Reproduced in part with permission from


Copyright [2014] American Chemical Society

And


Copyright [2015] The Royal Society of Chemistry

© 2016

SARANG M. BHAWAY

ALL RIGHTS RESERVED
FABRICATION OF BLOCK COPOLYMER TEMPLATED MESOPOROUS METAL OXIDE COMPOSITES FOR ENERGY STORAGE APPLICATIONS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Sarang M. Bhaway

August, 2016
FABRICATION OF BLOCK COPOLYMER TEMPLATED MESOPOROUS METAL OXIDE COMPOSITES FOR ENERGY STORAGE APPLICATIONS

Sarang M. Bhaway

Dissertation

Approved:                                               Accepted:

Advisor                                              Department Chair
Dr. Bryan D. Vogt                                      Dr. Sadhan Jana

Co-Advisor and Committee Member                       Dean of the College
Dr. Alamgir Karim                                      Dr. Eric J. Amis

Committee Chair                                       Dean of the Graduate School
Dr. Kevin A. Cavicchi                                  Dr. Chand K. Midha

Committee Member                                      Date
Dr. Yu Zhu

Committee Member
Dr. Jiahua Jack Zhu
ABSTRACT

Block copolymer templated mesoporous (2 nm-50 nm) metal oxides are considered promising electrode materials for energy storage devices such as electrochemical capacitors or lithium/sodium ion batteries. The mesoporous electrode morphology offers several advantages: (1) high surface area and porosity facilitate charge transfer across the electrolyte-electrode interface, (2) nanoscale-dimension of the oxide framework minimizes the solid state ion diffusion paths, and (3) interconnected porous morphology enables rapid electrolyte transport through the electrodes, leading to overall enhancement in charge storage capabilities. This research attempts to study the effect of mesoporosity and mesopore geometry on charge storage capabilities and cycling stability of ordered mesoporous metal oxide electrodes in energy storage devices.

The first part of this dissertation focuses on fabrication of ordered mesoporous metal oxide composites utilizing the Evaporation Induced Self-Assembly (EISA) and the Block Copolymer Micelle Templating (BCMT) strategy. Firstly, we demonstrate fabrication of ordered mesoporous carbon-vanadium oxide composites utilizing EISA of phenolic resin oligomer (resol), VOCl$_3$ and an amphiphilic triblock. We illustrate that carbon yield from resol carbonization can prevent break-out crystallization of vanadia during calcination and help maintain an ordered mesostructure. The mesoporous carbon-vanadia mesostructured thin films exhibit specific capacitance 7 times higher than their non-porous analog at high scan rates when tested as electrode in aqueous supercapacitor.
The second part of this thesis focuses on BCMT technique to fabricate ordered mesoporous mixed-metal oxide electrodes for battery applications. Ordered mesoporous Ni₄Co₃₋ₓO₄ thin films with varying chemical composition are fabricated using a metal nitrate-citric acid complex and an amphiphilic PEGMA-b-PBA block copolymer template. This templating strategy is further extended to fabricate porous and hierarchically structured, Ni encapsulated NiO/MnOₓ/carbon nanofiber composites based on electrospinning metal nitrate salts, citric acid, resol and PEGMA-b-PBA copolymer. The mesoporous structure is demonstrated to significantly enhance the composite materials performance as electrodes in sodium as well as lithium ion batteries.

To gain insights into the underlying mechanisms that enhance the charge storage capabilities of ordered mesoporous metal oxide anodes, final part of the dissertation focuses on in-operando grazing incidence small angle x-ray scattering and x-ray diffraction (GISAXS/GIXD) technique to monitor the structural evolution of a mesoporous NiCo₂O₄ anode during Li⁺ ion battery operation. We demonstrate mesopores smaller than ~10 nm collapse during the first 2 cycles of operation due to volume expansion/contraction that accompanies Li⁺ ion insertion/de-insertion. However, the mesopores in anodes with pore size > 15 nm are only partially lost during the first 2 cycles of operation. This limited structural change leads to efficient and reversible Li⁺ ion insertion/de-insertion, thereby improving the capacity retention and overall cycling stability of the anode. This in-operando study illustrates how changes at the atomic scale (lithium insertion) impact the mesostructure, and provides correlations between mesostructure and storage performance in ordered mesoporous metal oxide anodes.
DEDICATION

I dedicate this dissertation to my parents, Mukund Bhaway, Medha Bhaway and my sister, Sanyogeeta Bhaway, who have always been by my side through thick and thin.
ACKNOWLEDGMENTS

I would like to acknowledge and convey my sincere gratitude to each and every individual who has helped me during the past five years of my Ph.D. research. First and foremost, I would like to thank my co-advisors Dr. Bryan Vogt and Dr. Alamgir Karim for their invaluable guidance not only in terms of research, but molding me into the professional I have become today. I will always be grateful for their support, patience and encouragement during my initial days of adjusting to Ph.D. life at The University of Akron.

I would like to thank all my committee members, Dr. Alamgir Karim, Dr. Kevin Cavicchi, Dr. Yu Zhu and Dr. Jiahua Jack Zhu for being part of my dissertation committee, taking time to read my dissertation and for giving very useful suggestions to improve it. I am extremely thankful to Dr. Yu Zhu for his collaboration, guidance and help in carrying out lithium/sodium ion battery testing experiments. In this regard, I would also like to make a special mention of Yu-Ming Chen and Kewei Liu who have helped me during the course of these battery testing experiments. I would like to thank Dr. Vogt’s group members, past and present, for their useful suggestions and help throughout my PhD journey, with special mention to Dr. Jeongwoo Lee and Clinton Wiener. I also thank all my friends, whom I consider more of a family at this point of time. Finally, I am very thankful to my family for their constant love and support and motivating me to work harder and smarter every day.
TABLE OF CONTENTS

LIST OF FIGURES……………………………………………………………………………x

LIST OF TABLES……………………………………………………………………………….xvii

CHAPTER
I INTRODUCTION........................................................................................................1

II BACKGROUND AND LITERATURE REVIEW.........................................................8

  2.1 Energy storage devices ..........................................................................................8
  2.1.1 Electrochemical capacitors .............................................................................14
  2.1.2 Lithium ion battery ........................................................................................21
  2.1.3 Sodium ion battery .........................................................................................26

  2.2 Anode materials for Lithium/Sodium ion battery ..............................................28
  2.2.1 Carbon based anodes ......................................................................................28
  2.2.2 Anodes based on alloying-dealloying reactions............................................29
  2.2.3 Metal oxide based anodes .................................................................................30

  2.3 Mesoporous metal oxide anodes .........................................................................33
  2.3.1 Hard-templating of mesoporous metal oxide composites ..........................38
  2.3.2 Soft-templating of ordered mesoporous metal oxide composites .............40
VI IN-OPERANDO GISAXS/GIXD OF ORDERED MESOPOROUS NICKEL COBALTITE ANODES TO UNDERSTAND NANOSTRUCTURE CHANGES DURING LITHIUM ION BATTERY OPERATION………………………………….148

6.1 Introduction……………………………………………………………………...148

6.2 Experimental Section…………………………………………………………….151

6.3 Results and Discussion…………………………………………………………….156

6.4 Conclusion………………………………………………………………………176

VII OVERALL SUMMARY AND FUTURE STUDIES……………………………..178

REFERENCES……………………………………………………………………...185

APPENDIX…………………………………………………………………………..213
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Characterization of properties and performance of different battery systems utilized in current hybrid electric vehicles (HEV) and electric vehicles (EV)</td>
<td>10</td>
</tr>
<tr>
<td>2.2 Specific power (vs) Specific energy (Ragone plot) for electrical energy storage devices. Times shown on the Ragone plot correspond to time constant obtained on normalizing energy density by power density</td>
<td>11</td>
</tr>
<tr>
<td>2.3 (A) Schematic of porous carbon-metal oxide composite electrode providing electrolyte transport paths through the pores. (B) Comparison of specific capacitance of mesoporous tungsten oxide electrode with a bulk analog, indicating significantly higher specific capacitance in case of porous electrode architecture</td>
<td>12</td>
</tr>
<tr>
<td>2.4 Scheme of charge storage mechanism in (A) electric double-layer capacitors (EDLC) based on carbon electrodes and (B) redox-reactions based pseudo-capacitors</td>
<td>14</td>
</tr>
<tr>
<td>2.5 Scanning electron microscopy image of (A) polypyrrole microsheets utilized as precursor to porous carbon (B) 3D hierarchically porous, high-surface area (&gt; 2500 m²/g) carbon fabricated through KOH activation (C) Specific capacitance of 3D hierarchically porous carbon electrode as a function of current density (D) Cycling stability of 3D hierarchically porous carbon electrode at current density of 5 A.g⁻¹ over 10,000 cycles</td>
<td>16</td>
</tr>
<tr>
<td>2.6 Normalized capacitance as a function of pore size</td>
<td>17</td>
</tr>
<tr>
<td>2.7 Comparison of specific capacitance of carbon based double-layer capacitors and metal oxide based pseudo-capacitors illustrating the superior charge storage capabilities of metal oxide electrodes</td>
<td>18</td>
</tr>
<tr>
<td>2.8 Scheme for fabrication of block copolymer templated ordered mesoporous carbon-tungsten oxide hybrid electrochemical capacitor</td>
<td>20</td>
</tr>
<tr>
<td>2.9 Gravimetric energy density of different battery systems in comparison to gasoline</td>
<td>23</td>
</tr>
<tr>
<td>2.10 Schematic of lithium ion battery illustrating movement of electrons and Li⁺ ions during battery charge-discharge process</td>
<td>24</td>
</tr>
<tr>
<td>2.11 Theoretical capacities of various anode materials utilized in lithium ion batteries</td>
<td>32</td>
</tr>
<tr>
<td>2.12 Characterization of porous materials based on pore size</td>
<td>34</td>
</tr>
</tbody>
</table>
2.13 (A) Schematic of charge transfer process occurring in a porous electrode and the importance of nano-dimension in reducing Li$^+$ ion diffusion time\textsuperscript{10} (B) KLE-templated ordered mesoporous Li$_4$Ti$_5$O$_{12}$ anode possessing nano-dimension matrix demonstrating excellent capacity retention and high C-rate and performance..............................36

2.14 Schematic of hard-templating pathways to fabricate mesoporous oxides with (A) cylindrical (MCM-41) and (B) cubic geometry (MCM-48).................................39

2.15 Schematic of Evaporation Induced Self-Assembly (EISA) process during formation of mesoporous metal oxide thin films using amphiphilic block copolymers as soft-templates..................42

2.16 Schematic of CASH process to fabricate highly crystalline ordered mesoporous metal oxides ........................................................................................................43

2.17 Schematic of block copolymer micelle templating strategy to fabricate ordered mesoporous metal oxides ..................................................................................45

3.1 AFM phase images of OBO triblock-templated polymer-vanadia thin film (a) as cast, and after calcination in (b) Ar (CASH-450-Ar), (c) N$_2$(CASH-450-N$_2$), and (d) in air at 450 $^\circ$C. The mesostructure in the as-cast composite film is not preserved upon template removal, irrespective of calcining environment (scale bar – 200 nm)..........................57

3.2 AFM phase image of tri-constituent OBO triblock template, resol and vanadia composite (a) as cast film exhibiting spherical micelles ~26 nm in diameter, and (b) upon calcination in air at 450 $^\circ$C, leading to loss of the ordered mesostructure (scale bar – 350 nm). TGA trace for (c,d) the OBO triblock copolymer template in Ar (red) and N$_2$(blue) indicating similar degradation behavior with complete degradation of template at 475 $^\circ$C. (e, f) Thermopolymerized resol with a 56 wt% carbon yield at 800 $^\circ$C in Ar (red) and 58 wt% carbon yield in N$_2$(blue) environments. ..................................................................59

3.3 AFM phase images of resol-assisted tri-constituent thin films of (a) CV-450-N$_2$, (b) CV-450-Ar, (c) CV-600-N$_2$, (d) CV-600-Ar, (e) CV-800-N$_2$ and (f) CV-800-Ar. The templated mesoporous carbon-vanadium oxide morphology is partially preserved after calcination under N$_2$(scale bar – 200 nm). ........................................................................60

3.4 (A) 1-D plots extracted from the in-plane direction of GISAXS patterns at $\alpha = 0.2^\circ$ (above critical angle) for (a) CV-450-Ar, (b) CV-450-N$_2$, (c) CV-600-N$_2$, and (d) CV-800-N$_2$. (B) Comparison of GIXD 1-D profiles for (e) CV-600-N$_2$, (f) CV-600-Ar, (g) CV-800-N$_2$, and (h) CV-800-Ar.................................................................63

3.5 Evolution of film thickness and change in contraction for CV-x-N$_2$ at different processing temperatures........................................................................................................64

3.6 Exponential decay function (red) applied to the 1-D GISAXS plot for CV-800-N$_2$ to determine the background scattering and corresponding Lorentzian function used to determine the peak position (inset)........................................................................65
3.7 Cross-sectional TEM micrographs of (a) CV-600-N₂ (bright field), (b) CV-600-N₂ (dark field), (c) scrapped thin film of CV-600-N₂ (dark field), (d) scrapped thin film of CV-800- N₂ (dark field), (e) CV-800-N₂ and (f) CV-800-Ar illustrating the porous structure of these films. (f) Note the segregation of vanadia to the film surface on calcination in Ar..............................67

3.8 Toluene adsorption (black) and desorption (red) isotherms for (a) CV-600-N₂ and (b) CV-800-N₂. (c) Pore size distribution for CV-600-N₂ and CV-800-N₂ calculated from the adsorption isotherms by using the Kelvin equation. ....................................................... 69

3.9 (a) Mass evolution during calcination of thermopolymerized resol-vanadium oxide composites using Ar and N₂ as determined by TGA. There is significantly greater residue at 800 °C using N₂. (b) Determination of the vanadia content by heating in air of CV-800-N₂(28 wt%); heating of CV-800-Ar residue (red) in air demonstrates that the vanadium is not in its highest oxidation state as there is an increase in mass on heating above 500°C, indicative of further vanadium oxidation..........................71

3.10 (A) High resolution XPS profiles for V2p peaks for resol assisted tri-constituent thin films calcined under different environments for (a) CV-600-N₂, (b) CV-600-Ar, (c) CV-800-N₂, and (d) CV-800-Ar. N₂ calcined films contain predominately V⁵⁺ and Ar calcined films contain predominately V⁴⁺. (B) XPS survey spectrum for CV-800-N₂ is consistent with the presence of vanadium in V⁵⁺ oxidation state on the surface of the thin film along with carbon (C1s) and oxygen (O1s) peaks. 3.10(B) inset indicates presence of nitrogen (N1s) peak obtained around 397.2eV, corresponding to formation of small amount of vanadium oxynitride ................................................................. 73

3.11 FTIR spectra for resol assisted tri-constituent composite thin films of (a) CV-600-N₂, (b) CV-600-Ar, (c) CV-800-N₂, and (d) CV-800-Ar ...............................................................75

3.12 TGA trace for (a) thermopolymerized resol-vanadium oxide composites using ultrapure N₂ (less than 0.5 ppm O₂) (black) and N₂ containing<5 ppm O₂ content (blue) respectively. ........................................77

3.13 (a) FTIR spectra for CV-600-N₂ (black) and after calcination for 30 min (blue) and 90 min (green) in air at 400 °C. AFM phase image of CV-600-N₂ subjected to calcination in air at 400 °C for (b) 30 min and (c) 90 min. (d) FTIR spectra for CV-800-N₂ (black) subjected to calcination for 30 min (blue) and 90 min (green) in air at 400 °C. AFM phase image of CV-800-N₂ subjected to calcation in air at 400 °C for (e) 30 min and (f) 90 min. (Scale bar - 200 nm) ...........................................................................78

3.14 (a) Electronic conductivity of carbon-vanadium oxide composites calcined under argon environment (red triangles) and nitrogen environment (blue squares) at different processing temperatures indicating increasing conductivity of the composite with increased target calcining temperature. Note that the electrical conductivity of the composite is independent of the calcination environment. (b) Cyclic voltammetry curves for CV-800-N₂ at scan rate of 2mV/s (black), 10mV/s (red), 50mV/s (green) and 100mV/s (blue); (c) Normalized specific capacitance of OBO templated porous CV-800-
N₂ (relative to non-porous, non-templated carbon-vanadium oxide film) at different scan rates. ................................................................. 80

4.1 (A) TGA traces of metal nitrate-citric acid complex (x is mole fraction of nickel for the nitrates used) on heating in air. Decomposition of the metal nitrate-citric acid complex occurs in two distinct steps, corresponding to formation of metal carbonate (fuchsa) and decomposition of metal carbonate into corresponding metal oxide (chartreuse). (B) TGA trace (blue) and derivative (green) of mass loss for cobalt nitrate-citric acid complex, indicating two step degradation corresponding to formation of cobalt carbonate followed by decomposition of carbonate into cobalt oxide. (C) Onset temperature for formation of metal carbonate (circle) and metal oxide (triangle) with varying nickel content within the composite determined from TGA traces. ......................... 92

4.2 (A) FTIR spectra of PMPEGMA-b-PBA micelle templated metal nitrate-citric acid film containing with 50 mol% nickel for (a) as cast, (b) carbonate formation at 240 °C for 1 h, and (c) oxide formation at 350 °C for 30 min. (B) FTIR spectra of micelle templated mesoporous (d) Co(CO₃)₂, (e) NiCo₂(CO₃)₂, (f) Ni₁.₅Co₁.₅(CO₃)₂, (g) Ni₂Co(CO₃)₂, and (h) Ni(CO₃)₂. (C) FTIR spectra of micelle templated mesoporous (i) CoO₄, (j) NiCo₂O₄, (k) Ni₁.₅Co₁.₅O₄, (l) Ni₂CoO₄, and (m) NiO fabricated by first forming the carbonate (heating for 1 h) and subsequently the oxide (heating for 30 min) using the temperatures specified in Table 4.1................................................................. 94

4.3 (A) 1-D GIXD profiles for (a) Co₃O₄, (b) NiCo₂O₄, (c) Ni₁.₅Co₁.₅O₄, (d) Ni₂CoO₄, and (e) NiO. (B) Diffraction profiles from the (400) plane for (a) Co₃O₄, (b) NiCo₂O₄, (c) Ni₁.₅Co₁.₅O₄ and (d) Ni₂CoO₄. There is a shift in the (400) peak position to lower 2θ with increasing nickel content. ................................................................. 95

4.4 High resolution XPS profiles of (a) Ni2p (b) Co2p and (c) O1s peaks present in templated mesoporous Ni₁.₅Co₁.₅O₄ thin film. Ni and Co are found to be present as a mixture of 2⁺ and 3⁺ oxidation state in the MMO composite. (d) Variation in atomic % of Ni (red), Co (blue) and defect O concentration (black) in the MMO with varying nickel content........................................................................................................ 97

4.5 High resolution XPS profiles of (A) Ni2p (B) Co2p and (C) O1s peaks present in templated mesoporous Ni₁.₅Co₁.₅⁻xO₄ thin films along with deconvolution of peaks indicating Ni and Co to be present as a mixture of oxidation states in the MMO composite. ............................................................................................................................... 98

4.6 AFM micrographs of micelle templated (a) Co(CO₃)₂, (b) NiCo₂(CO₃)₂, (c) Ni₁.₅Co₁.₅(CO₃)₂, (d) Ni₂Co(CO₃)₂, and (e) Ni(CO₃)₂. A microphase separated morphology is present in all cases. (Scale bar = 200 nm in all micrographs) .......... 100

4.7 FTIR spectra tracking the removal of PMPEGMA-b-PBA block copolymer template from thin films of (A) Ni₂Co(CO₃)₂ and (B) Ni(CO₃)₂. AFM micrographs indicating an ordered mesoporous structure for (C) Ni₂Co(CO₃)₂ and (D) Ni(CO₃)₂. (Scale bar = 200 nm) .................................................................................................................. 101

4.8 AFM micrographs of templated mesoporous (a) Co₃O₄, (b) NiCo₂O₄, (c) Ni₁.₅Co₁.₅O₄, (d) Ni₂CoO₄, and (e) NiO. The templated porous structure is maintained after
decomposition of metal carbonate and complete removal of block copolymer template. (f) TEM micrograph of Ni$_{1.5}$Co$_{1.5}$O$_4$ film that has been scrapped from the substrate (Scale bar = 200 nm)..........................102

4.9 (A-E) 2-D GISAXS plots for mixed metal carbonates (Ni$_x$Co$_{(3-x)}$(CO$_3$)$_y$) and (F) 1-D plots extracted from GISAXS data for mixed metal carbonates (Ni$_x$Co$_{(3-x)}$(CO$_3$)$_y$) at 0.2° incident angle. .............................................................................................................104

4.10 (A-E) 2-D GISAXS plots for mixed metal oxides (Ni$_x$Co$_{(3-x)}$O$_4$) and (F) 1-D plots extracted from GISAXS data for mixed metal oxides (Ni$_x$Co$_{(3-x)}$O$_4$) at 0.2° incident angle. .............................................................................................................105

4.11 TEM micrographs of samples prepared from scrapped films of (A) Co$_3$O$_4$ (B) NiCo$_2$O$_4$ (C) Ni$_{1.5}$Co$_{1.5}$O$_4$ (D) Ni$_2$CoO$_4$ and (E) NiO. Ordered mesoporous structure with spherical pores (~ 14 nm) can be clearly seen in all the oxide film samples (Scale bar=100 nm) ................................................................................................................ 108

4.12 (A) Specific discharge capacity of mesoporous cobalt oxide (▲) and nickel oxide (●) film anodes for sodium ion batteries galvanostatically cycled at a current density of 1 A/g, (B) Volumetric and areal (inset) capacity of mesoporous cobalt oxide (▲) and nickel oxide (●) film anodes. Cyclic voltammetry curves for (C) Co$_3$O$_4$ and (D) NiO anodes carried out at a scan rate of 2 mV/s in the voltage range of 0.01-3.0 V .............109

4.13 (A) Comparison of the MMOs as anodes subjected to galvanostatic cycling over 10 cycles with a potential window of 0.01-3.0 V at current density of 1 A/g: NiCo$_2$O$_4$ (■), Ni$_{1.5}$Co$_{1.5}$O$_4$ (▲), and Ni$_2$CoO$_4$ (●). (B) Comparison of specific discharge capacities of templated mesoporous and non-porous Ni$_2$CoO$_4$ anode subjected to galvanostatic cycling at varying current densities (C) Volumetric and areal (inset) discharge capacities of Ni$_2$CoO$_4$ anode subjected to galvanostatic cycling at varying current densities. Cyclic voltammetry curves for (D) NiCo$_2$O$_4$ (E) Ni$_{1.5}$Co$_{1.5}$O$_4$ and (F) Ni$_2$CoO$_4$ carried out at a scan rate of 2 mV/s in the voltage range of 0.01-3.0 V ................................................. 112

4.14 (A) Enhancement in electronic conductivity of MMO thin films with varying nickel content in the composite determined using 4-point probe measurements (B) X-ray diffraction profiles of MMO thin film anodes subjected to galvanostatic cycling. ......115

5.1 SEM micrographs of (A, B) Ni$_{60}$-Mn$_{100}$/C; (D, E) Ni$_{33}$-Mn$_{66}$/C; (G, H) Ni$_{50}$-Mn$_{50}$/C; (J, K) Ni$_{66}$-Mn$_{33}$/C; and (M, N) Ni$_{100}$-Mn$_{0}$/C composite fibers. Size distribution of (C) Ni$_{60}$-Mn$_{0}$/C (F) Ni$_{33}$-Mn$_{66}$/C (I) Ni$_{50}$-Mn$_{50}$/C (L) Ni$_{66}$-Mn$_{33}$/C (O) Ni$_{100}$-Mn$_{0}$/C nanofiber composites..........................................................................................................................126

5.2 Scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) spectroscopy for surface elemental compositional analysis of (A) Ni$_{66}$-Mn$_{33}$/C (B) Ni$_{50}$-Mn$_{50}$/C (C) Ni$_{33}$-Mn$_{66}$/C fiber composites..........................................................................................................................128

5.3 High resolution x-ray photoelectron spectroscopy (XPS) profiles of Ni2p peaks for (A) Ni$_{33}$-Mn$_{66}$/C (B) Ni$_{50}$-Mn$_{50}$/C and (C) Ni$_{66}$-Mn$_{33}$/C fiber composites illustrating the
increase in surface Ni$^0$ content (peak at binding energy 852.5 eV) for Ni$_x$-Mn$_{100-x}$/C composites with increasing initial nickel dope. ............................................................

5.4 Thermogravimetric traces for (A) Ni$_{100}$/Mn$_0$/C (B) Ni$_{66}$/Mn$_{33}$/C (C) Ni$_{50}$/Mn$_{50}$/C (D) Ni$_{33}$/Mn$_{66}$/C (E) Ni$_0$/Mn$_{100}$/C composite fibers carried out in air indicating ~ 18 wt% carbon yield present in all Ni$_x$-Mn$_{100-x}$/C composites. (F) Evolution of Ni$_{66}$/Mn$_{33}$ mass during calcination in nitrogen (red) and air (blue) atmosphere........................................131

5.5 X-ray diffraction profiles of mesoporous Ni$_x$-Mn$_{100-x}$/C composite nanofibers calcined at 800 °C under nitrogen flow (■-Ni; ★-NiO; ▲-MnO; ♦-Mn$_3$O$_4$; ●-Graphite) ........ 132

5.6 (A) N$_2$ (■) adsorption and (○) desorption isotherms for the mesoporous Ni$_x$-Mn$_{100-x}$/C fiber composites. (B) Pore size distribution for the mesoporous Ni$_x$-Mn$_{100-x}$/C fibers determined from the adsorption isotherm. .................................................................... 135

5.7 Discharge capacity of Ni$_0$/Mn$_{100}$/C and Ni$_{100}$/Mn$_0$/C nanofiber anode subjected to galvanostatic cycling between 0.01-3.0 V vs Li/Li$^+$ at varying current densities. ..........137

5.8 (A) Discharge capacity of Ni$_x$-Mn$_{100-x}$/C fiber anodes subjected to varying current densities between 0.01-3.0 V vs Li/Li$^+$. (B) Specific discharge capacity of Ni$_x$-Mn$_{100-x}$/C nanofiber anode normalized by the weight of electroactive material when galvanostatically cycled at varying current densities. .................................................................138

5.9 Electrochemical impedance spectroscopy (EIS) of Ni$_x$-Mn$_{100-x}$/C fiber anodes at 0.1 - $10^5$ Hz prior to galvanostatic cycling. The overall impedance of composite anode is reduced with increasing Ni content. .................................................................................................141

5.10 Electrochemical impedance spectroscopy (EIS) and the simulated fits (A) Ni$_{100}$/Mn$_0$/C (B) Ni$_{66}$/Mn$_{33}$/C (C) Ni$_{50}$/Mn$_{50}$/C (D) Ni$_{33}$/Mn$_{66}$/C and (E) Ni$_0$/Mn$_{100}$/C composite fibers at 0.1 - $10^5$ Hz prior to galvanostatic cycling. (F) Equivalent circuit used to model the impedance data (Rs = solution resistance, R$_{SEI}$ = SEI resistance, C$_{SEI}$ = SEI capacitance, R$_{CT}$ = charge transfer resistance, W = Warburg impedance, Q = constant phase element, FD = finite length diffusion impedance) .............................................................142

5.11 Cyclic voltammetry curves for mesoporous (A) Ni$_{33}$/Mn$_{66}$/C (B) Ni$_{50}$/Mn$_{50}$/C (C) Ni$_{66}$/Mn$_{33}$/C fiber anodes carried out at a scan rate 0.5 mV/s. .................................................................143

5.12 Galvanostatic charge-discharge cycling of Ni$_x$-Mn$_{100-x}$/C fiber anodes at a constant current density of 0.1A/g. A current density of 0.05A/g was used for the first 5 charge-discharge cycles. .................................................................................................145

6.1 Custom-designed lithium ion cell and outer body to carry out in-operando GISAXS/GIXD and galvanostatic cycling of m-NCx anodes .................................................................155

6.2 AFM micrographs of (A) m-NC28 (B) m-NC16 and (C) m-NC9 films prior to galvanostatic cycling illustrating the variation in pore size........................................................157
6.3 (A) In-operando GISAXS-galvanostatic cycling runs on m-NC9 thin film anode (B) Quantitative analysis of change in d-spacing of m-NC9 anode during successive lithiation and de-lithiation segments ................................................................................................................................. 158

6.4 Quantitative mapping of (A) peak intensity and (B) full width-half max (FWHM) of primary scattering peak observed from 1-D GISAXS profiles of m-NC9 anode subjected to galvanostatic cycling vs Li/Li+ ........................................................................................................... 161

6.5 (A-C) Bright-field cross-sectional TEM images of m-NC9 thin film anode subjected to galvanostatic cycling for 2 cycles. (D, E) Scanning tunneling electron micrograph of m-NC9 and (F-I) elemental (Ni, Co, O and C) color map of corresponding region indicating relatively non-porous morphology and uniform distribution of Ni and Co elements ...................................................................................................................... 163

6.6 In-operando GISAXS-galvanostatic cycling runs of (A) m-NC16 and (B) m-NC28 thin film anode. (C) Quantitative mapping of change in d-spacing of m-NC16 and m-NC28 anodes based on analysis of primary scattering peak ................................................. 164

6.7 Galvanostatic charge-discharge curves of (A) m-NC16 and (B) m-NC28 thin film anodes illustrating the multi-step electrochemical reduction process. Quantitative mapping of primary scattering peak intensity observed from 1-D GISAXS profiles of (C) m-NC16 and (D) m-NC28 anode during galvanostatic cycling................................. 165

6.8 (A,B) Cross-sectional TEM micrographs of m-NC16 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling. (C) Scanning tunneling electron microscopy (STEM) micrograph of m-NC16 anode and corresponding area elemental color maps of (D) C (E) Ni (F) Co and (G) O elements in NiCo$_2$O$_4$ framework cross-sectional TEM micrographs of (A,B) m-NC16 and (C,D) m-NC28 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling......................... 167

6.9 (A-C) Cross-sectional TEM micrographs of m-NC28 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling. (D) Scanning tunneling electron microscopy (STEM) micrograph of m-NC28 anode and corresponding area elemental color maps of (E) Ni (F) Co (G) O and (H) C. (I) Merged elemental color map indicating C element primarily present on mesopore walls ........................................................... 168

6.10 In-operando variation of (A) NiCo$_2$O$_4$ nanoparticle size and (B) NiCo$_2$O$_4$ nanoparticle volume in m-NCx anodes during initial lithiation and de-lithiation segments .................................................................................................................................... 170

6.11 Azimuthally averaged in-operando 1D-GIXD profiles of m-NCx anodes subjected to galvanostatic cycling in custom-designed lithium ion battery (●-initial discharge, ●-1$^{st}$ charge, ●-1$^{st}$ discharge, ●-2$^{nd}$ charge segment) ................................................................................................................................. 172

6.12 Galvanostatic cycling stability of m-NC28 and m-NC9 anode subjected to constant current density of 600 mAh/g ........................................................................................................................................ 175
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Comparison of the chemical nature of Lithium and Sodium</td>
<td>27</td>
</tr>
<tr>
<td>4.1 Precursor compositions and processing conditions for fabrication of cobalt oxide, nickel oxide and their mixed-metal oxide (Ni_xCo_{(3-x)}O_4) composites</td>
<td>88</td>
</tr>
<tr>
<td>4.2 Atomic ratios in MMO films determined from XPS survey scans</td>
<td>99</td>
</tr>
<tr>
<td>5.1 Precursor composition for fabrication of the Ni_xMn_{100-x}/C electrospun nanofiber composites (excluding the solvents)</td>
<td>122</td>
</tr>
<tr>
<td>5.2 Energy-dispersive x-ray (EDX) spectroscopy for Ni_x-Mn_{100-x}/C nanofiber composites</td>
<td>127</td>
</tr>
<tr>
<td>5.3 Crystalline composition from Rietveld refinement of XRD profiles of Ni_x-Mn_{100-x}/C fibers</td>
<td>133</td>
</tr>
<tr>
<td>5.4 BET surface area and micropore volume of Ni_x-Mn_{100-x}/C fiber composites</td>
<td>136</td>
</tr>
<tr>
<td>5.5 Calculated theoretical capacity and obtained capacity based on MO_x composition</td>
<td>140</td>
</tr>
<tr>
<td>6.1 Chemical composition utilized for fabrication of m-NCx thin film anodes</td>
<td>153</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Mesoporous materials are defined as materials possessing pores in the range of 2 nm -50 nm according to International Union of Pure and Applied Chemistry (IUPAC). Research in the field of functional mesoporous materials originated from the early attempts at developing zeolite-like porous materials possessing with pore size greater than 2 nm. Since then, various efforts have been directed towards development of surfactant templated mesoporous metal oxides and metal oxide-carbon composites with precise control over pore geometry and size. The ability to tailor the properties of ordered mesoporous metal oxides based on chemical functionality, porosity and pore geometry has given rise to potential applications in fields such as energy storage, drug delivery, catalysis, gas sensors or functional coatings.

One of the major hurdles for the 21st century is energy conversion and storage. To reduce the ever-increasing gap between energy demand and supply, significant efforts are being directed towards developing next-generation, high efficiency energy storage devices such as electrochemical capacitors and lithium/sodium ion batteries. In an attempt to achieve this goal, these studies have primarily focused on improving our understanding of materials chemistry and correlating the effect of electrode morphology on performance of these energy storage devices.
Block copolymer templated mesoporous metal oxide electrodes, with precise control over chemical composition and morphology, is one way of improving charge storage performance and enhancing the efficiency in energy storage devices. Some of the important characteristics of block copolymer surfactant templated mesoporous metal oxide electrodes include high porosity, large pore volume, high surface area, nano-dimension metal oxide matrix accompanied by precise control over pore size and geometry. The mesoporous electrode morphology facilitates electrolyte diffusion, flexible porous architecture can provide stress relief during electrode volume expansion and nano-sized domains allow faster operation.

However, current methods based on hard-templating or sol-gel processing to fabricate ordered mesoporous metal oxide electrodes requires multiple processing steps and precise control over various reaction parameters, making large-scale production unviable. To overcome the shortcomings of existing synthesis protocols and fabricate mesoporous metal oxide electrodes with improved performance in energy storage devices acts as a major motivation in this thesis. Another key area of focus in this dissertation involves correlating mesopore geometry with charge storage performance of metal oxide anodes in electrochemical capacitors and lithium/sodium ion batteries. Mesoporous metal oxide electrodes with controlled nano-architecture exhibit excellent charge storage behavior but suffer capacity fade or inferior charge storage upon successive cycling. However, the factors contributing towards such capacity fade in nanostructured anodes is not clearly understood. To develop a mechanistic understanding of capacity fade exhibited by mesoporous metal oxide anodes in lithium/sodium ion battery devices acts as a major motivation in this thesis. This study will help develop design principles for
fabricating high energy density porous metal oxide electrodes demonstrating improved long-term performance. The primary goal of this research can be divided into two important aspects- (1) devising synthesis strategies to fabricate highly porous, high surface area metal oxide composite anodes to improve capacity and cycling efficiency of energy storage devices and (2) correlating effect of mesostructure on charge storage capabilities of mesoporous electrodes in supercapacitors and lithium/sodium ion battery.

In the first part of the dissertation, block copolymer templated mesoporous carbon-vanadia composite electrodes were fabricated by combining block copolymer self-assembly and sol-gel processing. Previous studies on fabrication of mesoporous vanadium oxide have reported collapse of ordered porous structure on template removal.\textsuperscript{24, 25} We demonstrate that the ordered mesoporous structure of vanadia can be maintained through cooperative self-assembly of resol (carbon precursor) along with block copolymer surfactant and vanadia precursor. The carbon yield derived from resol on carbonization confines the crystallization of vanadia and prevents mesostructure collapse even after heating the composite at 800 °C in a N\textsubscript{2} environment. The nanoporous (~9\%) morphology of block copolymer templated carbon-vanadia composite improves specific capacitance of mesoporous anode by a factor of 7.25 over its non-porous analog, when tested as anode in a supercapacitor. Such improved performance is observed even at high scan rates (100 mV.s\textsuperscript{-1}) due to easier access of electrolyte ions to the porous electroactive metal oxide surface and shorter diffusion paths.\textsuperscript{26}

Since sol-gel processing requires stringent control over various reaction parameters such as humidity, temperature, pH of solution, hydrolysis and condensation rates, second part of the dissertation deals with developing a new and simple synthesis
protocol for fabricating ordered mesoporous mixed-metal oxide composites. We discuss the block copolymer micelle templating strategy in detail, used to template mesoporous mixed-metal oxide composite thin films of Ni$_x$Co$_{(3-x)}$O$_4$. The amphiphilic block copolymer surfactant used in all following studies is poly[methoxy poly(ethylene glycol) methacrylate]–block–poly(butyl acrylate), PMPEGMA-b-PBA, synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization. This particular study focuses on electrode materials chemistry as well as the morphology, where we demonstrate Ni$_2$CoO$_4$ thin film anode, possessing higher nickel content on molar basis, exhibits the best performance in terms of charge storage and cycling stability at current densities in a sodium ion battery. The templated mesoporous Ni$_2$CoO$_4$ anode possess the highest electronic conductivity (0.23 S.cm$^{-1}$) among nanostructured Ni$_x$Co$_{(3-x)}$O$_4$ anodes, allowing efficient electron transport even at high current densities. We demonstrate the nanoporous morphology of Ni$_2$CoO$_4$ anode improves charge storage capabilities of the porous anode by a factor of 2 as compared to non-templated, non-porous Ni$_2$CoO$_4$ electrode. This block copolymer micelle templating method can be generalized for synthesis of variety of mixed-metal oxide composites, depending on them metal oxide precursors chosen.

An important criterion to improve electron and charge transport in metal oxide anodes and enhance charge storage capabilities of electrodes involves developing anodes with interconnected morphology. Fabricating anodes possessing interconnected nanofiber morphology is one method of preventing shorts and inactive material in the lithium/sodium ion battery electrodes. The 1-dimensional nanofiber morphology helps accommodate the strain associated with Li$^+$ intercalation and prevent metal oxide
pulverization during the cycling process.\textsuperscript{27} Taking into account these advantages of nanofiber morphology, the third part of this dissertation will focus on electrospinning high surface area and electronically conductive nanofiber composite anodes for lithium ion battery applications. Manganese oxide (MnO\textsubscript{x})\textsuperscript{28} and nickel oxide (NiO)\textsuperscript{29} possessing high theoretical capacities were selected as the reodx-active materials to electrospin the nanofiber composites, while carbon and metallic Ni were chosen to reduce overall impedance of the composite. Block copolymer (PMPEGMA-\textit{b}-PBA) micelle templating strategy will be utilized to introduce porosity and fabricate high surface area nanofiber anodes for lithium ion battery. Previous reports on electropsun metal oxide nanofibers have reported loss of fiber morphology on calcination at high temperatures.\textsuperscript{30} We demonstrate in this study that the nanofiber morphology can be maintained on calcination through the formation of an intermediate metal carbonate and presence of interdispersed resol. When testing these porous composite fibers as anode in lithium ion battery, we demonstrate nanofiber composite possessing highest surface metallic Ni content (19\%) exhibits the lowest impedance (238 $\Omega$) through formation of continuous electron transport paths. At the same time, efficient surface encapsulation of Ni\textsubscript{66}-Mn\textsubscript{33}/C nanofiber composite by metallic Ni significantly improves the energy density and cycling stability of these composite fiber anodes. The electrospinning methodology developed in this study can be easily extended for scaled-up for industrially relevant, roll-to-roll fabrication of 3-dimensionally interconnected, electronically conductive metal oxide nanofibers for varied applications.

Previous chapters have focused on the importance of templated nanoporous morphology and materials chemistry in improving the energy density of metal oxide
composite electrodes. However, the effect of mesopore dimensions and oxide wall thickness on charge storage performance of ordered mesoporous metal oxide anodes is not clearly understood. As mentioned in Chapter 4, block copolymer templated mesoporous NiCo$_2$O$_4$ anode improved high-rate performance as compared to its bulk analog in a sodium ion battery. However, it exhibits 79 % capacity fade on successive cycling and the origins of this capacity fade are also not clearly understood. Park et al. have suggested evolution of pore morphology in ordered mesoporous metal oxide anodes during cycling in a lithium ion battery, which contributes towards capacity fade.$^{31}$ However, the critical role of pore size and geometry on long-term cycling performance of mesoporous metal oxide anodes is still unknown. The last part of the dissertation aims at addressing these issues and correlating effect of mesostructure on long-term cycling performance of ordered mesoporous metal oxide anodes. To develop a better understanding of effect of pore geometry on long-term cycling efficiency in mesoporous metal oxide anodes, PMPEGMA-$b$-PBA templated NiCo$_2$O$_4$ anodes with pore size varying from 9 nm to 28 nm were fabricated. The evolution of the porous structure during battery operation was observed in-operando using a custom-designed lithium ion cell that permits collection of grazing incidence x-ray scattering (GISAXS/GIXD) profiles, while simultaneously charging-discharging the NiCo$_2$O$_4$ anode. Based on this in-operando study, we demonstrate that mesoporous NiCo$_2$O$_4$ anodes possessing pores smaller than 10 nm and oxide wall thickness ~ 6 nm significantly deform and the mesostructure collapses in the first few charge-discharge cycles, leading to significant capacity fade on successive cycling. However, NiCo$_2$O$_4$ anodes possessing larger pores (16 nm and 28 nm) and thicker oxide walls (10 nm and 20 nm) can accommodate the stresses formed during
cycling and can maintain their ordered porous structure during the cycling process. These anodes also exhibit improved long-term capacity retention when tested in the lithium ion battery. This suggests that below a critical pore dimension (~10 nm) and oxide framework thickness (~6 nm), the stresses developed in NiCo$_2$O$_4$ framework due to lithium insertion/de-insertion accompanied by volume expansion of NiCo$_2$O$_4$ matrix leads to collapse of the ordered mesoporous structure during battery cycling operation. The collapse of ordered porous structure is accompanied by significant capacity fade in the anode and inferior charge storage performance as compared to mesostructured NiCo$_2$O$_4$ anodes possessing larger mesopore dimensions and thicker oxide walls. Based on this study, we can develop design principles in terms of mesopore dimensions, oxide wall thickness and porosity for metal oxide anode nano-architecture necessary for high performance and stable lithium/sodium ion batteries.
CHAPTER II
BACKGROUND AND LITERATURE REVIEW

The background review presented in this chapter focuses on energy storage devices, namely electrochemical capacitors and lithium/sodium ion batteries. A thorough review on the electrode materials utilized in such energy storage devices is presented accompanied by factors affecting device performance. In addition, the chapter covers the crucial role of mesoporous electrode architecture, porosity and pore geometry on improved charge storage performance and its impact on device efficiency. Two different strategies to fabricate mesoporous metal oxide electrodes are presented, with special emphasis on “block copolymer micelle templating strategy” utilized extensively in this work.

2.1 Energy storage devices

One of the greatest challenges facing mankind in the 21st century is energy conversion and storage.\textsuperscript{10, 11} In 2006, the world’s primary energy consumption was estimated to be around 14 TW-y, while this figure is estimated to increase by 43% and reach 20 TW-y by the end of 2030.\textsuperscript{32} The ever-growing demand for energy has put tremendous strain on petroleum and coal industry to provide the essential resources for energy production. It is estimated that approximately 80% of energy usage is associated with carbon-intensive resources like oil, natural gas and coal.\textsuperscript{32}
However, the environmental concerns associated with use of such resources cannot be neglected while trying to satisfy energy demands. It is estimated that CO$_2$ levels have almost doubled between 1975 and 2005 leading to increase in global temperatures and dramatic climate changes.$^{33}$ To slow down global warming and avoid ill-effects associated with climate change, it necessary to reduce CO$_2$ emissions. The key to solving the energy crisis in a sustainable manner lies in developing highly efficient, high performance and low-cost energy conversion and storage devices in the form of solar cells, wind turbines, batteries or electrochemical capacitors.$^{32}$

As solar and wind energy cannot be captured continuously, efforts are being directed towards development of next-generation electrical energy storage systems. In this regard, lithium ion batteries and electrochemical capacitors are promising candidates to meet the requirements of high energy density, high power density, low cost and clean technology. These storage devices can deliver high energy on demand in stand-alone power plants or portable electronic devices. Energy storage devices such as lithium ion batteries can deliver high energy density (180 Whkg$^{-1}$) and are being considered as the best option to deliver energy in hybrid electric vehicles (HEV) and electric vehicles (EV).$^{34}$ Combining lithium ion batteries with internal combustion engines in HEVs have also helped improve fuel economy and reduce pollution.

As can be seen in Figure 2.1, the main propulsion system used in current HEVs is based on internal combustion engines. Low energy density Nickel-Metal Hydride (Ni-MH) batteries are utilized in such cars to provide electric propulsion for short driving distances ($\sim$ 15 km). These Ni-MH batteries offer the advantages of high rates, prolonged cycle life and excellent safety features as compared to lithium ion batteries.$^{35}$ However,
Ni-MH batteries cannot satisfy the needs of high energy density required in fully electric vehicles (EV) that will allow the cars to cover large distances on a single charge. In order to develop fully electric vehicles (EV) with no dependence on petroleum fuel, the ultimate goal is to develop high capacity, high energy density and light weight lithium ion batteries at reasonable cost.

<table>
<thead>
<tr>
<th>Modes of operation</th>
<th>battery capacity needed, kWh</th>
<th>Energy density, Wh/kg</th>
<th>Weight of battery, Kg</th>
<th>Speed, kilometres per hour</th>
<th>Distance on one charge, kilometres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid</td>
<td>&lt;3</td>
<td>40-50 (Ni-MH)</td>
<td>60 (Ni-MH)</td>
<td>100+</td>
<td>15</td>
</tr>
<tr>
<td>Plug in Hybrid</td>
<td>5.6-18</td>
<td>90-100 (Li-ion)</td>
<td>60-200 (Li-ion)</td>
<td>100+</td>
<td>10-60</td>
</tr>
<tr>
<td>Full EV</td>
<td>35-54</td>
<td>90-100 (Li-ion)</td>
<td>450 (Li-ion)</td>
<td>&gt;100</td>
<td>150-200</td>
</tr>
</tbody>
</table>

Figure 2.1 Characterization of properties and performance of different battery systems utilized in current hybrid electric vehicles (HEV) and electric vehicles (EV) [Reprinted with permission from Ref. 35]

Electrochemical capacitors, as opposed to lithium ion batteries, provide significantly higher power density (10 kWkg\(^{-1}\)) and are playing an important role in complementing battery technology used in EVs.\(^3\) These energy storage devices can provide instantaneous power for vehicle acceleration, and also recuperate energy during the braking operation.\(^3\) Electrochemical capacitors can also provide back-up energy for battery systems and fuel cells to provide uninterrupted and continuous power supply. As
a result, the US Department of Energy has designated these devices to be as important as battery systems for energy storage devices.\textsuperscript{34, 36} Figure 2.2 illustrates the Ragone plot most commonly followed for comparing performance of different electrical energy storage devices. The vertical axis on a Ragone plot describes how much energy can be provided by a device, while the horizontal axis illustrates how quickly the energy (power) can be delivered. Thus, a point on Ragone plot corresponds to the amount of time a particular quantity of energy can be provided at a given power. Lithium ion batteries, as mentioned earlier, possess high energy density but low power density.\textsuperscript{35} Electrochemical capacitors, conversely, possess high power density but low energy density (5 Whkg\(^{-1}\)). These electrochemical capacitors fill the gap between lithium ion batteries and conventional solid-state capacitors in terms of energy storage.\textsuperscript{34}

![Ragone plot](image)

Figure 2.2 Specific power (vs) Specific energy (Ragone plot) for electrical energy storage devices. Times shown on the Ragone plot correspond to time constant obtained on normalizing energy density by power density [Reprinted with permission from Ref. 37].
Since the introduction of lithium ion batteries in 1990 by Sony, significant efforts have been directed towards developing new electrode materials in the form of redox couples or insertion materials to enhance the capacities of batteries.\(^{38}\) However, very little progress has been achieved in terms of improving the battery life-time due to limited innovation in this field.\(^{33,39}\) Similarly, in case of electrochemical capacitors, there has only been an incremental improvement in performance over the last 30 years.\(^ {34}\) A major bottleneck in developing high performance devices is directly related to the chemistry of electrode materials utilized in these devices. In many cases, the synthesis protocols associated with developing new electrode materials requires many tedious steps, making the manufacturing process expensive. Developing inexpensive new materials and advancing our understanding of the electrochemical interface in these energy storage electrodes will help in improving the overall efficiency of these energy storage devices.

Figure 2.3 (A) Schematic of porous carbon-metal oxide composite electrode providing electrolyte transport paths through the pores. (B) Comparison of specific capacitance of mesoporous tungsten oxide electrode with a bulk analog, indicating significantly higher specific capacitance in case of porous electrode architecture [Reproduced with permission from Ref. 40 and Ref. 41].
Apart from electrode chemistry, significant efforts are now being directed towards design and fabrication of nanostructured materials to improve existing energy storage technology. Nanostructured and more specifically mesoporous electrode materials are considered promising candidates for energy storage applications as they provide much higher surface area as compared to their bulk analogs. The high surface area corresponds to high electro-active area, leading to enhancement in charge storage capabilities across the electrode. At the same time, the nano-dimension of the matrix and porous nature of electrode provides efficient electrolyte transport paths, allowing faster ion transfer across the electrode interface (Figure 2.3). For instance, Yoon et al. have illustrated the significant improvement in specific capacitance of mesoporous tungsten oxide (m-WO$_3$) anode as compared to its bulk (b-WO$_3$) counterpart through fabrication of mesostructured electrodes (Figure 2.3). The importance of mesoporous electrode morphology contributing towards the enhancement in charge storage capabilities of lithium/sodium ion battery or electrochemical capacitors will be discussed in greater detail in Section 2.3.

However, there is still substantial room for improvement to meet the requirements of portable electronics devices, electric vehicles or large industrial equipment. For example, the United States Advanced Battery Council (USABC) in the FreedomCAR research initiative (2002) set a goal for developing a 42 V battery that has a life-time of 15 years for hybrid electric vehicles (HEV) and 10 years for electric vehicles (EV). To attain these goals, efforts will have to be aimed at improving materials chemistry and their synthesis protocols to make large-scale production economically viable. Similarly,
efforts will also have to be directed towards understanding the effect of electrode nanostructure and morphology on charge storage performance.

2.1.1 Electrochemical capacitors

Electrochemical capacitors can be classified based on their charge storage mechanism and the electro-active materials used. Electrochemical double-layer capacitors primarily store charge based on ion adsorption, while pseudo-capacitors storage energy through fast surface redox reactions (Figure 2.4).³⁴

![Image of charge storage mechanism in (A) electric double-layer capacitors (EDLC) based on carbon electrodes and (B) redox-reactions based pseudo-capacitors. Reprinted with permission from Ref. 47.]

Figure 2.4 Scheme of charge storage mechanism in (A) electric double-layer capacitors (EDLC) based on carbon electrodes and (B) redox-reactions based pseudo-capacitors [Reprinted with permission from Ref. 47].

Electric double layer capacitors (EDLC) are most commonly based on high electronic conductivity materials such as activated carbon based electrodes possessing high surface area. The ease of availability, cheap cost and non-toxic nature of carbon materials makes these ideal materials for electrodes in EDLSs. Various studies have
focused on use of chemically activated nanoporous carbon\textsuperscript{48,49,50} or graphene,\textsuperscript{51,52} carbon nanotubes,\textsuperscript{53,54} carbon paper\textsuperscript{55,56} and nanofibers\textsuperscript{57,58} as electrodes in EDCLs. The charge storage mechanism in EDLCs is based on adsorption of electrolyte ions on the electrode surface (Figure 2.4). Electrostatic charge separation on the electrode surface leads to polarization of electrode-electrolyte interface, giving rise to the double-layer capacitance (C) according to the following equation-

\[ C_{EDLC} = \frac{\varepsilon_r \varepsilon_0 A}{d} \]  

(2.1)

where, \( \varepsilon_r \) is the electrolyte dielectric constant, \( \varepsilon_0 \) is the dielectric constant of the vacuum, \( d \) is the effective thickness of the double layer (charge separation distance) and \( A \) is the electrode surface area. As can be seen in equation 2.1, the double-layer capacitance is found to increase with increase in surface area of the electrode. Hence, significant efforts are being directed towards fabrication of high surface area electrodes based on templated and activated carbons. Such high surface area porous carbon electrodes have been fabricated utilizing biological templates\textsuperscript{59} as well as organic\textsuperscript{46, 60, 61} and inorganic templates.\textsuperscript{62} For instance, Qie et al. demonstrated, porous activated carbon electrodes possessing high surface area (> 2500 m\textsuperscript{2}/g) exhibited specific capacitance in excess of 200 F.g\textsuperscript{-1} at ultra fast scan rates of 50 A.g\textsuperscript{-1} and also excellent cycling stability (Figure 2.5).\textsuperscript{60}

However, it must be mentioned that there is no linear relationship between double-layer capacitance and surface area, as the capacitance can be limited by kinetics of ion transport as well as inaccessible surface area in the electrode. Instead, pore dimensions play an important role in the charge storage mechanism.\textsuperscript{49,50} Studies on effect
of pore size on specific capacitance have suggested materials possessing mesopores in the range of 2-50 nm to be most effective in demonstrating high surface area accompanied by high power density.\textsuperscript{63, 64} Mesopores improve ion mass transport across the pores and also provide easily accessibly electro-active area, leading to enhancement in power density and excellent cyclability.\textsuperscript{65}

Figure 2.5 Scanning electron microscopy image of (A) polypyrrole microsheets utilized as precursor to porous carbon (B) 3D hierarchically porous, high-surface area (> 2500 $\text{m}^2/\text{g}$) carbon fabricated through KOH activation (C) Specific capacitance of 3D hierarchically porous carbon electrode as a function of current density (D) Cycling stability of 3D hierarchically porous carbon electrode at current density of 5 A.$\text{g}^{-1}$ over 10,000 cycles [Reproduced with permission from Ref.60]
However, recent studies have demonstrated that partial desolvation of electrolyte ions can occur in microporous carbon electrodes allowing access to much smaller micropores (< 2 nm). As a result, larger number of ions can participate in the formation of electric double-layer across the micropore volume, leading to exponential increase of capacitance in microporous materials (Figure 2.6). The charge storage mechanism in such porous EDLCs does not involve any electrochemical conversion reactions. As a result, these capacitors provide fast energy uptake and delivery, and significantly enhanced power performance as compared to batteries.

![Figure 2.6](image)

Figure 2.6 Normalized capacitance as a function of pore size [Reprinted with permission from Ref.66, 67]

Apart from Electric Double-Layer Capacitors (EDLC), electrochemical capacitors based on faradic reactions at the electrode interface are known as Pseudo-capacitors. The Greek meaning of pseudo in case of these pseudo-capacitors refers to “not actually, but having the appearance of” a capacitor. The charge storage mechanism in such...
capacitors is primarily dominated by fast, reversible redox reactions occurring at the electrode surface. Metal oxides such as RuO$_2$, MnO$_2$, and Co$_3$O$_4$ have been extensively studied as pseudo-capacitive electrode materials. The theoretical capacitance in metal oxide electrodes is given as follows:

$$C_{\text{pseudo-capacitance}} = \frac{n \times F}{M \times V} \quad (2.2)$$

where, $n$ is the mean number of electrons transferred in the redox reaction, $F$ is the Faraday constant, $M$ is the molar mass of metal oxide and $V$ is the operating voltage window.

Figure 2.7 Comparison of specific capacitance of carbon based double-layer capacitors and metal oxide based pseudo-capacitors illustrating the superior charge storage capabilities of metal oxide electrodes [Reprinted with permission from Ref. 75].

In case of pseudo-capacitors, the surface functional groups, crystal defects and grain boundaries in metal oxides act as excellent redox sites for charge storage
The higher pseudo-capacitance of metal oxide based electrodes (300-1000 F.g\(^{-1}\)) as compared to double-layer capacitance from carbon electrodes (100-250 F.g\(^{-1}\)) has led to significant growth in this field of energy storage systems (Figure 2.7).

A common drawback associated with metal oxide pseudo-capacitors is their low electronic conductivity which limits their power density.\(^{67}\) At the same time, irreversible redox reactions at the electrode interface can also lead to poor cycling stability in such capacitors.\(^{75}\) The strain developed in the metal oxide during intercalation of ions can also lead to cracking of electrode and poor cycling stability.\(^{76, 77}\) This has given led to development of hybrid capacitors based on integrating metal oxides into porous carbon structures engineered at different dimensions.\(^{76, 78, 79}\) These hybrid capacitors combine the benefits of EDLC from carbon and pseudo-capacitance from metal oxide interfaces, providing high energy density, high power density and good cycling stability.

However, poor textural parameters (low porosity, roughness, non-uniform dispersion of metal oxide) of composite electrodes and unsupported metal oxides on carbon matrix cause inefficient supercapacitor performance. In this regard, block copolymer templated mesoporous carbon-metal oxide composites encompass an important class of electrode materials with precise control over pore dimensions and tunable chemical composition.\(^{2, 80, 81, 82, 83}\) Block copolymer templated mesoporous carbon-metal oxide composite electrodes can provide high surface area, large pore volume, easy transport paths for electrolyte ions and fast electron transfer. The mesoporous carbon structure also acts as a support for metal oxide sites and improves cycling stability of the electrode. These properties combined with the faradic redox reactions of metal oxide leads to overall enhancement in charge storage performance and
cycling stability of mesoporous metal oxide-carbon composite electrodes as compared to their bulk analog.\textsuperscript{80, 82} For instance, Jo et al. have reported fabrication of block copolymer templated mesoporous carbon-tungsten oxide hybrid electrochemical capacitors (Figure 2.8). The high surface area of these composite electrodes accompanied by low internal resistance give rise to high specific capacitance of 340 F.cm\textsuperscript{-3} at fast scan rates.\textsuperscript{84}

Figure 2.8 Scheme for fabrication of block copolymer templated ordered mesoporous carbon-tungsten oxide hybrid electrochemical capacitor [Reprinted with permission from Ref. 84].

Similarly, Dai et al. have demonstrated the synergistic effect of mesoporous carbon structure loaded with cobalt oxide nanoparticles, leading to enhancement in specific capacitance from 22 F.g\textsuperscript{-1} to 115 F.g\textsuperscript{-1} with excellent cycling stability up to 500 cycles.\textsuperscript{80} Similar to cobalt oxide, vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) is an important pseudocapacitive material exhibiting specific capacitance as high as 350 F.g\textsuperscript{-1} at high scan rates.
in aqueous electrolyte.\textsuperscript{85, 86} It undergoes the following redox reactions in aqueous electrolyte solutions-

$$V_2O_5 + 4H^+ + 4e^- \leftrightarrow H_2V_2O_5$$ \hspace{1cm} (2.3)

However, the intrinsically low electronic conductivity ($10^{-4}$-$10^{-2}$ S.cm\textsuperscript{-1})\textsuperscript{87} and poor cycling stability\textsuperscript{88} of $V_2O_5$ limits its use as high power density electrode for electrochemical capacitors. These drawbacks can be overcome by fabricating carbon-vanadium oxide composite electrodes.\textsuperscript{89, 90} Chapter 3 will discuss in the detail the fabrication of high surface area mesoporous carbon-vanadium oxide composites, with controlled nanoporous morphology for hybrid electrochemical capacitor applications. The effect of templated porosity and carbon matrix on enhancement in capacitance of mesoporous carbon-vanadia electrodes will be presented.

The key to achieving high power density and cycling stability in hybrid electrochemical capacitors will ultimately depend on development of composite electrode materials with rational design of porous structure and morphology.\textsuperscript{75}

2.1.2 Lithium ion battery

Lithium is the most electropositive (-3.04 V vs standard hydrogen electrode) and lightest metal (equivalent weight M = 6.94 g.mol\textsuperscript{-1}, specific gravity = 0.53 g.cm\textsuperscript{-3}) among the elements in the periodic table. The theoretical electrochemical capacity of Li/Li\textsuperscript{+} is 3860 mAhg\textsuperscript{-1}.\textsuperscript{42} As a result, energy storage systems based on lithium metal can theoretically provide high energy density and excellent charge storage capabilities. The first lithium ion battery prototype was developed in 1972 based on an anode consisting of lithium metal and cathode made up of electronically conductive dichalcogenide, titanium
disulfide (TiS$_2$). Electrochemical charge storage in titanium disulfide electrodes was primarily based on insertion of Li$^+$ ions between the crystal lattice planes of TiS$_2$ to form Li$_x$TiS$_2$ complex, without any redox reactions. Hence, these were termed as intercalation electrodes. However, the small operating potential window, high production cost and safety issues associated with lithium dendrite formation limited it commercial production. It took nearly two decades for Sony Corporation to commercialize the first lithium ion battery in 1991. The metallic lithium electrode was replaced by Li insertion material (such as Li$_x$MO$_2$, M= Co, Mn, Ni) to overcome issues related to dendrite formation and make these batteries safe for commercial use.

Current lithium ion batteries available commercially provide energy density almost 2-3 times higher than conventional nickel-cadmium or nickel metal-hydride batteries, making these the popular choice for use in various portable electronic devices such as cellphones, laptops, wrist watches, calculators and other consumer products. The worldwide production of lithium ion batteries in the year 2010 was worth approximately $11.8 billion, while the demand and growth is expected to exponentially increase to a market value of $53.7 billion by 2020.

Figure 2.9 illustrates the energy density of different batteries in comparison to gasoline. Lithium ion batteries clearly outperform current technologies based on lead acid or nickel based battery systems making them the primary choice of batteries for electric vehicles (EV). However, the energy density of current lithium ion batteries (~180 Whkg$^{-1}$) falls way short of the practical energy density of gasoline (1700 Whkg$^{-1}$) used in vehicles. Hence, to completely replace gasoline in vehicles, a 10 fold increase in energy density of lithium ion batteries would be required. Additionally, the light weight of
lithium ion batteries as compared to gasoline would also contribute towards significant improvement in overall fuel efficiency in electric vehicles (EVs). Hence, tremendous efforts are being devoted towards improving the electrochemical performance of lithium ion batteries through use of nanotechnology,\textsuperscript{95} optimizing electrode morphology\textsuperscript{14} as well as seeking new materials chemistry.\textsuperscript{91, 93, 96}

Figure 2.9 Gravimetric energy density of different battery systems in comparison to gasoline [Reprinted with permission from Ref. 93].

2.1.2.1 Basics concepts and principles of lithium ion battery

Lithium ion battery is a rechargeable battery consisting of three main components- positive electrode (cathode), negative electrode (anode) and an electrolyte which enables ion transport across the two electrodes. Commercial lithium ion batteries consist of a positive cathode is made up of lithium containing layered metal oxide as such lithium cobaltite (LiCoO\textsubscript{2}), lithium iron phosphate (LiFePO\textsubscript{4}) or lithium manganese oxide
The layered oxide structure allows easy Li\(^+\) ion insertion between the crystal planes. Cathodes primarily act as a source of Li\(^+\) ions and must be air-stable intercalation compounds to prevent lithium oxidation and safety concerns related to fire.\(^{38}\)

The negatively charged anode in commercial lithium ion batteries is typically made up of graphite based electrodes.\(^{94}\) The two electrodes are separated by Li\(^+\) ion conducting electrolyte solution made up of a salt of lithium hexafluorophosphate (LiPF\(_6\)) or lithium perchlorate (LiClO\(_4\)) dissolved in organic solvents such as ethylene carbonate, dimethyl carbonate or propylene carbonate. The choice of lithium salt and organic solvent depends on the dielectric constant, ionic conductivity, viscosity and operating potential window of the electrolyte, which affects the overall charge storage and rate performance of the battery.\(^{98}\)

---

Figure 2.10 Schematic of lithium ion battery illustrating movement of electrons and Li\(^+\) ions during battery charge-discharge process [Reprinted with permission from Ref. 100]
Considering the case of commercially available lithium ion cells, Li\(^+\) ions intercalate into the graphite anode and electrons are released in the external circuit during battery discharging (Figure 2.10). The opposite reaction takes place during the charging process and the overall electrochemical reactions taking place at the electrodes can be summarized as follows-

\[
6C + xLi^+ + xe^- \leftrightarrow Li_xC_6 ; (0 < x \leq 1) : \text{Anode} \tag{2.4}
\]

\[
LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- ; (0 < x \leq 1) : \text{Cathode} \tag{2.5}
\]

The charge storage capabilities of a lithium ion battery primarily depend on the chemistry of cathode and anode electrodes as well as electrolyte system used. Developing electrodes with high Li\(^+\) ion intercalation capabilities and a large electrochemical potential window allows for enhanced energy density. Cathodic electrodes based on LiCoO\(_2\) (theoretical capacity = 273 mAhg\(^{-1}\)) have been extensively studied in the past and are commercially used in lithium ion batteries as they avoid dendrite formation and are considered inherently safer compared to metallic lithium.\(^99\) Anodes used in commercial lithium ion batteries are primarily based on graphitic carbon. However, these electrode materials possess a low theoretical capacity of 372 mAhg\(^{-1}\), which is considered as a major bottleneck to develop high energy density battery systems.\(^100\) Hence, significant efforts have been directed towards developing new intercalation, alloying and conversion type anode materials whose theoretical capacities are significantly higher than those of graphitic carbons.\(^94,101\) Charge storage mechanisms in such alternate anode materials will be discussed in detail in Section 2.2. Coupled with developing new materials chemistry, fabrication of nanostructured anodes with controlled porous morphology is a promising
strategy to achieve further improvements in specific capacities over current lithium ion battery systems. \textsuperscript{10, 11, 42, 95, 102} Importance of anode nanostructure and porous morphology will be discussed in detail in Section 2.3.

2.1.3 Sodium ion battery

Lithium ion batteries are light in weight, compact and provide energy density much greater than nickel-cadmium or nickel metal-hydride batteries. However, lithium reserves in the Earth’s crust are limited to only 20 ppm.\textsuperscript{103, 104} At the same time, lithium resources are primarily located in South America, due to which import of these resources becomes necessary for global manufacturing of lithium ion batteries. This has led to almost 40\% increase in cost of these resources in the last 15 years, leading to overall rise in prices of lithium ion batteries.\textsuperscript{104} Sodium is being considered as a potential candidate to replace lithium, primarily because of its abundant availability, low cost and electrochemical redox potential which is similar to lithium (-2.71 V vs standard hydrogen electrode).\textsuperscript{104} The battery components used in sodium ion and lithium ion batteries are similar, while Na\textsuperscript{+} ion intercalation chemistry is very similar to Li\textsuperscript{+} ion intercalation. Hence, switching from lithium based batteries to sodium metal can be achieved in an economical manner. However, the gravimetric capacity of sodium (1165 mAhg\textsuperscript{−1}) is much lower than that of lithium (3829 mAhg\textsuperscript{−1}),\textsuperscript{104} due to the larger size of Na\textsuperscript{+} ion as compared to Li\textsuperscript{+} ion accompanied by lower standard reduction potential (-2.70 V vs SHE). As a result, the energy density obtained from sodium ion batteries is inherently lower than lithium ion batteries. At the same time, the larger size of Na\textsuperscript{+} ion leads to slower diffusivity as compared to Li\textsuperscript{+} ions, which results in inferior rate capabilities and longer battery charging duration. The larger size of Na\textsuperscript{+} ion also requires larger interstitial
spaces to intercalate and allow reversible Na\(^+\) ion insertion and de-insertion.\(^{12}\) The differences between lithium and sodium are presented in Table 2.1.

Table 2.1 Comparison of the chemical nature of Lithium and Sodium\(^{12}\)

<table>
<thead>
<tr>
<th>Characteristic property</th>
<th>(\text{Li})</th>
<th>(\text{Na})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation radius ((\text{Å}))</td>
<td>0.68</td>
<td>0.97</td>
</tr>
<tr>
<td>Atomic weight (g.mol(^{-1}))</td>
<td>6.9</td>
<td>23.0</td>
</tr>
<tr>
<td>(E^0) (V vs SHE)</td>
<td>-3.04</td>
<td>-2.70</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>180.5</td>
<td>97.7</td>
</tr>
<tr>
<td>Capacity (mAhg(^{-1}), metal)</td>
<td>3829</td>
<td>1165</td>
</tr>
<tr>
<td>Cost, carbonates ($/ton)</td>
<td>4000</td>
<td>120</td>
</tr>
<tr>
<td>Material abundance in Earth’s crust (ppm)</td>
<td>20</td>
<td>23,600</td>
</tr>
<tr>
<td>Distribution</td>
<td>70% in South America</td>
<td>Everywhere</td>
</tr>
</tbody>
</table>

Some of the drawbacks associated with larger Na\(^+\) ion size can be overcome by fabricating nano-architectured anodes that reduce the path length of Na\(^+\) ion diffusion.\(^{10,95}\) However, in order to develop high energy density energy storage systems based on sodium ion battery, there is a need to develop new electrode materials with controlled nano-morphology. Chapter 4 will discuss in detail how we are addressing these challenges by developing a simple and cost-effective technique to fabricate mesoporous architectured metal oxide electrodes for high-rate sodium ion battery applications.
2.2 Anode materials for Lithium/Sodium ion battery

Section 2.2 will discuss in detail different classes of anode materials utilized as electrodes in lithium/sodium ion batteries and their characteristic charge storage mechanisms.

2.2.1 Carbon based anodes

Graphite is the most common negative electrode used in lithium ion batteries. The reversible intercalation of Li\(^{+}\) ion forms LiC\(_6\) providing a theoretical capacity of 372 mAhg\(^{-1}\) in the process. The low charge storage capacity of graphite results in low volume changes (~ 10%) and excellent cycling stability depending on the current rate used. Graphitic carbon also allows rapid Li permeation and combined with its high electronic conductivity leads to excellent high rate capabilities when tested as anodes in lithium ion batteries. Similarly, nanoporous carbons possessing much higher surface area can provide much higher capacities through the formation of Li\(_2\) molecules between graphene layers, by the presence of charged Li\(^{+}\) clusters in the cavities or micropores, or through adsorption of Li\(^{+}\) ions on the surface and edges of graphite grains.

Various studies have focused on the effect of carbon nanostructure on enhanced charge storage capabilities in lithium ion battery anodes. Previous studies on use of carbon nanotubes, carbon nanofibers, graphene, ordered mesoporous carbons or hierarchically structured carbons have correlated the effect of nano-architecture, morphology and porosity on improvement in charge storage performance. In case of ordered porous carbon and three-dimensionally structured porous carbon electrodes, porosity gives rise to electrolyte transport paths and higher electro-active
surface area. As a result, the rate-limiting step in terms of chemical diffusion of Li$^+$ is avoided, providing excellent rate capabilities. Zhou et al. have reported a high discharge capacity of 850 mAhg$^{-1}$ at 100 mAg$^{-1}$ current density utilizing an ordered mesoporous carbon anode in a lithium ion battery.\textsuperscript{114} The excellent discharge capacity reported is higher than the theoretical capacity of graphite, and the enhancement in charge storage performance was attributed to the continuous electron transport paths in the three-dimensionally interconnected anode accompanied by ion transport paths.

It must be mentioned that graphite is electrochemically less active in sodium ion cells due to limited intercalation of large-size Na$^+$ ions between the graphite lattices.\textsuperscript{103, 115} However, Doeff et al. and Stevens et al. were among the first to demonstrate that disordered, soft\textsuperscript{115} and hard carbon\textsuperscript{116} anodes in a sodium ion battery can exhibit capacities similar to graphite electrodes used in lithium ion batteries. Nonetheless, these discharge capacities fall way short of the theoretical values that can be achieved using metal oxide based anodes due to limited Na$^+$ ion intercalation in the carbon framework.

2.2.2 Anodes based on alloying-dealloying reactions

These anodes are class of elements (A) or metals (M) that can alloy with Li (Li$_x$A or Li$_i$M) or Na metal and form crystal structure whose properties are different than the original materials. Anodes based on pure silicon (Si), tin (Sn), antimony (Sb), germanium (Ge) or zinc (Zn) have been extensively studied in this case as these metals are abundantly available, cheap and environmentally friendly.\textsuperscript{117} Such alloying electrodes exhibit significantly higher specific capacities as compared to graphite and titania anodes, as the charge storage mechanism involves interstitial alloying of larger number of Li$^+/Na^+$ ions between the metal crystal planes as compared to intercalation in graphite
and titania. Among these alloying compounds, silicon possesses the higher theoretical capacity of 4200 mAhg\(^{-1}\) and 954 mAhg\(^{-1}\) when tested as anode in lithium and sodium ion battery respectively.\(^{27,118,119}\) However, the large volume changes (320% on Li\(^{+}\) ion alloying and 144% on Na\(^{+}\) ion alloying) occurring during successive alloying and de-alloying process leads to pulverization of anode followed by significant capacity fade and poor cycling stability.\(^{117}\) To overcome some of these issues, intermetallic compounds (active material in inactive host) are being developed to alleviate the stresses formed during volume expansion.\(^{120,121}\) Similarly, efforts are being directed towards fabrication of carbon encapsulated composites, where the volume expansion of alloying anode is confined by the carbon matrix thereby preventing anode pulverization and improving cycling stability of the anode.\(^{122,123,124}\)

2.2.3 Metal oxide based anodes

Metal oxides can possess a variety of crystal structures with electronic behavior that may resemble an insulator, semiconductor or metallic characteristics. The diverse physical and chemical properties of metal oxides make them attractive candidates for lithium and sodium ion battery anodes.\(^{42}\) Metal oxide anodes used in lithium/sodium ion batteries primarily follow two types of charge storage mechanisms- (1) intercalation and de-intercalation and (2) conversion mechanism. Efforts to enhance the capacities of battery anodes have led to discovery of a host of metal oxide materials which possess theoretical capacities significantly higher that commercially used graphite electrodes as illustrated in Figure 2.11.\(^{125}\)

Intercalation electrodes based on transition metal oxides possess two-dimensional layered structure or three-dimensional network structure that allow Li\(^{+}/Na^{+}\) ion to
reversibly intercalate and de-intercalate between the crystal lattice planes. Titania based anodes are an important class of intercalation electrodes extensively studied in case of such anodes.\textsuperscript{126, 127, 128} A major drawback associated with titania and intercalation anodes is their low theoretical capacities (335 mAh g\textsuperscript{-1})\textsuperscript{94} as compared to other metal oxide electrodes.\textsuperscript{27}

Conversion metal oxide anodes on the other hand store charge through redox reactions and formation of an intermediate Li\textsubscript{2}O compound. The primary charge storage mechanism is related to the reversible formation and decomposition of Li\textsubscript{2}O according to the following equation-

\[ MO_x + 2xLi^+ + 2xe^- \leftrightarrow M + xLi_2O \] \hspace{1cm} (2.6)

where, M = Fe, Mn, Co, Ni, Cu and others. The multiple electron transfer reactions taking place during the redox process gives rise to high theoretical capacities in these conversion anodes.\textsuperscript{95, 116, 129} Many metal oxide and mixed-metal oxides have been explored in this field possessing high theoretical capacities (Figure 2.11).\textsuperscript{12, 94, 95, 101, 105, 129}
A common drawback associated with metal oxide anodes is their low electronic conductivity, which limits their high rate performance. At the same time, the volume expansion occurring during charging-discharging process leads to pulverization of anode and capacity fading on successive cycling.\textsuperscript{130, 131} To overcome some of these issues, carbon-metal oxide composites with controlled nano-architecture have been extensively studied.\textsuperscript{28, 79, 132, 133, 134} Composite anodes based on carbon and metal oxide can combine the advantages of long cycle life, high energy density accompanied by improved high rate performance.\textsuperscript{10, 45, 135} For instance, cobalt oxide (Co\textsubscript{3}O\textsubscript{4}) exhibits a high theoretical capacity of 890 mA\textsubscript{h}g\textsuperscript{-1} but suffers from significant volume changes leading to pulverization and capacity fade. However, Zhi et. al demonstrated a reversible capacity of 940 mA\textsubscript{h}g\textsuperscript{-1} could be achieved for over 20 cycles through fabrication of carbon coated cobalt oxide composite anodes.\textsuperscript{136} The higher discharge capacity of carbon coated Co\textsubscript{3}O\textsubscript{4}
as compared to the theoretical capacity of pure Co₃O₄ (890 mAh⁻¹) was due to the contribution of carbon towards some discharge capacity. The conformal carbon layers on cobalt oxide prevented pulverization of anode by restricting the volume expansion of oxide during the cycling process and also improved electronic conductivity of cobalt oxide, leading to enhancement in capacity. Similar carbon-metal oxide composites have been fabricated using carbon nanotubes, graphene and mesoporous carbon to improve performance of conversion metal oxide anodes. In each case, the role of carbon in enhancing electronic conductivity of composite and preventing pulverization of oxide anode during volume expansion has been highlighted.

2.3 Mesoporous metal oxide anodes

Mesoporous materials according to IUPAC definition are materials possessing pore size in the range of 2-50 nm. Materials with pore size smaller than 2 nm are referred to as microporous materials, while materials possessing pores larger than 50 nm are defined as macroporous materials (Figure 2.12). Mesoporous materials possess combination of unique properties such as high porosity, high surface area, interconnected nanoporous morphology and low density, which makes them ideal candidates for electrodes in electrochemical capacitors and lithium/sodium ion batteries. When tested as electrodes in energy storage devices, the mesoporous morphology provides transport paths for electrolyte ions and easy access to the electrode surface. The nano-dimension of mesoporous electrode also facilitates charge transfer across the electrode-electrolyte interface.
Fabricating ordered mesoporous anodes utilizing block copolymer templating is one strategy that has been extensively studied. Precise control over pore morphology, pore size, porosity or nano-dimensions of matrix wall are some of the advantages that makes block copolymer templating strategy very popular. Fabrication of block copolymer templated ordered mesoporous electrodes has permitted drawing correlations between porosity and pore geometry on electrode performance. For instance, Ren et al. demonstrated that in case KIT-6 templated mesoporous $\beta$-MnO$_2$ anodes possessing the same pore dimensions, increasing the oxide wall thickness led to inferior Li$^+$ ion charge storage capabilities at varying current densities. Similarly, Lin et al. demonstrated the shorter pore length and small nanoparticle size in SBA-15 templated $\text{Co}_3\text{O}_4$ mesoporous anodes led to enhancement in discharge capacities when tested in lithium ion batteries. However, drawing such conclusions using non-ordered porous anodes would not have been possible. Apart from control over pore geometry and surface area, the interconnected mesoporous structure also accommodates the volumetric stress.
developed in the metal oxide anode during lithium/sodium ion battery operation.\textsuperscript{147}, \textsuperscript{148} Feng et al. have reported 50% improvement in discharge capacity and cycling stability of ordered mesoporous Li-Mn-O spinel electrode as compared to its bulk analog.\textsuperscript{148} The enhancement in cycling stability was attributed to the ordered 3D mesoporous structure that can accommodate the strain associated with lithium intercalation process.\textsuperscript{148} However, the evolution of mesopore morphology during battery operation and underlying mechanisms contributing towards enhanced charge storage in mesoporous metal oxide anodes is not clearly understood. Insights into the evolution of pore geometry during battery operation and its effect on cycling stability of mesoporous metal oxide anodes will be discussed in great detail in Chapter 6.

The dimensions of mesoporous metal oxide wall thickness play a very important role when testing these porous materials as anodes in lithium/sodium ion battery. Charge storage mechanisms in lithium/sodium ion battery anodes involve Li$^+$/Na$^+$ ion diffusion and electronic conduction processes, which occur simultaneously. The characteristic time ($\tau$) required for lithium/sodium ion diffusion in host anode is represented as follows-

$$\tau = \frac{L_{ion}^2}{D_{Li/Na}} \quad (2.7)$$

where, $L_{ion}$ is lithium/sodium ion diffusion length and $D_{Li/Na}$ is the lithium/sodium ion diffusion co-efficient. The lithium/sodium ion diffusion co-efficient depends on the nature of the host anode material.\textsuperscript{10} For instance, the lithium-ion diffusion co-efficient in LiCoO$_2$ is $10^{-11}$-$10^{-10}$ cm$^2$ s$^{-1}$, while in case of graphite anode it varies from $10^{-11}$-$10^{-9}$ cm$^2$ s$^{-1}$.\textsuperscript{10}
Figure 2.13 (A) Schematic of charge transfer process occurring in a porous electrode and the importance of nano-dimension in reducing Li\(^+\) ion diffusion time\(^\text{10}\) (B) KLE-templated ordered mesoporous Li\(_4\)Ti\(_5\)O\(_{12}\) anode possessing nano-dimension matrix demonstrating excellent capacity retention and high C-rate and performance [Reproduced with permission from Ref. 10 and Ref. 143].

As can be seen in equation 2.7, the characteristic time required for Li\(^+\)/Na\(^+\) intercalation in anode varies proportionally to the square of the diffusion length. Hence, reducing the dimensions of the redox-active anode reduces the effective Li\(^+\)/Na\(^+\) ion diffusion length and can help charging of anode materials at a faster rate. Utilizing block copolymer templating strategy, the mesoporous metal oxide wall thickness can be easily tuned in the nano-dimension. As a result, these templated and ordered porous materials exhibit excellent high-rate performance when tested as anodes in lithium/sodium ion batteries (Figure 2.13).\(^\text{15, 32, 45, 141}\) The contribution of nanoporous metal oxide morphology towards improved high-rate performance of sodium ion battery anodes will be discussed in detail in Chapter 4.

As mentioned in Section 2.2.3, the inherently low electronic conductivity of metal oxide anodes leads to inferior charge storage capabilities at high current densities (high
C-rates) in lithium/sodium ion batteries. Hence, significant efforts are being directed towards fabricating block copolymer templated ordered mesoporous carbon-metal oxide composites. Block copolymer templating allows easy control over metal oxide pore dimensions, pore geometry, oxide wall thickness as well as control over porosity. To improve the electronic conductivity of metal oxide, ideally carbon black is used along with the metal oxide to form a percolating conductive network. However, carbon phase can also be directly integrated with the redox active metal oxide in a single step process utilizing resol-assisted block copolymer templating methods.\(^{29, 141, 145}\) This allows for fabricating highly porous and conductive carbon-metal oxide composite electrodes in a simple one-step process.

The advantages associated with block copolymer templated mesoporous carbon-metal oxide composite anodes can be summarized as follows-

- High porosity of templated composite anodes provides efficient electrolyte transport through the anode
- High surface area of porous electrode facilitates charge transfer across electrode-electrolyte interface, enhancing charge storage capabilities of the electrode
- Nano-dimension matrix reduces the transport path for Li\(^+\) ion allowing faster charging rates
- Nanosized metal oxide particles that make up the composite matrix can suppress irreversible phase transformations that occur in microcrystalline anodes
- Interconnected nanoporous morphology accompanied by carbon matrix provides strain relief to metal oxide volume expansion during the cycling process
• Carbon present in the composite increase the inherent electronic conductivity of the composite enhancing the charge transfer capabilities of the anode

• Mesoporous carbon-metal oxide composite anodes can be utilized as binder-free anodes

Ordered mesoporous metal oxide composites are fabricated either using Hard-templating or Soft-templating strategies. These templating methods will be discussed in greater detail in Section 2.3.1 and 2.3.2.

2.3.1 Hard-templating of mesoporous metal oxide composites

Hard-templating strategy involves use of porous “hard” inorganic templates such as zeolites, alumina, silica or carbon. The Mobil Composition of Matter (MCM) “hard” silica templates were the first family of mesoporous templates fabricated using a surfactant-assisted synthesis strategy called liquid-crystal templating. The discovery of these interconnected and ordered porous silicates with controlled pore geometry paved the path for discovery of various other hard-templates such as Santa Barbara Amorphous (SBA-15, SBA-16), KIT-6, FDU-12 and CMK-6 based templates. Since the first report on these MCM-type mesoporous silicates, various reports have emerged on the fabrication of mesoporous metal oxide composites using hard-templating strategies.
Figure 2.14 Schematic of hard-templating pathways to fabricate mesoporous oxides with (A) cylindrical (MCM-41) and (B) cubic geometry (MCM-48) [Reprinted with permission from Ref. 4].

Hard-templating is a confined-space assembly approach and involves replicating the topological structure of the host to derive the guest replica.\textsuperscript{154} Hard-templating strategies are also called nanocasting, exotemplating or repeated templating.\textsuperscript{155} The basic process involves infiltrating the hard-templates with metal ion precursors using sorption, phase transition, ion exchange or covalent grafting (Figure 2.14).\textsuperscript{156} The infiltration step is followed by heat treatment to thermally decompose the metal ion precursors and form hard-template infiltrated metal oxide. The thermal treatment step also causes the metal oxide nanoparticles to grow in size, interconnect during the heating process and form a continuous framework. Finally the hard-template is removed by chemical etching to obtain interconnected mesoporous metal oxide structures. Zhu et al. reported for the first time the use of SBA-15 hard-templates to fabricate mesoporous Cr$_2$O$_3$ in 2003.\textsuperscript{157} Since then, there have been multiple reports of mesoporous metal oxide and mixed-metal oxide fabrication utilizing hard-templating pathways.\textsuperscript{151, 153, 158, 159}
An advantage of hard-templating strategy is the ability to precisely control the pore geometry of templated mesoporous metal oxides by tuning the pore size and wall thickness of hard-template. For instance, Rumplecker et al. developed methodologies to precisely control the mesopore size and wall thicknesses of mesoporous Co$_3$O$_4$ utilizing different KIT-6 templates. However, to effectively template the mesoporous metal oxide, it is important to achieve efficient and complete infiltration of hard-template with precursor solution. Hence, the hydrogen bonding, coulombic, coordination and Van der Waals interactions between the hard-template and metal ion precursor need to be carefully tuned to efficiently infiltrate the template. Similarly, hard-templating strategy involves multiples steps such as hard-template synthesis, metal ion infiltration, calcination, which is then followed by silica dissolution using HF solution or carbon template oxidation. To overcome the disadvantages of multi-step hard-templating synthesis strategy and develop a simple, single-step fabrication method served as a major motivation for use of soft-templated synthesis protocols.

2.3.2 Soft-templating of ordered mesoporous metal oxide composites

Soft-templating strategy involves use of “soft” precursor species such as organic surfactants, virus or block copolymers. Soft-templating strategy to fabricate ordered mesoporous metal oxides relies on the cooperative assembly of soft-templates like block copolymer surfactants and inorganic species. Various ionic as well as non-ionic amphiphilic block copolymer surfactants have also been used to template ordered mesoporous metal oxide composites. Block copolymer templating is considered a simple approach to fabricate ordered mesoporous materials because the pore shape, geometry and pore size can be easily controlled based on quantity of the inorganic
species present, molecular weight of block copolymer template and by tuning their interactions with the templating surfactant.

The first report on synthesis of soft-templated mesoporous materials was based on fabrication of MCM-41S family of mesostructured silica. However, the first report on fabrication of ordered mesoporous transition metal oxide (TiO$_2$) utilizing long chain alkylamine surfactant was reported by Ying et al. This study was soon followed by reports on fabrication of surfactant templated ordered mesoporous niobium oxide (Nb$_2$O$_5$) utilizing a ligand-assisted templating method. Following these reports, various studies on synthesis of ordered mesoporous metal oxides fabricated using commercially available poly(alkylene oxide) block copolymers and Evaporation Induced Self-Assembly (EISA) mechanism were reported. Using the principles of EISA technique, the pioneering work carried out by Brinker et al. led to success in the synthesis of ordered mesoporous silica thin films and metal oxide thin films.

The basic mechanism of EISA involves initially controlling the interactions between the hydrophilic block of the soft-template surfactant and inorganic moiety via chemical or hydrogen bonding in the homogenous solution. The block copolymer surfactant concentration ($C_0$) in the homogenous solution stage is below the critical micellar concentration ($C_0 < CMC$). As the volatile solvent in the homogenous system begins to evaporate, surfactant concentration gradually increases above the CMC concentration leading to formation of self-assembled mesostructures. Progressive increase in surfactant concentration drives self-assembly and organization of inorganic species and block copolymer into liquid crystalline mesophases (Figure 2.15).
Figure 2.15 Schematic of Evaporation Induced Self-Assembly (EISA) process during formation of mesoporous metal oxide thin films using amphiphilic block copolymers as soft-templates [Reproduced with permission from Ref.176].

Thermal treatment of these inorganic-surfactant mesostructures at high temperatures leads to consolidation of framework, template degradation and removal followed metal oxide crystallization. The strategy can be utilized for fabrication of mesoporous metal oxide monoliths as well ordered mesoporous thin films. Combining chemical solution deposition techniques (dip coating or flow coating) along with EISA, variety of ordered mesoporous metal oxide and mixed-metal oxide thin films fabrication has been demonstrated.

The EISA method has also been extensively used to fabricate ordered mesoporous carbons and mesoporous carbon-metal oxide composites. A recent study by Schuster et al. has reported that ordered mesoporous carbon formation
follows Thermally-Induced Self-Assembly mechanism rather than EISA. Carbon precursors such as phenolic resin (resol), resorcinol-formaldehyde or furfuryl alcohol are commonly added during the self-assembly process to fabricate mesoporous carbon-metal oxide composites. These hydrophilic precursors provide high carbon yield (~ 55%) on calcination under inert environment, which makes them ideal candidates as carbon precursors. By controlling the relative concentrations of inorganic species and surfactant concentration, the block copolymer interface can be tuned to fabricate variety of ordered mesostructures varying from cubic (spherical pores), 2D hexagonal (cylindrical pores), gyroidal or wormlike (elongated pores). The pore size in such composites can also be controlled based on the molecular weight of the block copolymer template or by using various pore expanders like 1,3,5-trimethylbenzene (TMB). Hydrophobic pore expanders such as TMB reduce the curvature of block copolymer-resol composite or block copolymer-inorganic species, increase relative hydrophobic volume fraction and thereby increase the pore size of the mesostructure. Chapter 3 will discuss in detail the synthesis of ordered mesoporous carbon-vanadium oxide composites fabricated using sol-gel chemistry combined with block copolymer templating.

Figure 2.16 Schematic of CASH process to fabricate highly crystalline ordered mesoporous metal oxides [Reprinted with permission from Ref. 145]
However, block copolymer self-assembly combined with sol-gel chemistry requires precise control over various parameters such as pH of the solution, moisture, temperature, condensation and reaction times, interactions of inorganic precursor with organic polymer template and aging times.\textsuperscript{154, 168} Uncontrolled condensation rates can lead to “freezing” of mesostructure with no mechanical integrity of inorganic framework on template removal.\textsuperscript{168, 181} This can lead to collapse of inorganic mesostructure during the thermal treatment stage. Also, commonly used Pluronic (PEO-PPO-PEO) block copolymer soft-templates decompose at low temperatures (200 °C-350 °C) and possess limited mechanical integrity, which leads to collapse of ordered mesostructure due to growth of metal oxide crystals through the mesopores during the crystallization stage.\textsuperscript{19} To overcome some of these disadvantages, Lee et al. developed the Combined Assembly by Soft and Hard (CASH) chemistries approach (Figure 2.16). This synthesis strategy involves use of block copolymer surfactant (such as PI-$b$-PEO or PEO-$b$-PAN), in which the hydrophobic block contains a sp$^2$-hybridized carbon. Cooperative self-assembly of block copolymer with inorganic species followed by calcination at high temperatures leads to \textit{in-situ} formation of carbon yield due to thermal decomposition of the hydrophobic block.\textsuperscript{145, 182} This carbon yield provides additional mechanical integrity to the ordered structure and can prevent metal oxide crystallization through the mesopores, allowing fabrication of highly crystalline ordered mesoporous metal oxides.\textsuperscript{145, 183}
Using the CASH strategy, ordered mesoporous carbon-metal oxide composites or highly crystalline metal oxides can be synthesized in a single step. However, the success of this method depends on the complex chemistry involved in synthesizing sp\(^2\)-hybrized carbon containing block copolymer template. Eckhardt et al. developed a simpler and scalable approach to fabricate highly ordered mesoporous metal oxide composites using block copolymer micelle templating (Figure 2.17).\(^{184,185}\)

Block copolymer micelle templating strategy can be considered as a combination of three processes- initial steps of metal ion complex formation using Pechini method, metal carbonate thermal decomposition and pore templating using block copolymer micelle templates.\(^{184}\) Block copolymer soft-template used is usually an amphiphilic surfactant capable of forming spherical micelles in solution. This templating strategy involves use of metal nitrate and citric acid that form chelate complexes of metal ions following the Pechini method,\(^{186}\) and interact with the hydrophilic shell of the block copolymer micelle through hydrogen bonding in solution. Slow evaporation of volatile organic solvent from the solution drives self-assembly of block copolymer surfactant
micelles into ordered mesostructures dispersed in a matrix of metal nitrate-citric acid complex.\textsuperscript{184, 185} An important step in this synthesis strategy involves formation of an intermediate metal carbonate through the thermal reaction of metal nitrate and citric complex. This intermediate metal carbonate “freezes” the morphology and provides mechanical integrity to the ordered mesostructure even beyond the decomposition temperature of the block copolymer surfactant.\textsuperscript{187} On heating the micelle templated metal carbonate composite beyond the thermal decomposition temperature of organic block copolymer, well-ordered mesoporous metal carbonate and metal oxide nanostructures can be fabricated.

In case of block copolymer self-assembly combined with sol-gel processing of inorganic species, the relative rates of surfactant self-assembly and hydrolysis/condensation rates of inorganic species have to be controlled to obtain well ordered mesostructures. As block copolymer micelle templating decouples these two stages of surfactant self-assembly and mesostructure reinforcement through an intermediate metal carbonate formation stage, it is considered as an easier technique to synthesize ordered mesoporous metal oxide composites. This method can also be generalized to fabricate variety of ordered mesoporous metal oxide and mixed-metal oxide nanostructures with controlled pore geometry.\textsuperscript{184, 188, 189, 190} However, only spherical mesostructures have been fabricated using this methodology till date\textsuperscript{179, 184, 187} due to limited choice of solvents that permit dissolution of metal nitrate, citric acid and surfactant without forming spherical micelles in solution.

Block copolymer micelle templating strategy does not require synthesizing block copolymer templates with complex chemistry or difficult synthesis procedures. An
amphiphilic surfactant, containing a hydrophilic block capable of hydrogen-bonding and forming micelles in solution can be used to effectively template a variety of mesoporous metal oxides. Chapter 4 will discuss in detail the extension of block copolymer micelle templating strategy to fabricate ordered mesoporous mixed-metal oxides and their application in energy storage devices. Using this strategy, the drawbacks associated with sol-gel processing of two metal oxide precursors and long aging times can be avoided. In chapter 5, this strategy will be further extended to fabricate highly porous, high surface area inorganic nanofiber composites.
CHAPTER III
MESOPOROUS CARBON-VANADIAUM OXIDE FILMS BY RESOL-ASSISTED, TRIBLOCK COPOLYMER-TEMPLATED COOPERATIVE SELF-ASSEMBLY

3.1 Introduction

Significant efforts\textsuperscript{19, 44, 191} have increased the chemical diversity\textsuperscript{16} of soft templated, ordered mesoporous materials, since the original report of the Mobil Composition of Matter (MCM)\textsuperscript{1} family of silicate materials. However, the scalable synthesis of well-defined mesoporous materials with highly crystalline frameworks under high temperature processing conditions remains challenging.\textsuperscript{192} Commercially available organic templates, such as Pluronic\textsuperscript{®} poly(ether) triblock copolymers, generally decompose prior to significant inorganic framework crystallization, leading to losses in templated porosity as the crystals break out and grow through the pores.\textsuperscript{193} Thus, most frameworks in mesoporous materials are at best semi-crystalline with numerous grain boundaries,\textsuperscript{16, 25, 166} which limits their electronic and electrochemical applications.\textsuperscript{194} Hard templating\textsuperscript{195} by mesoporous silica\textsuperscript{160} or carbon\textsuperscript{196} provides a means of increasing crystallite size and overall crystallinity, yet the increased time and costs associated with template synthesis and its post-processing removal render this method inefficient.
The poorly crystalline framework of a mesoporous material may be alternatively coated with carbon and silica for elevated temperature crystallization without loss of porosity, again at increased time and expense.\textsuperscript{197} Wiesner and coworkers pioneered the Combined Assemblies of Soft and Hard chemistries (CASH) methodology for mesoporous metal oxide synthesis, in which inorganic framework crystallization breakout into the mesopores is physically prevented by carbon derived from the block copolymer template.\textsuperscript{145} Thus, the CASH method enables the synthesis of a broad variety of mesoporous transition metal oxides.\textsuperscript{198} For example, a titania sol templated by a poly(isoprene-\textit{b}-ethylene oxide) (PI-\textit{b}-PEO) copolymer was calcined under argon to effectively crystallize TiO\textsubscript{2} with the mesostructure protected during crystallization by carbon generated \textit{in-situ} from the PI segment of the template.\textsuperscript{145} Calcination under air instead led to loss of porosity due to full degradation of the block copolymer and subsequent titania sintering.\textsuperscript{193} In spite these advances afforded by the CASH method, most reports of ordered mesoporous metal oxides with highly crystallizable frameworks have focused on low temperature calcination/crystallization\textsuperscript{199} or alternative processing techniques, such as microwave-assisted synthesis\textsuperscript{126} and the addition of nucleation aids,\textsuperscript{200} to mitigate loss of porosity by breakout crystallization.

Ideally, the CASH method\textsuperscript{3} should furnish robust route for generating thin carbon coatings on the desired framework chemistry to generate well defined metal oxide-carbon composites. These metal oxide-carbon composites are particularly promising for electrical energy storage applications.\textsuperscript{2, 80, 133, 201} For example, introduction of low concentrations of vanadia (< 20 wt\%) into mesoporous carbon dramatically increases its supercapacitor performance.\textsuperscript{80} Vanadium oxide electrodes also exhibit low electrical
conductivities and poor cycling stabilities, which may be ameliorated by the formation of carbon-vanadia composite electrodes.

The transformation of soft templated vanadia into an ordered mesoporous structure is challenged due to the low temperature crystallization of vanadium oxide at ~250 °C under an inert atmosphere. A rapid calcination protocol can overcome this limitation to retain the mesoporous vanadia structure using a poly(ethylene oxide-\textit{b}-polystyrene) (PS-\textit{b}-PEO) template that yields large pore sizes (30–35 nm). More recently, multicomponent mixtures comprising a metal oxide sol, a block copolymer template, and the carbonizable precursor resol provide a route to fabricate high porosity mesoporous materials of easily crystallizable metal oxides even upon elevated temperature processing. In this case, the resol provides carbon yield in the framework, not just at the interface with the template as in the standard CASH method. However, access to ordered mesoporous materials with significantly higher concentrations of vanadium oxide poses the significant challenge of maintaining porosity upon template removal. For example, addition of vanadium oxide in excess of 35wt% induces partial macrophase separation of the inorganic components from the block copolymer template.

Herein to address these limitations, we examine the efficacy of the CASH method for generating mesoporous carbon-vanadia composite films using vanadium (V) oxychloride and poly(ethylene oxide-\textit{b}-1,4-butadiene-\textit{b}-ethylene oxide) (OBO) triblock copolymer as the template, whereby the \textit{B} segment provides the carbon yield requisite for CASH. As an alternative, the tri-constituent cooperative assembly of an OBO triblock with both resol and \text{VOCl}_3 is shown to significantly increase the carbon content in the
final product, simply by tuning of the VOCl₃:resol ratio in the precursor solution (as a resol-assisted CASH method). We find that preservation of the templated mesostructure during elevated temperature calcination sensitively depends on the judicious choice of calcining environment: nitrogen or argon. Calcination under nitrogen leads to the greatest mesostructure retention upon inclusion of resol in the synthesis, while argon leads to a complete loss of the templated mesostructure at high temperatures. Through structural, chemical and thermal analyses of the films, we show that this calcination environment-dependent morphology difference stems from the ready carbothermal reduction of the vanadia in argon. Under a nitrogen atmosphere, vanadia carbothermal reduction is apparently inhibited by the formation of a small fraction of a vanadium oxynitride that leads to mesostructure retention even upon heating to 800 °C. This mesoporous morphology significantly improves the electrochemical capacitance of the resulting vanadium oxide-carbon composite in NaSO₄ (aq) at high rates as determined by cyclic voltammetry. Thus, resol-assisted assembly of the vanadium oxide preserves the block copolymer-templated mesostructure at elevated temperatures in a manner unachievable with the CASH method alone.

3.2 Experimental Section

**Materials:** Phenol (>99%), formaldehyde (ACS reagent, 37 wt% (aq) with 10-15% methanol stabilizer), NaOH (ACS reagent, >97%), conc. hydrochloric acid (ACS reagent, 37 wt% (aq)), vanadium (V) oxychloride (99%), 2-butanol (ACS reagent, >99 %) were purchased from Sigma-Aldrich and used as received. Chloroform (Technical grade, 0.75% ethanol preservative) was purchased from Fisher Scientific.
To template the mesostructure, poly(ethylene oxide-\textit{b}-1,4-butadiene-\textit{b}-ethylene oxide) (OBO) triblock copolymer with $M_n = 16$ kg/mol and $f_{\text{PEO}} = 0.36$ was used. The synthesis of this block copolymer was previously reported.\textsuperscript{205} While this block copolymer has a broader dispersity $D = M_w/M_n = 1.46$ than typical copolymer templates, this material generates a well-defined nanoscale morphology. We note that broad copolymer dispersity results in increased domain sizes for the center $B$ block even at low molecular weights.\textsuperscript{206}

For the carbonizable precursor, phenol and formaldehyde were condensed using NaOH to form a low molecular weight, thermally cross-linkable Resol phenolic resin as described previously.\textsuperscript{46} The reaction mixture was neutralized using 1M HCl(\textit{aq}) to $\sim$ pH 7. Water was removed from the synthesized resol by rotary evaporation at 46 °C under vacuum. The resulting liquid resol was dissolved in 2-butanol to yield a 20 wt\% solution, and any precipitated NaCl(\textit{s}) was removed from the solution using a 0.45 \textmu m glass filter.

Silicon wafers (Silicon, Inc.) were used as substrates and were cleaned using ultraviolet (UV) ozone (Jelight, model no. 42) for 1 h prior to use. Two different silicon wafers were used depending on the experiment. For FTIR measurements, high resistivity ($>10$ $\Omega\cdot$cm), 500 \textmu m thick double side polished Si wafers were used, while cyclic voltammetry measurements employed highly conductive 600 \textmu m thick silicon wafers (resistivity = 0.01-0.02 $\Omega\cdot$cm).

**Sample Preparation:** Films were prepared by first dissolving 20 mg of OBO triblock copolymer in 2 ml CHCl$_3$ at 22 °C. For the CASH method, 75 mg of VOCl$_3$ was added slowly to 0.15 g 2-butanol and stirred for 10 min, after which 2 ml CHCl$_3$ solution containing 20 mg of OBO copolymer was passed through a 0.45 \textmu m glass filter and
added to the vanadia sol. After aging the sol gel solution for 1 h, thin films were cast by flow coating$^{207}$ at 40 mm/s and a relative humidity of ~ 30-40%. For resol-assisted assembly, 20 mg of VOCl$_3$ was added slowly to 0.2 g of 20 wt% resol in 2-butanol and stirred for 10 min in a separate vial. After 10 min, 2 ml CHCl$_3$ solution containing 20 mg of OBO copolymer was passed through a 0.45 μm glass filter and added to the resol-vanadia sol. The final mass ratios of the solids, resol:VOCl$_3$:OBO copolymer was fixed at 2:1:1 for all films shown here. This solution was subjected to continuous vigorous stirring for 1 h at 22 °C prior to film casting. Thin films were then immediately cast from the solution by flow coating$^{207}$ at 40 mm/s and a relative humidity of ~ 30-40%.

All coated films were allowed to age for 10-12 h at ambient temperature and humidity (~30-40% RH). Subsequently, all the films were heated at 120 °C for 24 h. The purpose of this heating is to crosslink the resol following prior protocols,$^{46}$ but all films irrespective of resol content were processed identically for consistency. The template was removed by calcination in a tube furnace (SentroTech Corp.) with a gas purge of either nitrogen (Praxair, Industrial Grade, [O$_2$] < 5 ppm) or argon (Praxair, Grade AR5.0 UH, [O$_2$]< 1 ppm) at 100 mL/min. The heating schedule for template removal was an initial ramp to 350 °Cat 1°C/min and a 2 h hold at 350 °C, followed by heating at 1°C/min to the final target temperature with an additional 1h hold at that temperature. Samples were then cooled to ambient temperature at 1°C/min. Three different target temperatures were used to fabricate mesoporous polymer-vanadium oxide (450°C) or carbon-vanadium oxide thin films (600 °C or 800 °C). We use the sample nomenclature “CV-x-y”, where CV denotes the carbon-vanadia composite, $x$ denotes the target temperature and $y$ represents the gas environment used: nitrogen (N$_2$) or argon (Ar). For thin films cast
following the CASH method without any resol, an analogous heating protocol in an Ar environment was employed. These thin films are named as CASH-x-Ar, using the previously described convention.

**Characterization:** Spectroscopic ellipsometry (M-2000, J.A. Woollam) was used to elucidate the thickness and refractive index of the films after each processing step. Ellipsometric porosimetry (EP) was used to assess the porosity and pore size distribution of the composite thin films. Toluene was used as the probe solvent for EP. The change in refractive index as a function of the partial pressure of toluene was monitored by *in-situ* ellipsometry, where the sample is contained in a cell with quartz windows at 70° relative to the normal. The pore size distribution was estimated using the Kelvin equation for the adsorption isotherm.\(^{208}\) The surface morphology was also investigated at each step (as cast, thermopolymerized, and calcined) using atomic force microscopy (AFM, Dimension ICON, Veeco). Grazing incidence small angle X-ray scattering (GISAXS) was performed at beamline 8-ID-E at the Advanced Photon Source (APS) of Argonne National Laboratory and the X9 beamline of National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). At APS, the films were illuminated with 7.35 keV radiation at incident angles (\(\alpha_i\)) of 0.1°–0.2° under vacuum; the off-specular scattering was recorded with a Pilatus 1MF pixel array detector (pixel size = 172 μm) with a sample-to-detector distance of 2175 mm. At NSLS, an incident X-ray beam of energy of 13.5 keV was used and scattering data were collected using a charged-coupled device (CCD) detector at a distance of 4.73 m. All samples under vacuum (≈40 Pa) were measured at multiple angles both below and above the critical angle. The crystal structures of the films were assessed with grazing incidence x-ray diffraction (GIXD).
GIXD was carried out at NSLS using incident X-ray energy of 13.5 keV and the scattering data was collected on a CCD detector. Complementary real space images were obtained by transmission electron microscopy (TEM) using a JEOL JEM2100F microscope in both bright- and dark-field imaging modes. The TEM samples were prepared using the focused ion beam (FIB) *in-situ* lift-out specimen technique.\(^{209}\) Additionally, nitrogen calcined films were scrapped off from the silicon wafer and pulverized into fine powder. The powdered sample was dispersed in ethanol solvent and subjected to ultrasonication, followed by transferring onto a carbon coated copper grid. Transmission electron microscopy (TEM) was performed on a Tecnai G2 20S-TWIN apparatus at an accelerating voltage of 200 kV.

To investigate the carbon and vanadium oxide contents in the calcined composites, we performed thermogravimetric analysis on crushed powders of resol and vanadium oxide composites. Crushed powders were prepared by first forming a sol of resol and VOCl\(_3\), having the same initial composition as that used for casting thin films; the only difference being the absence of the OBO block copolymer template in the sol. This sol was poured into a dish and the solvent was allowed to evaporate at 22 °C for 8-10 h, followed by thermopolymerization of resol at 120 °C for 24 h. Thermogravimetric analysis (TGA, TA Instruments, TGA-Q50) was performed on these thermopolymerized resol-vanadia powders with either nitrogen or argon purge over a temperature range of 22–800 °C. The heating schedule (rate and hold) for these TGA measurements was identical to that used for the fabrication of the films described previously. These carbonized powders were subsequently analyzed with an air purge to determine the
vanadium oxide content of the materials after carbonization at a heating rate of 10 °C/min.

In order to assess the chemical composition of the calcined composite thin films, X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa probe II scanning XPS microprobe, ULVAC-PHI Inc.) with high-resolution scans at energies associated with C1s, O1s and V2p was performed using 0.05 eV step size and pass energy of 11.75 eV. The scans were recorded at a take-off angle of 45°, probing approximately 10 nm into the surface of the thin films. The peaks associated with V2p were deconvoluted using peak fitting (IGOR Pro, Wavemetrics) in order to determine the oxidation states of vanadium in the films. Additionally, FTIR spectra (Thermo Scientific, Nicolet iS50 FT-IR) were obtained in transmission mode on the thin films using 256 scans with a resolution of 4 cm⁻¹ using a DeuteratedTriGlycine Sulfate (DTGS) detector. Spectra were baseline corrected using the OMNIC software.

The electrical conductivity of the carbon-vanadium oxide thin films was determined by four-point probe measurement (Pro-4, Lucas Labs) with a Keithley Series 2400 Source Meter. The spacing between the pins on the probe head was 0.04 inch. The electrical conductivity was corrected for the film thickness using typical geometric arguments. In order to assess the electrochemical capacitance of the films, cyclic voltammetry using a three-electrode cell with Pt wire as the counter electrode and Ag/AgCl as the reference electrode was performed with a CHI630 electrochemical analyzer (CH Instruments). The cyclic voltammetry experiments used 1 M Na₂SO₄ (aq) as the electrolyte at ambient temperature and the impact of scan rate (2-100 mV/s) on charge storage was investigated. The apparent capacity of the CV-800-N₂ film was
compared to the capacity of a non-templated, non-porous film prepared using identical processing conditions without the OBO triblock.

3.3 Results and Discussion

Figure 3.1 illustrates the change in the surface morphology of films at various stages of the fabrication process following the CASH protocol (without any addition of resol). Initially, the OBO triblock leads to poorly defined micelles templated into the vanadia composite (Figure 3.1a). The templated structure lacks any long range order, yet a common length scale of ~ 24 nm associated with the microphase separation of the OBO template is observed in the as-cast films.

Figure 3.1 AFM phase images of OBO triblock-templated polymer-vanadia thin film (a) as cast, and after calcination in (b) Ar (CASH-450-Ar), (c) N₂ (CASH-450-N₂), and (d) in
air at 450 °C. The mesostructure in the as-cast composite film is not preserved upon template removal, irrespective of calcining environment (scale bar – 200 nm).

Calcination in an argon environment per the standard CASH protocol\textsuperscript{145} leads to loss of this nanostructure at 450 °C (CASH-450-Ar), as shown in Figure 3.1b. This CASH protocol leads to formation of large vanadia crystals that are approximately 60-75 nm across, which are significantly larger than in the original templated structure. This loss of the templated morphology suggests that the CASH method is incapable of preventing break-out crystallization in this system.

OBO triblock-templated vanadia thin films instead calcined under N\textsubscript{2} at 450 °C exhibited a similar loss of mesostructure (Figure 3.1c). The thermal stability of the OBO template in Ar and N\textsubscript{2} environments is found to be similar, with a degradation onset temperature of approximately 400 °C (Figure 3.2(c,d)). In spite of the similar degradation behaviors of OBO template under both Ar and N\textsubscript{2}, the size of the evolved vanadia crystals on the surface is significantly smaller using N\textsubscript{2} (35-50 nm) as opposed to Ar (60-75 nm). Moreover, direct calcination in air leads to significantly larger crystals at the same processing conditions (Figure 3.1d), implying that there is some suppression in the crystal growth in the ‘inert’ atmospheres with the N\textsubscript{2} being surprisingly more effective. Nonetheless, the structure templated by the OBO triblock is lost in all cases on calcination at 450 °C, even when following the CASH protocol.\textsuperscript{145}

Previous work has demonstrated similar loss of surfactant-templated mesostructure on calcination of vanadia-based systems. This destruction of the mesostructure on template removal is attributed to the low-temperature crystallization of
vanadium oxide and the associated break-out crystallization that is accompanied by collapse of the porous mesostructure.\textsuperscript{24, 25} However, the CASH method\textsuperscript{145} is designed to prevent this crystallization break-out through \textit{in-situ} carbon generation ("carbon yield") that leads to hard templating of the metal oxide component.\textsuperscript{198} The failure of CASH under these circumstances suggests that the carbon yield is insufficient for effective templating. Therefore, we reasoned that introduction of an additional component that would enhance the carbon yield upon thermal treatment in the CASH process might enable more effective hard templating to produce mesoporous vanadia films. Consequently, we devised a resol-assisted multi-component assembly, wherein resol serves as a precursor that enhances the carbon yield to provide a more effective template.

Figure 3.2 AFM phase image of tri-constituent OBO triblock template, resol and vanadia composite (a) as cast film exhibiting spherical micelles ~26 nm in diameter, and (b) upon calcination in air at 450 °C, leading to loss of the ordered mesostructure (scale bar –350 nm). TGA trace for (c,d) the OBO triblock copolymer template in Ar (red) and N\textsubscript{2} (blue) indicating similar degradation behavior with complete degradation of template at 475 °C. (e, f) Thermopolymerized resol with a 56 wt\% carbon yield at 800 °C in Ar (red) and 58 wt\% carbon yield in N\textsubscript{2} (blue) environments.
Thermally polymerized resol, a resin derived from phenol and formaldehyde, on its own can provide up to 58 wt% carbon upon heating at 800 °C in N₂ or Ar gas environment (Figure 3.2(e,f)). The mesoporous structure shown in the AFM image in Figure 3.2a arose from the tri-constituent thin film composites of OBO triblock template, resol and vanadia. Calcining this composite thin film in air at 450 °C led to complete loss of ordered mesostructure accompanied by break-out crystallization of vanadia on the surface (Figure 3.2b) due to oxidation of pyrolyzed resol. This result further corroborated the importance of carbon yield necessary to maintain an ordered mesostructure. Hence, future experiments were carried out in inert N₂(g) or Ar calcining environment.

![AFM phase images of resol-assisted tri-constituent thin films](image)

Figure 3.3 AFM phase images of resol-assisted tri-constituent thin films of (a) CV-450-N₂, (b) CV-450-Ar, (c) CV-600-N₂, (d) CV-600-Ar, (e) CV-800-N₂ and (f) CV-800-Ar. The templated mesoporous carbon-vanadium oxide morphology is partially preserved after calcination under N₂ (scale bar – 200 nm).
Unlike the previous samples lacking resol (Figure 3.1), removal of the template by calcination at 450 °C under N₂ (CV-450-N₂, Figure 3.3a) or Ar (CV-450-Ar, Figure 3.3b) leads to a mesostructured porous film that retains the triblock copolymer-templated structure. This result suggests that the additional carbon yield from the resol prevents the break-out crystallization and helps maintain the ordered structure. The hydrophobic nature of poly(1,4-butadiene) segment in the OBO copolymer ideally promotes formation of spherical micelles in chloroform. These micelles tend to pack in a cubic (BCC) mesostructure when the concentration of the BCP is increased.¹⁸⁴ The spherical features observed in Figure 3.3 are consistent with this expected cubic mesostructure. Note that block copolymer-templated vanadium oxide calcined in argon at 400 °C appears porous under these conditions, thus it appears possible to maintain some porosity without resol by careful control of the calcination conditions.²¹¹ However, the addition of resol appears to provide a more facile and tolerant approach to robust mesoporous structures containing vanadium oxide. An important point to note is that the VOCl₃ concentration in the precursor is crucial to obtain an ordered porous structure. Higher loadings of VOCl₃ led to a loss of the mesostructure on heating and template removal at 450 °C.

For the porous films reported thus far, the resol remains polymeric and thus non-conducting upon heating to 450 °C. Increasing the calcination temperature to 600 °C, at which the resol becomes carbonaceous, markedly transforms the observed morphology depending on the calcination atmosphere. When calcined in N₂ at 600 °C, mesoscale order remains after resol carbonization (CV-600-N₂, Figure 3.3c). The average pore diameter decreases slightly from 22.5 nm to 20 nm based on AFM images, as the calcination temperature is increased from 450 °C to 600 °C, respectively. Similarly, the
average $d$-spacing estimated from the FFT of the AFM micrographs indicates a 9.2% decrease in the $d$-spacing from 32.8 nm for CV-450-N$_2$ to 29.8 nm for CV-600-N$_2$. However, calcination under Ar at 600 °C destroys the templated structure (CV-600-Ar, Figure 3.3d), due to formation of large vanadia crystals (~60–75 nm in size). Further increasing the calcination temperature to 800 °C under N$_2$ worsens the mesoscale ordering (CV-800-N$_2$, Figure 3.3e), with only partial preservation of the copolymer-templated structure. As expected, break-out crystallization occurs in Ar at this same temperature (CV-800-Ar, Figure 3.3f). Both morphologies arising from break-out crystallization (CV-600-Ar and CV-800-Ar) appear similar to the mesostructure obtained using CASH-450-Ar. Thus, the presence of carbon alone is not sufficient to preserve porous architecture and the inert calcining environment plays a crucial role in this regard.

In order to confirm that the surface features observed by AFM reflects the bulk morphology of the thin film, we conducted grazing-incidence small angle X-ray scattering (GISAXS) on the templated thin films. As shown in Figure 3.4, a single, broad scattering peak associated with the in-plane correlation of the mesoporous structure is observed in 1-D $I(q)$ vs. $q$ plots extracted from the 2D GISAXS images. Since the angle of the incident X-ray beam (0.2°) is greater than the critical angle of vanadium oxide, these measurements probe the entire depth of the composite film to provide an average correlation length therein. The absence of higher order Bragg peaks in the scattering data is not unexpected, based on the short-range translational order observed by AFM. The broad primary peak at $q_x \approx 0.188$ nm$^{-1}$ for CV-450-Ar (Figure 3.4a) corresponds to a $d$-spacing of 33.4 nm, while scattering from CV-450-N$_2$ (Figure 3.4b) exhibits a similar broad peak in the in-plane direction at $q_x \approx 0.19$ nm$^{-1}$ ($d = 33.1$ nm). This comparative
scattering analysis of CV-450-Ar and CV-450-N\textsubscript{2} agrees well with the similar short-range ordered porous polymer-vanadium oxide thin films determined from the AFM micrographs (Figure 3.3). The similarities in these scattering features indicate that the calcination environment (N\textsubscript{2} or Ar) does not significantly impact the ordering length scale of the mesoporous polymer-vanadium oxide structure at 450 °C.

![Figure 3.4](image)

Figure 3.4 (A) 1-D plots extracted from the in-plane direction of GISAXS patterns at $\alpha = 0.2^\circ$ (above critical angle) for (a) CV-450-Ar, (b) CV-450-N\textsubscript{2}, (c) CV-600-N\textsubscript{2}, and (d) CV-800-N\textsubscript{2}. (B) Comparison of GIXD 1-D profiles for (e) CV-600-N\textsubscript{2}, (f) CV-600-Ar, (g) CV-800-N\textsubscript{2}, and (h) CV-800-Ar

As the calcination temperature is increased to 600 °C, the scattering peak shifts to a higher $q_x = 0.212$ nm\textsuperscript{-1} for CV-600-N\textsubscript{2} (Figure 3.4c), corresponding to a decrease in the $d$-spacing to 29.6 nm from 33.1 nm at 450 °C. These results agree well with the characteristic length scales calculated from the FFT of the AFM micrographs (Figure 3.3) as the spacing decreases from 32.8 nm for CV-450-N\textsubscript{2} to 29.8 nm for CV-600-N\textsubscript{2}. We ascribe this $d$-spacing decrease to shrinkage of pores and contraction of the composite carbon-vanadium oxide thin film on calcination. It is interesting that the in-plane $d$-
spacing decreases during this processing, as uniaxial contraction is typically observed for templated mesoporous thin films of silica,\textsuperscript{213} other metal oxides,\textsuperscript{184} and carbon.\textsuperscript{214} We can compare this contraction in the in-plane $d$-spacing to the contraction in the film thickness, which typically is well correlated with the changes in the out-of-plane $d$-spacing (this cannot be determined as these out-of-plane diffraction peaks are weak and thus hidden by the beamstop in these GISAXS measurements).

![Figure 3.5 Evolution of film thickness and change in contraction for CV-$x$-$N_2$ at different processing temperatures](image)

The film contraction for CV-450-$N_2$ from ellipsometric measurements is 53% in comparison to the as-cast film (330 nm), while the film of CV-600-$N_2$ exhibits 64% contraction (Figure 3.5). Between 450 °C and 600 °C, there is a 10% decrease in the in-plane $d$-spacing, while the film thickness decreases by 23%. Thus, there is a preferred contraction of the film through its thickness, but there is still a substantial decrease of the in-plane dimension. This analysis suggests that the structure of these templated resolvanadia composite films continue to evolve during thermal processing.
For CV-800-N₂ composite films, only a single, very weak and broad scattering peak is observed (Figure 3.4d). In order to estimate the peak position, the 1-D scattering profile was fit with a combination of an exponential decay (to describe the background scattering) and a Lorentzian function (Figure 3.6).

![Figure 3.6 Exponential decay function (red) applied to the 1-D GISAXS plot for CV-800-N₂ to determine the background scattering and corresponding Lorentzian function used to determine the peak position (inset).](image)

From this procedure, the \( d \)-spacing is estimated to be 30.8 nm for CV-800-N₂. This weak scattering signature is consistent with the poor short range ordering observed by AFM for CV-800-N₂. It should be noted that no significant scattering, outside of the background associated with a non-templated film, is obtained for CV-600-Ar and CV-800-Ar due to loss of the self-assembled mesostructure on calcination.

To further understand how processing impacts the evolution of vanadia crystal structure, Figure 3.4B illustrates the grazing incidence x-ray diffraction (GIXD) for these films. All calcined films exhibit a broad diffraction peak at \( 2\theta \approx 12.8^\circ \), which corresponds
to the (002) reflection of amorphous carbon. Metal oxides are known to promote partial graphitization on heating in excess of 750 °C. However, the broad carbon peak indicates that limited graphitization for these carbon-vanadia composites, even after heating to 800°C. No clear diffraction peaks associated with vanadia are visible in the spectrum. This implies that the vanadia is primarily amorphous for these mesoporous composites in N₂, or the vanadia crystals are too small in size to be detected through GIXD.

To further analyze the nanoporous morphology of these carbon-vanadium oxide composites, cross-sectional TEM micrographs were obtained for the calcined thin films to elucidate the lateral structure through the thickness of the film (Figure 3.7). After calcination at 600 °C, CV-600-N₂ exhibits asymmetric ellipsoidal pores with their semi-major axes (22 ± 4 nm) oriented parallel to the silicon substrate as shown in the bright field micrograph in Figure 3.7a. This long-axis dimension is consistent with the surface structure obtained from AFM (Figure 3.3c). The asymmetric pore dimensions arise due to enhanced contraction through the thickness of the inorganic film. The ratio of semi-major to semi-minor axes (~ 2.4) of these pores compares favorably with the change in d-spacing (9.2 %) from AFM and thickness contraction (64 %) from ellipsometry, from which one would predict an asymmetry ratio of 1.9. Similar pore anisotropy has been reported previously for surfactant templated inorganic silica and mesoporous carbon thin films, yet the contraction is generally considered to be unidirectional. From the bright-field image, there are small (~ 2 nm) dark spots that are attributed to the vanadia due to its large Z. The dark-field imaging (Figure 3.7b) illustrates small bright spots of similar sizes (~ 2 ± 1 nm), providing confirmation that these features are due to vanadia.
Figure 3.7 Cross-sectional TEM micrographs of (a) CV-600-N$_2$ (bright field), (b) CV-600-N$_2$ (dark field), (c) scrapped thin film of CV-600-N$_2$ (dark field), (d) scrapped thin film of CV-800-N$_2$ (dark field), (e) CV-800-N$_2$ and (f) CV-800-Ar illustrating the porous structure of these films. (f) Note the segregation of vanadia to the film surface on calcination in Ar.

Upon increasing the calcination temperature to 800 °C, the ordered porous structure deteriorates with significant pore shrinkage (dark spots in the dark-field image) as shown in Figure 3.7e. The average diameter of the pores along the semi-major axis is estimated to be 15 ± 4 nm. At the same time, isolated vanadia nanoparticles (bright white spots, 3.5 ± 1.5 nm) are mostly dispersed in film; this increase in size of vanadia nanoparticles with increasing temperature is consistent with modest coarsening of the nanoparticles. The ordering of this porous system is quite poor and the multiple length
scales associated with the vanadia nanoparticles in the wall matrix are consistent with the GISAXS data for CV-800-N\(_2\) (Figure 3.4). Additionally, there is apparently some aggregation of the vanadia into polycrystalline structures that are on the order of 100 nm in isolated regions in the film.

In case of CV-800-Ar, significantly larger vanadia particles are observed and these appear to segregate to the free surface of the thin film (Figure 3.7f). This segregation of vanadia at the film surface helps to explain the disordered surface morphology observed from AFM for CV-600-Ar and CV-800-Ar (Figure 3.3). As the initial cast films are identical for the two calcination environments, this segregation of vanadia must occur during the calcination. In comparing CV-800-N\(_2\) (Figure 3.7e) and CV-800-Ar (Figure 3.7f), the thickness of the film is significantly less for CV-800-Ar, which suggests loss of carbon. If the carbon is preferentially removed from the surface, this would effectively concentrate the remaining vanadia, which would explain the apparent surface segregation. Interestingly, CV-800-Ar also exhibits ellipsoidal pores (dark spots) of highly variable size within the film. The overall mesostructure is slightly altered by distortion from film contraction on calcination. One additional change is the decrease in wall thickness that accompanies the transformation of resol to carbon. This effect is likely exacerbated by the carbothermal reduction that leads to further carbon loss and ultimately loss of structure.

To further investigate the porous structure of the films calcined in N\(_2\), Figure 3.8 illustrates the adsorption-desorption isotherms using ellipsometric porosimetry (EP) to elucidate the porosity and pores size distribution of these mesostructured films.\(^{208}\) Figure 3.8a illustrates that the CV-600-N\(_2\) film exhibits a type- IV isotherm with a H\(_1\)-type
hysteresis loop. The sharp rise in the adsorption isotherm in the range \(0.7 < \frac{p}{p_0} < 0.8\) corresponds to capillary condensation in the mesopores.

Figure 3.8 Toluene adsorption (black) and desorption (red) isotherms for (a) CV-600-N\(_2\) and (b) CV-800-N\(_2\) (c) Pore size distribution for CV-600-N\(_2\) and CV-800-N\(_2\) calculated from the adsorption isotherms by using the Kelvin equation.

The Lorentz-Lorenz effective medium approximation (EMA) is used to convert the refractive index into volume fraction of adsorbed toluene.\(^{218}\) Assuming all of the pores are filled by the adsorbed toluene, the porosity is estimated to be 13.6% porosity for CV-600-N\(_2\) and 8.5% for CV-800-N\(_2\) (Figure 3.8b). This porosity estimate assumes a uniform porosity through the film, but prior work with mesoporous carbon has suggested that the surface is less porous.\(^{219}\) The refractive index of optically opaque films is strongly weighed towards the film surface, so these reported porosities are a lower limit. Figure 3.8c illustrates the pore size distribution for these films. CV-600-N\(_2\) exhibits a bimodal pore size distribution with the primary peak centered around \(\kappa \approx 9.5\) nm and a minor peak centered around 5 nm. This compares well with the AFM image for CV-600-N\(_2\) (Figure 3.3c) which indicated spherical pore diameter of around 20 nm \(\left(r_{pore,AFM} \approx 10\right)\). Increasing the calcination temperature reduces the Kelvin radius to an average \(\kappa\) of approximately 5 nm (Figure 3.8c). A minor pore size in the bimodal distribution is still
observed around 2 nm. The shrinkage of both pore size is consistent between both the minor and major component.

In order to more clearly understand the dependence of the morphological differences of the vanadium oxide composites on the calcination environment, we examined the calcination process in greater detail. Figure 3.9a illustrates the TGA traces for simulated calcination to 800 °C in both N\textsubscript{2} and Ar atmospheres using dried and crushed powders of thermopolymerized resol-vanadia sols with identical initial composition as that of the templated thin films in the absence of the OBO copolymer template. The same heating conditions are utilized in the TGA as the calcining conditions used in the tube furnace, which results in the observed mass loss at 350 °C due to the hold at this temperature. There is a clear difference in the mass loss between the two environments. At temperatures below 350 °C, the mass loss in Ar is slightly less than the mass loss under N\textsubscript{2}. However, on holding these powders at 350 °C, the loss in Ar begins to exceed that in N\textsubscript{2} with the difference in mass loss increasing as temperature increases. The carbon-vanadium oxide residue is 56 wt\% at 800 °C when processed in N\textsubscript{2} (CV-800-N\textsubscript{2}), while calcination in argon yields only 32 wt\% residue on heating to 800 °C (CV-800-Ar). This additional mass loss in Ar is likely due to carbothermal reduction of the vanadium oxide. In N\textsubscript{2}, there is a possibility for the incorporation of N to form vanadium oxynitrides, although this typically does not occur at temperatures less than 1500 °C.\textsuperscript{220}

To both determine the vanadium oxide content and to assess whether any carbothermal reduction occurred within these calcined composites, the above residues from thermogravimetry were heated in air at 10 °C/min to remove the residual carbon by oxidation as shown in Figure 3.9b. Both residues exhibit almost no changes until 360 °C,
above which the residue obtained from carbonization in N$_2$ (CV-800-N$_2$) begins to lose mass. The residue obtained in Ar remains thermally stable until 410 °C.

Careful inspection of the TGA traces associated with the above residues indicates significant differences in their shapes. The TGA trace for the sample fabricated under N$_2$ follows a typical sigmoid associated with the oxidative removal of the carbon in air, to yield 28 wt% residual vanadium oxide (Figure 3.9b). On the other hand, the mass of the residue obtained in Ar reaches a minimum near 500 °C on heating CV-800-Ar in air. At temperatures greater than 500 °C, the apparent sample mass increases, which is attributed to the oxidation of vanadium to the V$^{5+}$ oxidation state.$^{221,222,223}$ The continuous increase in mass suggests that the oxidation of vanadium to the V$^{5+}$ oxidation state remains incomplete after heating to 800 °C. This behavior is in contrast to the CV-800-N$_2$ residue, which lacks any apparent increase in mass; this suggests that the vanadium oxide is V$_2$O$_5$ when calcined in N$_2$. These TGA traces indicate that CV-800-N$_2$ is initially 72 wt% carbon, while CV-800-Ar is estimated to contain only approximately 25 wt% carbon.

Figure 3.9 (a) Mass evolution during calcination of thermopolymerized resol-vanadium oxide composites using Ar and N$_2$ as determined by TGA. There is significantly greater residue at 800 °C using N$_2$. (b) Determination of the vanadia content by heating in air of
CV-800-N₂(28 wt%); heating of CV-800-Ar residue (red) in air demonstrates that the vanadium is not in its highest oxidation state as there is an increase in mass on heating above 500°C, indicative of further vanadium oxidation.

The significantly lower carbon content for CV-800-Ar along with its apparent lower oxidation state for the vanadium suggests that the Ar environment promotes carbothermal reduction of vanadium oxide. In the process of carbothermal reduction, the released oxygen lowers the carbon content in the composite through formation of CO(g) and CO₂(g). These differences in the carbon yield between the Ar and N₂ environments are likely responsible for the significant differences in morphology observed in the templated films as shown in Figure 3.3, especially at the higher temperatures.

To directly demonstrate the differences in the oxidation state of vanadium between those calcined in Ar and N₂, we performed high resolution XPS scans associated with the vanadium V2p peaks for the calcined carbon-vanadium oxide thin films as shown in Figure 3.10. The films calcined in N₂ exhibit a distinct V2p³/² peak at 517.3 eV and a V2p¹/² peak at 524.7 eV; these peak locations are attributed to vanadium oxide in the V⁵⁺ oxidation state.²²⁴,²²⁵ This occurrence of the V⁵⁺ oxidation state also agrees well with the TGA data for sample calcined in N₂, wherein no increase in mass is observed at elevated temperatures upon heating in air. The V2p peak positions are independent of temperature for calcination in N₂. Resolving the V2p³/² peak indicates ~ 97% of the vanadium oxide population is present as V⁵⁺ with less than 3% vanadium to be present in lower V⁴⁺ oxidation state (515.8 eV).
Figure 3.10 (A) High resolution XPS profiles for V2p peaks for resol assisted tri-
constituent thin films calcined under different environments for (a) CV-600-N₂, (b) CV-
600-Ar, (c) CV-800-N₂, and (d) CV-800-Ar. N₂ calcined films contain predominately V⁵⁺
and Ar calcined films contain predominately V⁴⁺. (B) XPS survey spectrum for CV-800-
N₂ is consistent with the presence of vanadium in V⁵⁺ oxidation state on the surface of the
thin film along with carbon (C1s) and oxygen (O1s) peaks. Figure 3.10(B) inset indicates
presence of nitrogen (N1s) peak obtained around 397.2eV, corresponding to formation of
small amount of vanadium oxynitride.

One alternative reason for the increased stability of the nanostructure in N₂ is the
formation of an oxynitride²²⁰ that is less reactive for the oxidation of carbon. A high
resolution scan for N1s illustrates a small peak at 397.2eV (Figure 3.10B). The elemental
composition of nitrogen is calculated to be 1.8% on the basis of these XPS measurements. Thus, a small amount of nitrogen is incorporated within the vanadium oxide-carbon composite during the calcination process; however, the absence of vanadium nitride V2p\(_{3/2}\) peak at 513.3 eV\(^{226,227}\) suggests that negligible vanadium nitride is formed at 800 °C under N\(_2\) calcination.

Interestingly, there is a shift in the V2p\(_{3/2}\) peak towards lower binding energy (515.9 eV) for the films calcined in Ar at 600 °C and 800 °C (Figure 3.10), corresponding to vanadium oxide in the V\(^{4+}\) oxidation state. The V2p\(_{1/2}\) peak is also at a lower binding energy of 523.2 eV as compared to N\(_2\) calcined thin films at equivalent temperature. After resolving the V2p\(_{3/2}\) peak, CV-600-Ar and CV-800-Ar indicate approximately 94 % vanadium to be present in as V\(^{4+}\), with 6 % vanadium in an even lower oxidation state. This decreased oxidation state of the vanadium oxide in the argon calcined thin films confirms that the Ar environment promotes carbothermal reduction at much lower temperatures when compared to nitrogen. Similar conclusions can be drawn based on the FTIR spectra (Figure 3.11) of the calcined carbon-vanadia composites.

Figure 3.11 illustrates the FTIR spectra of carbon-vanadia thin films used to examine the V=O stretching and V-O-V deformation modes at 1020 cm\(^{-1}\) and 764 cm\(^{-1}\) respectively, of vanadium oxide.\(^{228,229,230}\) For thin films calcined in N\(_2\) (CV-600-N\(_2\) and CV-800-N\(_2\)), these peaks are shifted to lower frequencies (990 cm\(^{-1}\) and 758 cm\(^{-1}\)). A similar shift has been reported for amorphous vanadium oxide supported on titanium oxide.\(^{231}\) However, the general ease of crystallizing of vanadia, especially at elevated temperatures (800 °C), would be inconsistent with the formation of amorphous vanadia.
Figure 3.11 FTIR spectra for resol assisted tri-constituent composite thin films of (a) CV-600-N₂, (b) CV-600-Ar, (c) CV-800-N₂, and (d) CV-800-Ar.

For films calcined in Ar (CV-600-Ar and CV-800-Ar), a significant difference in the peak positions corresponding to V=O stretch and V-O-V deformation is observed in comparison to those fabricated in N₂. The peak associated with the V=O stretch is further shifted to lower wavenumber (966 cm⁻¹), while no peak is observed near 760 cm⁻¹. The short V=O bonds in V(V)-oxo compounds exhibit a peak at 1020 cm⁻¹, while the vibrational band characteristic of V-O bond in V(IV) oxovanadium compounds is located near 920 cm⁻¹. The shift in V=O stretching frequency for CV-600-Ar and CV-800-Ar towards lower frequencies indicates distortion in the configuration of polyvanadate species, with a lower wavenumber associated with a greater concentration of the V⁴⁺ oxidation state. The peak associated with the vibrations of bound oxygen in V-O-V near 840 cm⁻¹, which is associated with V⁵⁺, also shifts slightly to lower wavenumbers of 838
cm$^{-1}$ and 836 cm$^{-1}$ after N$_2$ and Ar calcination, respectively. As the change in oxidation state of vanadia is accompanied by carbon loss, the larger shift in the vibrational bands for the films calcined in Ar is consistent with the loss of the mesostructure on heating in excess of 600 °C in Ar due to break-out crystallization.

To attempt to explain the difference in morphology based on the calcination environment, prior work associated with the carbothermal reduction of vanadia has been examined. Nitride formation actually promotes the formation of the vanadium carbide at lower temperatures than analogous carbothermal reduction in Ar,$^{232}$ but these focused on temperatures in excess of 1000 °C. The partial carbothermal reduction of lithium vanadates at 585 °C has been reported for lithium ion battery electrodes, but the impact of the atmosphere was not discussed.$^{233}$ Thus, this difference in carbothermal reduction of vanadia in Ar and N$_2$ at low temperatures appears to be relatively unexplored.

For the data presented herein, one additional difference between the Ar and N$_2$ is the oxygen content, which is < 1 ppm and < 5 ppm respectively. To understand if this residual oxygen is responsible for the significant difference in the carbon yield and resultant morphology, the calcination of the vanadium oxide – crosslinked resol is examined in ultrapure N$_2$ (<0.5 ppm O$_2$). Based on the TGA traces, calcining the composite under ultrapure nitrogen provides carbon-vanadia residue of 58 wt%, while 56 wt% yield is obtained using nitrogen atmosphere with < 5 ppm O$_2$ (Figure 3.12). The corresponding vanadium oxide contents are 26 wt% and 28 wt% (Figure 3.12). This indicates that limited difference in O$_2$ content is not responsible for the differences observed. Thus, we attribute these differences in the carbothermal reduction of vanadia at
temperatures less than 800 °C to the formation of a small amount of oxynitride when processed using N₂.

Figure 3.12 TGA trace for (a) thermopolymerized resol-vanadium oxide composites using ultrapure N₂ (less than 0.5 ppm O₂) (black) and N₂ containing<5 ppm O₂ content (blue) respectively.

Thus, the carbothermal reduction of carbon-vanadia composite thin films leads to loss of templated mesostructure on argon calcining. Hence, the standard protocol of argon calcinations used in the CASH method is not appropriate for templating mesoporous vanadium oxide. However, N₂ calcination process in the presence of resol provides an alternate route to obtain templated mesoporous carbon-vanadium oxide composites. This resol assisted tri-constituent assembly ideally should provide a strategy to develop wide range of mesoporous metal oxides by removal of carbon matrix.
Figure 3.13 (a) FTIR spectra for CV-600-N\textsubscript{2} (black) and after calcination for 30 min (blue) and 90 min (green) in air at 400 °C. AFM phase image of CV-600-N\textsubscript{2} subjected to calcination in air at 400 °C for (b) 30 min and (c) 90 min. (d) FTIR spectra for CV-800-N\textsubscript{2} (black) subjected to calcination for 30 min (blue) and 90 min (green) in air at 400 °C. AFM phase image of CV-800-N\textsubscript{2} subjected to calcation in air at 400 °C for (e) 30 min and (f) 90 min. (Scale bar - 200 nm)

Any attempts to remove carbon from CV-x-N\textsubscript{2} composite and form a porous vanadia structure lead to loss of the ordered mesoporous structure (Figure 3.13) further emphasizing the importance of carbon framework in maintaining the ordered structure. This is likely due to the high carbon content (72 wt\%) in the composite. In Figure 3.13, removal of carbon on heating CV-x-N\textsubscript{2} composite in air at 400 °C is tracked using FTIR. For both spectra, the peak height corresponding to the peak centered around 1230 cm\textsuperscript{-1}(C-
O bond stretching) is diminished after 30 min indicating loss of some carbon from the composite after heating in air at 400 °C. After 90 min heating in air, the peaks centered around 1730 cm\(^{-1}\) and 1610 cm\(^{-1}\) (C-C bond vibrations and stretching from aromatic ring) completely vanish indicating complete removal of carbon.\(^8\) At the same time, distinct peaks associated with V=O stretching and V-O-V deformation modes can be seen at 1017 cm\(^{-1}\) and 515 cm\(^{-1}\).\(^{230}\) From Figure 3.13b, the porous architecture begins to collapse, which is accompanied by growth of vanadia crystals on heating CV-600-N\(_2\) for 30 min in air. On heating CV-600-N\(_2\) for 90 min in air, the ordered mesoporous structure is completely lost after removal of carbon from the composite (Figure 3.13c). A similar trend is observed for CV-800-N\(_2\), however, larger vanadia crystals are formed after heating for 90 min at 400 °C in air (Figure 3.13f).

One issue with vanadium oxide as the electro-active material in energy storage devices is its inherently low electrical conductivity.\(^{87}\) This resol-assisted synthesis provides carbon yield that should endow these materials with enhanced electrical conductivities in order to overcome vanadia limitations for potential electrochemical applications. Interestingly, despite the large differences in carbon yields, the electrical conductivities of samples with a given calcination temperature are almost unaffected by the calcining atmosphere (Figure 3.14a). At 600 °C, the electrical conductivity is relatively low (0.6 ± 0.2 S/cm), but this increases significantly on calcining at 800°C to 8.2 ± 0.4 S/cm and 14 ± 4 S/cm for CV-800-N\(_2\) and CV-800-Ar, respectively. This conductivity is approximately 3 orders of magnitude greater than that of pure vanadium oxide,\(^{234}\) yet the conductivity is slightly less than that reported for mesoporous carbon thin films processed at 800 °C (~ 20 S/cm).\(^{217}\)
Figure 3.14 (a) Electronic conductivity of carbon-vanadium oxide composites calcined under argon environment (red triangles) and nitrogen environment (blue squares) at different processing temperatures indicating increasing conductivity of the composite with increased target calcining temperature. Note that the electrical conductivity of the composite is independent of the calcination environment. (b) Cyclic voltammetry curves for CV-800-N$_2$ at scan rate of 2mV/s (black), 10mV/s (red), 50mV/s (green) and 100mV/s (blue); (c) Normalized specific capacitance of OBO templated porous CV-800-N$_2$ (relative to non-porous, non-templated carbon-vanadium oxide film) at different scan rates.

To test the impact of the improved electrical conductivity and templated porosity on the electrochemical energy storage capabilities for the vanadium oxide, cyclic
voltammetry in 1 M Na$_2$SO$_4$(aq) electrolyte was used to determine the capacitance of the mesoporous carbon-vanadium oxide composite (CV-800-N$_2$) as shown in Figure 3.14b. At a slow scan rate of 2 mV/s, a specific capacitance of 136.1 F/cm$^3$ is obtained for the templated film. This specific capacitance decreases significantly to 43.4 F/cm$^3$ at 50 mV/s and 17.4 F/cm$^3$ at 100 mV/s with increasing scan rates.

The effect of porosity on the charge storage capabilities of carbon-vanadium oxide thin film electrodes is shown in Figure 3.14c by comparison of the specific capacitance of the templated CV-800-N$_2$ to the non-templated analog. At the slowest scan rate examined (2 mV/s), the specific capacitance of the non-templated composite film (133.6 F/cm$^3$) is nearly identical to that of the templated film. This illustrates that the primary charge storage mechanism is likely pseudo-capacitance through the redox reactions with vanadium oxide.$^{235}$ As these reactions are not diffusion limited under these conditions, the capacitance of these films is nearly identical at slower scan rates (2 mV/s). However at faster scan rates, the impact of porosity becomes apparent. As the scan rate increases, the difference between the templated and non-templated film increases due to the decreased diffusion length associated with the porous structure.$^{236}$ When the scan rate reaches 50 mV/s, the specific capacitance obtained from CV-800-N$_2$ is almost 7.25 times greater than that of the non-porous composite. This difference does not continue to grow as the rate is further increased to 100 mV/s. The porous architecture allows improved access of electrolyte ions to the vanadium oxide, but at sufficiently large rates (~ 50 mV/s) the charge insertion becomes diffusion limited and thus no additional improvements in relative performance are observed.
3.4 Conclusion

In this work, we demonstrated the importance of processing conditions in the formation and stabilization of porous carbon-vanadium oxide thin films. Using the standard CASH method, carbothermal reduction of vanadia occurs in the presence of argon leading to loss of the block copolymer-templated porous architecture. However, using a resol-assisted approach and by calcining under a nitrogen atmosphere, ordered porous carbon-vanadium oxide thin films were obtained at temperatures up to 800 °C. Generally, the exact nature of the inert calcining environments is not considered when synthesizing such mesoporous materials. However, this study illustrates the crucial role played by the calcining environment in the development of surfactant templated metal oxides to the action of the limited incorporation of N into the vanadium oxide framework, which prevents its carbothermal reduction. The mesoporous carbon-vanadium oxide composites calcined in nitrogen at 800 °C are found to have electrical conductivity as high as 8.2 S/cm, which is around 3 orders of magnitude higher than that of pure vanadium oxide.
CHAPTER IV
HIGH RATE SODIUM ION BATTERY ANODES FROM BLOCK COPOLYMER TEMPLATED MESOPOROUS NICKEL-COBALT CARBONATES AND OXIDES

4.1 Introduction

Soft-templating based on the cooperative assembly of block copolymers and precursors provides a convenient route to fabricate mesoporous metal oxides with precise control over pore size and surface area. These nanostructured porous materials can be applied to diverse applications, such as energy storage, gas absorption, catalysis, and drug delivery. For energy storage applications, the nanoscale dimensions associated with metal oxide matrix and interconnected mesopores provide short diffusion paths through the active materials and minimize ion transport issues when compared to bulk non-porous analogs. These properties can enable high capacity and cycling stability at high charge-discharge rates for templated mesoporous metal oxides electrodes in lithium ion batteries.

More recently, sodium ion battery technologies have garnered interest as a low cost alternative to lithium ion batteries. Layered (e.g., titanium oxide) or spinel (e.g., cobalt oxide and iron oxide) transition metal oxides are low cost materials for negative electrodes in sodium ion batteries.
However, more complex transition metal oxides, such as nickel cobaltite (NiCo$_2$O$_4$),$^{247}$ enable improved theoretical performance, but the performance, is intimately coupled to its nanoscale architecture.$^{248,249,250}$ In this context, a wide variety of nanoscale binary metal oxides have been fabricated in the form of nanoparticles, nanoribbons and disordered mesoporous materials.$^{101,248,251}$ Ordered mesoporous structures provide an advantage of controlled transport paths, but fabrication of ordered nickel cobaltite has been generally limited to hard templating.$^{152}$ Although hard templating is effective, the procedure requires multiple steps and is not readily scalable for commercialization. The soft templating of highly ordered mixed metal oxides of nickel cobaltite is generally challenged by the differences in hydrolysis and condensation rates of the oxide precursors for sol-gel processing.$^{181,252}$ Stucky and co-workers demonstrated that non-aqueous soft templating with metal chlorides is an effective route to generate ordered mesoporous transition metal oxides including binary and ternary metal oxides.$^{25}$ However, the long aging time (~ 2 days) significantly limits the commercial potential due to costs associated with the extended fabrication time. Syntheses of binary or ternary oxides using sol-gel precursors are limited by uncontrolled condensation that can lead to “freezing” of a metastable mesostructure possessing little or no structural integrity on template removal.$^{181}$ In these cases, the final mesostructure is generally very sensitive to a variety of factors: pH of precursor sol, interactions of precursor with template, moisture and processing conditions used. This sensitivity can render the sol-gel strategy tedious for fabricating ordered mesoporous metal oxides.$^{165,253}$

To overcome these issues and develop a simple and scalable synthesis approach, here we describe a citric acid mediated route for fabrication of ordered mesoporous
nickel-cobalt mixed-metal carbonates \( \text{Ni}_x\text{Co}_{(3-x)}(\text{CO}_3)_y \) and mixed-metal oxides \( \text{Ni}_x\text{Co}_{(3-x)}\text{O}_4 \). This method utilizes a complex of metal nitrate and citric acid that has been shown to yield a variety of soft templated mesoporous carbonates and oxides, such as those of cobalt, \(^{184}\) aluminium, \(^{184}\) copper, \(^{190}\) and manganese. \(^{190}\) We selected this route for the fabrication mesoporous mixed-metal oxides (MMO) due to the lack of an aging requirement, which eliminates a shortcoming of other soft templating methods. Here, we demonstrate this synthesis strategy for the fabrication of ordered mesoporous \( \text{Ni}_x\text{Co}_{(3-x)}\text{O}_4 \) through the formation of an intermediate mixed-metal carbonate (MMC) \( \text{Ni}_x\text{Co}_{(3-x)}(\text{CO}_3)_y \). This intermediate provides an additional opportunity as transition metal carbonates of cobalt \(^{254}\) and manganese \(^{255}\) are promising candidates as anodes in lithium ion batteries, but very few reports on use of mixed-metal carbonate (MMC) anodes exist in literature. \(^{256, 257, 258}\) Thus, this methodology should be able to be extended to the synthesis of a wide variety of mesoporous MMCs and MMOs for battery electrodes. We demonstrate that these ordered mesoporous \( \text{Ni}_x\text{Co}_{(3-x)}\text{O}_4 \) films act as potentially promising sodium ion battery anodes providing high specific capacity (> 200 mAh/g) at high current densities (> 1 A/g).

4.2 Experimental Section

**Materials**: Cobalt (II) nitrate hexahydrate (reagent grade, 98 %), nickel (II) nitrate hexahydrate (puriss. p.a., ≥ 98.5 %), citric acid (ACS reagent, ≥ 99.5 %), ethanol (ACS reagent, ≥ 99.5 % 200 proof, absolute), tetrahydrofuran (THF, ACS reagent, ≥ 99.0 %, containing 250 ppm BHT as inhibitor), mercaptosuccinic acid (97 %), methoxy poly(ethylene glycol) methacrylate (PMPEGMA, 475 g mol\(^{-1}\)), butyl acrylate (> 99 %), N, N-Dimethylformamide (DMF) (anhydrous, 99.8 %), and hexane (anhydrous, 95 %)
were purchased from Sigma-Aldrich and used as received. 2,2’-Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich, 98 %) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to prior reports in the literature.\textsuperscript{259} Deuterated chloroform (CDCl\textsubscript{3}) (Cambridge Isotope Laboratories, Inc.) was used as received.

For battery testing, sodium perchlorate (NaClO\textsubscript{4}, ACS reagent, \(\geq 98.0\%\)), ethylene carbonate (EC, anhydrous, 99\%) and propylene carbonate (PC, reagent plus, 99.7\%) were purchased from Sigma-Aldrich. Sodium metal (99.8\% Acros Organics) was used as the reference and counter electrode. For piranha cleaning of the substrates, sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 95-98\%, J.T. Baker) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30\%, Fisher Scientific) was used.

**Sample preparation**: Three different substrates were used in these studies: single side polished silicon wafers (Silicon, Inc.), high resistivity (1-10 \(\Omega\cdot\text{cm}\)), 600 \(\mu\text{m}\) thick double side polished (DSP) Si wafers for FTIR measurements, and 250 \(\mu\text{m}\) thick quartz slides (GM Associates Inc.) sputter coated with gold for electrochemical measurements. The silicon wafers were cleaned with Piranha solution (H\textsubscript{2}SO\textsubscript{4}: H\textsubscript{2}O\textsubscript{2} = 3:1 v/v) at 90 °C for 45 min, followed by multiple rinses with deionized water. These wafers were dried using nitrogen prior to film casting. The gold coated quartz slides were first treated with 10 mM ethanoic mercaptosuccinic acid for 24 h to produce a hydrophilic surface. After 24 h, the quartz substrates were rinsed multiple times with ethanol and dried with nitrogen prior to coating.
To fabricate block copolymer micelle templated thin films, poly[methoxy poly(ethylene glycol) methacrylate]–block–poly(butyl acrylate), PMPEGMA-b-PBA was used as the structure directing agent. PMPEGMA-b-PBA block copolymer template was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization following protocol mentioned elsewhere. The number average molecular weight ($M_n$) for PMPEGMA-b-PBA is $5.9 \times 10^4$ g mol$^{-1}$ with dispersity ($D_M$) of 1.3. The mole fraction of hydrophilic component ($f_{PMPEGMA}$) in the copolymer is approximately 0.1 as calculated from $^1$H-NMR.

Thin films were prepared by first dissolving 188 mg of metal (cobalt and/or nickel) nitrate in 0.6 g ethanol solution. After mixing for 15 min, 62 mg citric acid was added to the nitrate solution and stirred at room temperature for an additional 1 h. In a separate vial, 50 mg of PMPEGMA-b-PBA template was dissolved in 1.8 g THF and stirred for 1 h. After mixing for 1 h, the nitrate solution was added dropwise to the block copolymer solution and then stirred for 4-5 h at room temperature prior to film casting. Table 4.1 lists the solids composition for each of the precursor solutions used to fabricate the films in this work. Films were cast by flow coating at 40 mm/s and a relative humidity of ~40-50% RH. The coated films were allowed to dry for 30 min at ambient temperature. The cast films were placed in a preheated muffle furnace (Ney Vulcan 3-130) and heated for 1 h to fabricate the micelle templated carbonates. The calcination conditions are dependent on the composition as shown in Table 4.1. The calcination temperature for fabricating carbonates was well above the onset temperature of carbonate formation to ensure complete conversion of metal nitrate-citric acid into corresponding metal carbonate. After 1 h, the furnace was passively cooled to room temperature. To
generate ordered mesoporous carbonates of $\text{Ni}_2\text{Co(CO}_3)_y$ and $\text{Ni(CO}_3)_y$, micelle templated carbonates of $\text{Ni}_2\text{Co(CO}_3)_y$ and $\text{Ni(CO}_3)_y$ obtained previously were calcined in a preheated furnace at 300 °C for additional 20 min and quenched to room temperature. To generate mesoporous metal oxide thin films, a higher temperature was used for calcination of the micelle templated carbonate films (see Table 4.1) in a preheated furnace for 30 min. For the oxides, the films were rapidly quenched to room temperature after heating for 30 min. The metal oxide film thickness was 110 ± 15 nm irrespective of composition to enable direct comparisons.

Table 4.1 Precursor compositions and processing conditions for fabrication of cobalt oxide, nickel oxide and their mixed-metal oxide ($\text{Ni}_x\text{Co}_{(3-x)}\text{O}_4$) composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{Co(NO}_3)_2.6\text{H}_2\text{O}$ (mg)</th>
<th>$\text{Ni(NO}_3)_2.6\text{H}_2\text{O}$ (mg)</th>
<th>Citric acid (mg)</th>
<th>BCP template (mg)</th>
<th>Carbonate calcination (°C)</th>
<th>Oxide Calcination (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_3\text{O}_4$</td>
<td>188</td>
<td>-</td>
<td>62</td>
<td>50</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>$\text{NiCo}_2\text{O}_4$</td>
<td>143</td>
<td>51</td>
<td>63</td>
<td>53</td>
<td>220</td>
<td>325</td>
</tr>
<tr>
<td>$\text{Ni}<em>{1.5}\text{Co}</em>{1.5}\text{O}_4$</td>
<td>94</td>
<td>96</td>
<td>63</td>
<td>52</td>
<td>240</td>
<td>350</td>
</tr>
<tr>
<td>$\text{Ni}_2\text{CoO}_4$</td>
<td>42</td>
<td>148</td>
<td>62</td>
<td>55</td>
<td>260</td>
<td>365</td>
</tr>
<tr>
<td>$\text{NiO}$</td>
<td>-</td>
<td>191</td>
<td>66</td>
<td>53</td>
<td>265</td>
<td>375</td>
</tr>
</tbody>
</table>

**Characterization:** The molecular weight and dispersity of the macro RAFT agent and PMPEGMA-$b$-PBA block copolymer were determined by gel permeation chromatography (GPC). Three water system columns were used for GPC with a HR4,
HT2, HR1, HR0.5 styragel, and 500 Å ultrastyragel columns connected in series. GPC analyses in distilled tetrahydrofuran (THF) were performed at 35 °C using 0.1% (w/v) polymer solutions. Solutions were filtered (0.45 µm) and 200 µL was injected into the column at an effluent flow rate of 1.0 mL min⁻¹. The chromatograph was collected using a light scattering detector. The data were interpreted using Omnicsec software v.4.7.0.406. The compositions of PMPEGMA and PMPEGMA-b-PBA template were determined using ¹H-NMR (Varian NMRS-500 nuclear magnetic resonance instrument) operating at 500 MHz using deuterated chloroform (CDCl₃) as a solvent.

In order to determine the carbonate and oxide formation temperature by thermogravimetric analysis (TGA, TA Instruments, TGA-Q50), crushed powders of the metal nitrate and citric acid were prepared by drying the metal nitrate and citric acid in ethanol / THF mixture without the PMPEGMA-b-PBA template at 22 °C for 8-10 h, followed by heating under vacuum at 50 °C for another 10 h. TGA was performed using an air purge with 5 °C/min ramp rate. The onset of carbonate or oxide formation was determined by the derivative of the mass with respect to temperature, based on three TGA experiments.

Spectroscopic ellipsometry (M-2000, J.A. Woollam) was used to determine the thickness of the metal carbonate and oxide films. The optical properties were modelled with a generalized Kramers-Kronig consistent methodology (GenOsc) in CompleteEASE softwave (J.A. Woollam) using the wavelength range of 350-1100 nm. The surface morphology of the composite thin films was investigated after each processing step (carbonate and metal oxide) using atomic force microscopy (AFM, Dimension ICON, Veeco). Grazing incidence small angle X-ray scattering (GISAXS) was performed at the
X9 beamline of National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). An incident X-ray beam of energy of 13.5 keV (\(\lambda = 0.0918 \text{ nm}\)) was used and the scattering data were collected using a Pilatus detector at a distance of 4.73 m. All samples were measured under vacuum (\(\approx 40 \text{ Pa}\)) at multiple angles, both below and above the critical angle of the sample. Grazing incidence X-ray diffraction (GIXD) was also performed at the X9 beamline of NSLS at BNL to determine the crystal structure of the MMO films. Incident x-ray energy of 13.5 keV was utilized and the scattered intensity was collected on a charged couple device (CCD) WAXS detector. The average crystal size was estimated applying the Scherrer equation\(^{262}\) to the most intense diffraction peak and assuming \(\beta = 0.9\). Fourier Transform Infrared (FTIR) spectra (Thermo Scientific, Nicolet iS50 FT-IR) were obtained in transmission mode through the DSP silicon wafers, collecting 512 scans with a resolution of 8 cm\(^{-1}\) using a Deuterated TriGlycine Sulfate (DTGS) detector. The baseline of the FTIR spectra was corrected using OMNIC software. X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa probe II scanning XPS microprobe, ULVAC-PHI Inc.) with high-resolution scans at energies associated with Ni2p, Co2p and O1s was performed using 0.2 eV step size and pass energy of 23.5 eV. The scans were recorded at a take-off angle of 45\(^\circ\). Peaks associated with Ni2p, Co2p and O1s were deconvoluted using Multipeak fitting software applying a Shirley baseline correction to quantify the oxidation states of nickel and cobalt in the films.

The electrical conductivity of the mesoporous thin films was determined using four-point probe measurement (Pro-4, Lucas Labs) with a Keithley Series 2400 SourceMeter. The spacing between the pins on the probe head was 1 mm. The
The electrochemical behavior of the mesoporous films was quantified in a three-electrode system using the mesoporous MMO thin films on gold-coated quartz substrates as the active electrode material and sodium metal as both the counter and reference electrodes. Galvanostatic charge-discharge measurements (CHI660D electrochemical analyzer, CH Instruments) were performed in argon-filled glove box (O$_2$ < 2.5 ppm, H$_2$O < 0.5 ppm) using a voltage range of 0.01-3.0 V vs Na/Na$^+$. 1 M NaClO$_4$ in ethylene carbonate: propylene carbonate (EC: PC, 1:1 v/v) served as the electrolyte for the electrochemical measurements. The film anodes were galvanostatically cycled 10 times at current densities varying from 1 A/g to 4 A/g.

4.3 Results and Discussion

Metal nitrate-citric acid complexes of nickel and cobalt degrade in a two step process on heating in air; first generating a metal carbonate, which subsequently decomposes into the corresponding metal oxide at higher temperatures.$^{184}$ Figure 4.1 illustrates the compositional dependence on these transformations. Irrespective of composition, two distinct weight-loss steps are visible in all the TGA traces. The first drop corresponds to decomposition of the metal nitrate-citric acid complex to the carbonate. Further heating leads to a near constant mass after formation of the metal carbonate (higher temperatures in the fuchsia region in Figure 4.1).

The onset temperature associated with the carbonate formation is determined from the derivative of this TGA trace. The onset temperature for carbonate formation increases with increasing nickel content in the composite (Figure 4.1B). Cobalt carbonate formation begins around 135 °C while the peak for nickel carbonate occurs at much higher temperature (260 °C). A plateau region following the carbonate onset is observed
for these mixed-metal nitrate-citric acid composites instead of two distinct plateaus associated with the pure cobalt and pure nickel carbonate formation. However, the decrease in mass is more gradual for the mixtures, which makes it difficult to assess if only one single phase mixed-metal carbonate (MMC) \((\text{Ni}_x\text{Co}_{(3-x)}(\text{CO}_3)_y)\) is formed.

Figure 4.1 (A) TGA traces of metal nitrate-citric acid complex (x is mole fraction of nickel for the nitrates used) on heating in air. Decomposition of the metal nitrate-citric acid complex occurs in two distinct steps, corresponding to formation of metal carbonate (fuchsia) and decomposition of metal carbonate into corresponding metal oxide (chartreuse). (B) TGA trace (blue) and derivative (green) of mass loss for cobalt nitrate-citric acid complex, indicating two step degradation corresponding to formation of cobalt carbonate followed by decomposition of carbonate into cobalt oxide (C) Onset temperature for formation of metal carbonate (circle) and metal oxide (triangle) with varying nickel content within the composite determined from TGA traces.
At higher temperatures, a second drop in weight is attributed to the decomposition of the metal carbonate into its corresponding metal oxide (chartreuse shading in Figure 4.1). This decrease is much sharper for the cobalt-nickel mixtures than that associated with the formation of the carbonate. The compositional dependence of the onset temperature of oxide formation is similar to that for the carbonate (Figure 4.1C). For example, the onset temperature for cobalt oxide is approximately 245 °C, but this increases to around 375 °C for nickel oxide. The increase in onset temperature for carbonate or oxide formation with increasing nickel content illustrates that nickel increases the activation energy required for carbonate or oxide formation. The temperature window between the formation of metal carbonate and corresponding metal oxide is around 100 °C. With only two distinct decreases in mass, the TGA analysis suggests that this simple fabrication route can generate single phase $\text{Ni}_x\text{Co}_{(3-x)}\text{O}_4$ composites.

Insight into the compositional changes during processing is obtained from FTIR. Figure 4.2A illustrates the FTIR spectra for micelle templated films containing 50:50 (mol:mol) cobalt and nickel nitrate in the precursor through the different stages of the synthesis. The degradation of the template can be confirmed by the loss of the peak at 1740 cm$^{-1}$, which corresponds to the C=O vibration from the acrylate. Heating at 240 °C for 1 h leads to significant loss of the template, but does not completely degrade the template. At this temperature, the carbonate is formed as evidenced by the evolution of peaks at 1412 cm$^{-1}$ and 1587 cm$^{-1}$ corresponding to C-O bonds.
Figure 4.2 (A) FTIR spectra of PMPEGMA-\(b\)-PBA micelle templated metal nitrate-citric acid film containing with 50 mol\% nickel for (a) as cast, (b) carbonate formation at 240 °C for 1 h, and (c) oxide formation at 350 °C for 30 min. (B) FTIR spectra of micelle templated mesoporous (d) Co(CO\(_3\))\(_{y}\), (e) NiCo\(_2\)(CO\(_3\))\(_{y}\), (f) Ni\(_{1.5}\)Co\(_{1.5}\)(CO\(_3\))\(_{y}\), (g) Ni\(_2\)Co(CO\(_3\))\(_{y}\), and (h) Ni(CO\(_3\))\(_{y}\). (C) FTIR spectra of micelle templated mesoporous (i) Co\(_3\)O\(_4\), (j) NiCo\(_2\)O\(_4\), (k) Ni\(_{1.5}\)Co\(_{1.5}\)O\(_4\), (l) Ni\(_2\)CoO\(_4\), and (m) NiO fabricated by first forming the carbonate (heating for 1 h) and subsequently the oxide (heating for 30 min) using the temperatures specified in Table 4.1.

It should be noted that these peak positions are slightly shifted from pure cobalt carbonate.\(^{184}\) Similar FTIR spectra are observed for the other compositions for the fabrication of the MMCs (Figure 4.2B). After heating this carbonate film at 350 °C for 30 min, the template is now fully decomposed and the peaks associated with the carbonate peaks at 1412 cm\(^{-1}\) and 1587 cm\(^{-1}\) disappear, consistent with decomposition of the carbonate. New peaks centered around 634 cm\(^{-1}\) and 475 cm\(^{-1}\) appear in the spectra corresponding to M-O vibrations from Co-O and Ni-O in Ni\(_{1.5}\)Co\(_{1.5}\)O\(_4\).\(^{263}\) Figure 4.2C illustrates the change in the FTIR spectra for the MMOs with varying nickel content. Only peaks at low wavenumbers are observed due to M-O stretching vibrations from tetrahedral and octahedral sites characteristic of cobaltites in the MMO.\(^{184, 264, 265}\) As the
nickel content increases, there is a gradual shift of the peaks associated with the M-O vibrations to lower wavenumbers. These spectra are consistent with a single oxide phase.

Figure 4.3 (A) 1-D GIXD profiles for (a) Co$_3$O$_4$, (b) NiCo$_2$O$_4$, (c) Ni$_{1.5}$Co$_{1.5}$O$_4$, (d) Ni$_2$CoO$_4$, and (e) NiO. (B) Diffraction profiles from the (400) plane for (a) Co$_3$O$_4$, (b) NiCo$_2$O$_4$, (c) Ni$_{1.5}$Co$_{1.5}$O$_4$ and (d) Ni$_2$CoO$_4$. There is a shift in the (400) peak position to lower 2θ with increasing nickel content.

To further confirm the formation of single phase MMOs, Figure 4.3 illustrates the diffraction patterns obtained from GIXD. These profiles exhibit peaks assigned to (111), (220), (311) and (400) planes of the cubic Co$_3$O$_4$ (PDF card no. 01-078-1969) and MMOs (PDF card no. 01-073-1702), consistent with the formation of $Fd-3m$ spinel phase. Examination of the (400) peak position (Figure 4.3B) illustrates that a single peak is present in each case and this peak gradually shifts from 26.03° for Co$_3$O$_4$ to 25.04° for Ni$_2$CoO$_4$. The shift in peak position towards lower 2θ indicates an increase in lattice spacing between the (400) planes from 2.04 Å (NiCo$_2$O$_4$) to 2.11 Å (Ni$_2$CoO$_4$) with increasing nickel content, which is consistent with prior reports for the spinel phase of these MMOs. Diffraction peaks in NiO can be assigned to (111) and (200) planes of
the Fm-3m cubic crystal structure (PDF card no. 00-004-0835). Applying the Scherrer equation\textsuperscript{262} to the most intense peak from GIXD data of MMOs, the average crystallite size decreases from 4.2 nm for Co\textsubscript{3}O\textsubscript{4} to 2.3 nm for NiO. The average crystallite size formed in mesoporous NiCo\textsubscript{2}O\textsubscript{4} thin film is 3.6 nm while in case of Ni\textsubscript{2}CoO\textsubscript{4}, much smaller crystals of average size 2.3 nm are formed. This indicates that the crystallization behavior of the MMOs is impacted by the chemical composition of the composite and the processing conditions utilized.

To further characterize the chemical composition of the mesoporous composites, x-ray photoelectron spectroscopy (XPS) was performed on the MMO thin films. Figure 4.4 illustrates the high resolution scans for Ni2p and Co2p regions along with O1s region for Ni\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4}. As can be seen in Figure 4.4a, the Ni2p spectra is composed to two spin-orbit doublets corresponding to 2 different oxidation states (Ni\textsuperscript{3+} and Ni\textsuperscript{2+}) along with 2 satellite peaks corresponding to each oxidation state within the Ni\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4}.\textsuperscript{268, 269} Quantitative analysis of Ni2p peak indicates 55.4 % population of Ni\textsuperscript{3+} oxidation state within the porous MMO. Similarly, the Co2p spectrum also exhibits two spin-orbit doublets indicating cobalt to be present as Co\textsuperscript{3+} (41.5 %) and Co\textsuperscript{2+} (58.8 %) within Ni\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4}. The O1s spectra on the other hand, can be deconvoluted into 4 distinct peaks with peak positions centered around 528.8 eV, 530.6 eV, 532 eV and 533.3 eV. Each of these peaks corresponds to oxygen bound in different environment, namely oxygen-metal bond, oxygen present in the hydroxyl group, defect oxygen sites within the MMO and physisorbed or chemisorbed water molecules on the thin film surface.
Figure 4.4 High resolution XPS profiles of (a) Ni2p (b) Co2p and (c) O1s peaks present in templated mesoporous Ni$_{1.5}$Co$_{1.5}$O$_4$ thin film. Ni and Co are found to be present as a mixture of 2$^+$ and 3$^+$ oxidation state in the MMO composite. (d) Variation in atomic % of Ni (red), Co (blue) and defect O concentration (black) in the MMO with varying nickel content.

To gain further insights into chemical compositions of the MMO thin films, high resolution XPS scans were recorded on NiCo$_2$O$_4$ and Ni$_2$CoO$_4$ (Figure 4.5). From Figure 4.5 and Figure 4.4d, we can see that the population of Ni$^{3+}$ monotonically increases, while Co$^{3+}$ population decreases with increase in nickel content within the MMO. At the same time, the defect oxygen concentration in the MMO also increases with increase in nickel content within the MMO composite.
Figure 4.5 High resolution XPS profiles of (A) Ni2p (B) Co2p and (C) O1s peaks present in templated mesoporous Ni\textsubscript{x}Co\textsubscript{3-x}O\textsubscript{4} thin films along with deconvolution of peaks indicating Ni and Co to be present as a mixture of oxidation states in the MMO composite.

When additional nickel is added to the nickel-cobalt composite, Ni\textsuperscript{2+} ions begin to occupy the Co lattice sites, where Co\textsuperscript{3+} was initially present in the MMO. This leads to deficiency of positive charges and to maintain charge neutrality, Ni\textsuperscript{2+} transforms to Ni\textsuperscript{3+}.\textsuperscript{267} As a result, the Ni\textsuperscript{3+} population is found to increase while Co\textsuperscript{3+} decreases with
increasing nickel content within the MMO. The increase in oxygen defect concentration with nickel content again indicates intercalation of nickel within the cobalt lattice and formation of a single phase $\text{Ni}_x\text{Co}_{(3-x)}\text{O}_4$. Moreover, the chemical composition of MMOs determined from XPS survey scans is found to be close to the theoretical values from the initial precursor solutions (Error! Not a valid bookmark self-reference.).

Table 4.2 Atomic ratios in MMO films determined from XPS survey scans

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ni:Co:O)</td>
</tr>
<tr>
<td>$\text{NiCo}_2\text{O}_4$</td>
<td>1 : 2.18 : 4</td>
</tr>
<tr>
<td>$\text{Ni}<em>{1.5}\text{Co}</em>{1.5}\text{O}_4$</td>
<td>1.72 : 1.53 : 4</td>
</tr>
<tr>
<td>$\text{Ni}_2\text{CoO}_4$</td>
<td>2.28 : 0.84 : 4</td>
</tr>
</tbody>
</table>

The surface morphology of these films is characterized by Atomic Force Microscopy (AFM). Figure 4.6 illustrates the surface morphology of the micelle templated films after carbonate formation. All materials exhibit clear evidence of templating by spherical PMPEGMA-$b$-PBA micelles. A common length-scale associated with the center-to-center packing of the micelles is observed: 33.2 nm for $\text{Co}(\text{CO}_3)_y$ and 31.3 nm for $\text{Ni}(\text{CO}_3)_y$. In case of the MMCs, this distance does not systematically vary with nickel content (32.7 nm for $\text{NiCo}_2(\text{CO}_3)_y$, 31.2 nm for $\text{Ni}_{1.5}\text{Co}_{1.5}(\text{CO}_3)_y$ and 32.3 nm for $\text{Ni}_2\text{Co}(\text{CO}_3)_y$). The relative invariance of the structure with composition suggests that the micelle self-assembly process is not significantly impacted by precursor selection. Note that these films still contain some of the block copolymer template (Figure 4.2).
Figure 4.6 AFM micrographs of micelle templated (a) Co(CO$_3$)$_y$, (b) NiCo$_2$(CO$_3$)$_y$, (c) Ni$_{1.5}$Co$_{1.5}$(CO$_3$)$_y$, (d) Ni$_2$Co(CO$_3$)$_y$, and (e) Ni(CO$_3$)$_y$. A microphase separated morphology is present in all cases. (Scale bar = 200 nm in all micrographs)

To obtain template-free mesoporous Ni$_2$Co(CO$_3$)$_y$ and Ni(CO$_3$)$_y$ films, the micelle templated carbonates (Figure 4.6) were heated for additional 20 min at 300 °C. The removal of PMPEGMA-$b$-PBA template was confirmed by FTIR spectroscopy (Figure 4.7). The templated structure is maintained in the carbonates even after complete removal of block copolymer template (Figure 4.7C,D). Mesoporous Co(CO$_3$)$_y$, NiCo$_2$(CO$_3$)$_y$ and Ni$_{1.5}$Co$_{1.5}$(CO$_3$)$_y$ could not be fabricated due to decomposition of carbonate to its corresponding oxide prior to complete removal of the block copolymer template.
Figure 4.7 FTIR spectra tracking the removal of PMPEGMA-b-PBA block copolymer template from thin films of (A) Ni$_2$Co(CO$_3$)$_y$ and (B) Ni(CO$_3$)$_y$. AFM micrographs indicating an ordered mesoporous structure for (C) Ni$_2$Co(CO$_3$)$_y$ and (D) Ni(CO$_3$)$_y$. (Scale bar = 200 nm)

Figure 4.8 illustrates the surface morphology of the mesoporous oxides. The carbonate decomposition appears to degrade the packing of the micelles and lead to some small cracks. The extent of cracking increases for the higher nickel content films (which are subjected to higher calcination temperatures).
Figure 4.8 AFM micrographs of templated mesoporous (a) Co$_3$O$_4$, (b) NiCo$_2$O$_4$, (c) Ni$_{1.5}$Co$_{1.5}$O$_4$, (d) Ni$_2$CoO$_4$, and (e) NiO. The templated porous structure is maintained after decomposition of metal carbonate and complete removal of block copolymer template. (f) TEM micrograph of Ni$_{1.5}$Co$_{1.5}$O$_4$ film that has been scrapped from the substrate (Scale bar = 200 nm)

Although these higher temperatures will lead to larger stresses due to mismatch in the coefficient of thermal expansion between the mesoporous material and the silicon substrate, we attribute the cracks primarily to the confined inorganic framework shrinkage in these supported films. This leads to anisotropic shrinkage$^{214,270}$ and potential loss of the ordered nanostructure.$^{271}$ This shrinkage leads to a decrease in common length scale associated with micelle packing from 33.2 nm for cobalt carbonate to 28.6 nm for cobalt oxide, while the center-to-center distance between pores decreases from 31.3 nm
for nickel carbonate to 29.6 nm for nickel oxide. Similar decrease in length scale is also observed on conversion of the MMCs to corresponding MMOs. The templated mesopores formed in all the MMO thin films are $15 \pm 3$ nm wide based on AFM micrographs. These pore diameters agree with the pore size ($14 \pm 4$ nm) observed in the TEM micrograph (Figure 4.8f). Despite the large stresses applied during template removal and conversion to oxide, the templated porous structure is maintained in all the films (Figure 4.8) based on surface topography.

However, these AFM micrographs only provide information about the surface of these templated films. GISAXS interrogates the structure through the thickness over a large area. Figure 4.9F illustrates the 1-D in-plane GISAXS profiles obtained for the templated MMCs films; a broad primary peak and a weak secondary peak are present. Based on the primary peak position, the $d$-spacing is nearly invariant of composition decreasing from 33.9 nm for Co(CO$_3$)$_y$ to 31.7 nm for Ni(CO$_3$)$_y$, consistent with the spacing determined from AFM (33.2 nm and 31.3 nm, respectively). The secondary peak in the GISAXS profiles illustrates the long-range order in these MMC thin films. However, with increasing nickel content, this second order peak becomes broader indicating some loss of in-plane correlations. The ellipsoidal SAXS pattern of MMCs indicates presence of distorted body-centered cubic (bcc) mesostructure in the MMC thin films, with film shrinkage primarily occurring in the out-of-plane direction (normal to the substrate) during the carbonate heating stage. The primary and secondary peaks can be indexed to (110) and (220) bcc planes, respectively.
Figure 4.9 (A-E) 2-D GISAXS plots for mixed metal carbonates (Ni$_x$Co$_{3-x}$(CO$_3$)$_y$) and (F) 1-D plots extracted from GISAXS data for mixed metal carbonates (Ni$_x$Co$_{3-x}$(CO$_3$)$_y$) at 0.2° incident angle.
Figure 4.10 (A-E) 2-D GISAXS plots for mixed metal oxides (Ni$_x$Co$_{(3-x)}$O$_4$) and (F) 1-D plots extracted from GISAXS data for mixed metal oxides (Ni$_x$Co$_{(3-x)}$O$_4$) at 0.2° incident angle.
Figure 4.10F illustrates the GISAXS profiles for the mesoporous MMOs. A distinct primary peak corresponding to (110) plane is observed in all cases, which indicates that the cubic mesostructure is maintained through template removal and oxide formation. However, the primary peak position shifts to a higher $q_x$, compared to the corresponding metal carbonates. In case of pure cobalt oxide, the $d$-spacings decreases from 33.9 nm for the carbonate to 28.9 nm for the oxide; a 14.6% decrease in the in-plane correlations. A similar decrease (13.8%) in $d$-spacing due to shrinkage of inorganic framework was also observed in AFM. Interestingly, the largest $d$-spacing for the oxides is found for Ni$_{1.5}$Co$_{1.5}$O$_4$ (30.9 nm), which corresponds to 8.6% contraction from the carbonate to the oxide. This indicates that the structure of templated films evolves during decomposition of carbonate into corresponding mesoporous metal oxide. Similar to MMCs, a weak second order peak is also visible in the scattering profiles for these mesoporous MMO films.

To confirm the porous structure of the mixed-metal oxides, thin films were scrapped from silicon wafers and powdered samples were prepared for TEM imaging (Figure 4.11). All the images illustrate well-ordered and templated porous architectures for these oxides. The average pore diameter obtained in these mesoporous oxides is 14 ± 4 nm, which matches well with the pore width determined from AFM micrographs (Figure 4.8). Also the inorganic walls are comprised of individual nanoparticles that are 4.5 ± 1.5 nm in diameter, which is similar to the size scale suggested by the GIXD analysis.
Figure 4.11 TEM micrographs of samples prepared from scrapped films of (A) Co$_3$O$_4$ (B) NiCo$_2$O$_4$ (C) Ni$_{1.5}$Co$_{1.5}$O$_4$ (D) Ni$_2$CoO$_4$ and (E) NiO. Ordered mesoporous structure with spherical pores (~14 nm) can be clearly seen in all the oxide film samples (Scale bar=100 nm).

Block copolymer templated mesoporous metal oxides are known to enhance the performance of battery anode materials as compared with non-porous analogs due to facile electrolyte diffusion and high surface area.\textsuperscript{143, 148} The well-defined nanoporous architecture of these MMO thin films should allow for efficient charge storage at high current densities.\textsuperscript{45, 143, 144} This metal nitrate-citric acid route can fabricate ordered mesoporous metal oxide with porosities as high as 40%.\textsuperscript{261} To test the impact of this
porosity and interconnected porous architecture on the charge storage capabilities in sodium ion battery, ordered mesoporous Co$_3$O$_4$ and NiO thin film anodes were galvanostatically cycled at a high current density of 1A/g (Figure 4.12). The current densities utilized here are much higher than those reported in previous studies for use of Co$_3$O$_4$, NiO or NiCo$_2$O$_4$ anodes in sodium ion battery.$^{129,245,247}$ In this case, the thin film geometry provides a facile route to screen the MMO compositions to avoid convolution with the effect associated with binder chemistry, carbon black and slurry preparation.

Figure 4.12 (A) Specific discharge capacity of mesoporous cobalt oxide (▲) and nickel oxide (●) film anodes for sodium ion batteries galvanostatically cycled at a current density of 1 A/g, (B) Volumetric and areal (inset) capacity of mesoporous cobalt oxide (▲) and nickel oxide (●) film anodes. Cyclic voltammetry curves for (C) Co$_3$O$_4$ and (D) NiO anodes carried out at a scan rate of 2 mV/s in the voltage range of 0.01-3.0 V.
Mesoporous cobalt oxide and nickel oxide thin film anodes provide a high initial discharge capacity of 602 mAh/g and 619 mAh/g, respectively. Based on the oxide film thickness (~110 nm) and anode dimensions, the volumetric capacity of these active materials in the first discharge cycle is found to be 2488 mAh/cm$^3$ (Co$_3$O$_4$) and 2572 mAh/cm$^3$ (NiO) (Figure 4.12B). These initial discharge capacity values are higher than those previously reported, despite the higher current density employed here.$^{129, 245}$ High current densities lead to electrolyte ion mass transfer issues and generally low capacity. We attribute the higher specific capacity$^{16, 269}$ of these mesoporous cobalt oxide and nickel oxide at high current densities to the interconnected porous structure, short paths within the metal oxide and the continuous nature of the film. The interconnected porous electrode architecture helps to alleviate mass transfer issues and the nano-dimension of the inorganic walls provides shorter diffusion paths for sodium ions, which should lead to enhancement in performance of metal oxide anode.$^{15, 45}$

These metal oxide anodes, however, suffer significant capacity fade providing a low specific capacity of 59 mAh/g (242 mAh/cm$^3$) in case of Co$_3$O$_4$ and 132 mAh/g (483 mAh/cm$^3$) in case of NiO after 10 cycles. Ideally, anode materials are galvanostatically cycled at low current densities to form a stable solid electrolyte interface (SEI) layer on the electrode, followed by charging-discharging at high current densities in subsequent cycles. However, the high current density (1 A/g) used in our system likely hinders the formation of a stable solid electrolyte interface, which may contribute partially to the large capacity fade in these mesoporous anodes. The initial drop in specific capacity can also be attributed to side reactions occurring with the electrolyte and irreversible conversion reactions taking place in the first few cycles.$^{66}$ Cyclic voltammetry of the
mesoporous thin films (Figure 4.12C,D) at a scan rate of 2 mV/s provides further insight into the conversion reactions and capacity fade taking place in Co$_3$O$_4$ and NiO anodes. The mesoporous Co$_3$O$_4$ anode exhibits an intense cathodic peak at 0.46 V corresponding to partial reduction of Co$^{3+}$ and Co$^{2+}$ to metallic Co. The broad peak centered around 0.8 V corresponds to Na$_2$O formation accompanied by electrolyte decomposition.\textsuperscript{19} The anodic peak corresponding to Co oxidation occurs at approximately 1.5 V. As illustrated in Figure 4.12, the area under the CV curves progressively decreases upon successive cycling, consistent with the poor cycling stability of Co$_3$O$_4$ anode (Figure 4.12) at high rates.

In the case of the mesoporous NiO anode (Figure 4.12D), the cyclic voltammogram exhibits a broad peak centred around 1.0 V corresponding to the reduction of NiO to metallic Ni, while the broad cathodic peak in voltage range of 0.1-0.3 V corresponds to SEI formation and conversion reactions.\textsuperscript{132} The anodic peak corresponding to Ni oxidation is observed around 1.2 V and 1.7 V in the anodic curve. The low intensity of cathodic peak in the subsequent cycles indicates irreversible conversion reactions taking place in the NiO anode at high rates, leading to poor cycling stability of the mesoporous electrode. Theoretically, the reversible conversion reactions during sodium insertion-deinsertion in the metal oxides can be described as:

\[
\text{Co}_3\text{O}_4 + 8\text{Na}^+ + 8e^- \leftrightarrow 4\text{Na}_2\text{O} + 3\text{Co} \quad (4.1)
\]

\[
\text{NiO} + 2\text{Na}^+ + 2e^- \leftrightarrow \text{Na}_2\text{O} + \text{Ni} \quad (4.2)
\]

On galvanostatically cycling of the mesoporous MMO anodes of NiCo$_2$O$_4$ and Ni$_{1.5}$Co$_{1.5}$O$_4$ a high initial capacity of 538 mAh/g and 591 mAh/g is obtained but these
anodes exhibit poor capacity retention (only 21% and 25%) at the end of 10 cycles (Figure 4.13A). The equivalent volumetric capacity for the first discharge cycle is 2275 mAh/cm$^3$ in case of NiCo$_2$O$_4$ and 2671 mAh/cm$^3$ for Ni$_{1.5}$Co$_{1.5}$O$_4$.

Figure 4.13 (A) Comparison of the MMOs as anodes subjected to galvanostatic cycling over 10 cycles with a potential window of 0.01-3.0 V at current density of 1 A/g: NiCo$_2$O$_4$ (■), Ni$_{1.5}$Co$_{1.5}$O$_4$ (▲), and Ni$_2$CoO$_4$ (∗). (B) Comparison of specific discharge capacities of templated mesoporous and non-porous Ni$_2$CoO$_4$ anode subjected to...
galvanostatic cycling at varying current densities (C) Volumetric and areal (inset) discharge capacities of Ni$_2$CoO$_4$ anode subjected to galvanostatic cycling at varying current densities. Cyclic voltammetry curves for (D) NiCo$_2$O$_4$ (E) Ni$_{1.5}$Co$_{1.5}$O$_4$ and (F) Ni$_2$CoO$_4$ carried out at a scan rate of 2 mV/s in the voltage range of 0.01-3.0 V

Doping of cobalt oxide films with nickel ideally leads to significantly enhanced electronic conductivity of Ni$_x$Co$_{(3-x)}$O$_4$. Similar enhancement in electronic conductivity is observed in our case as the conductivity increases from 0.06 ± 0.02 S cm$^{-1}$ for NiCo$_2$O$_4$ to 0.23 ± 0.06 S cm$^{-1}$ for Ni$_2$CoO$_4$ (Figure 4.14). Such increase in electronic conductivity is typically associated with increase in doping of Ni$^{3+}$ within the octahedral sites of Ni$_x$Co$_{(3-x)}$O$_4$. This agrees with the XPS measurements (Figure 4.4), which illustrated an increase in Ni$^{3+}$ concentration within the crystal lattice upon increasing the nickel component in the MMO. The enhancement in electronic conductivity should provide faster electron transport in the mesoporous Ni$_x$Co$_{(3-x)}$O$_4$ anodes, but this still does not lead to improved high rate performance. Nonetheless, the crystal structure remains after cycling as shown in Figure 4.14B. The diffraction peak centered around 44.5° arises due to (400) crystal plane indicating that the crystal structure of the MMO is not destroyed following multiple insertion-deinsertion of Na$^+$ ions in the thin film anodes. The broad and intense peak centered at 38° arises due to gold sputtered on the quartz substrate. NiCo$_2$O$_4$ reference crystal planes are indicated by black lines (PDF card no. 01-073-1702) in Figure 4.14. Cyclic voltammetry curves (Figure 4.13C,D) further indicate poor cycling capabilities of these MMO anodes at high rates, as evidenced by decrease in redox peak intensities with successive cycling.
The mesoporous Ni$_2$CoO$_4$ anode, on the other hand, provides a lower initial discharge capacity 352 mAh/g (1711 mAh/cm$^3$) but maintains 68% of its initial capacity at the end of 10 cycles. This represents a significant improvement on the capacity retention of previously reported NiCo$_2$O$_4$ anode, which exhibited only 32% capacity retention after 2 cycles.$^{21}$ Cyclic voltammetry curve of Ni$_2$CoO$_4$ thin film anode further illustrates enhanced cycling capabilities of this MMO composition, where the CV curves almost overlap each other after 10 cycles (Figure 4.13F). Even on galvanostatically cycling Ni$_2$CoO$_4$ anode at significantly high current density of 2 A/g, a discharge capacity of 118 mAh/g (560 mAh/cm$^3$) is obtained while at 4 A/g current density. This value decreases to 24 mAh/g (114 mAh/cm$^3$) with 88% capacity retention after 10 cycles on cycling at 4 A/g. In comparison, a non-templated, non-porous Ni$_2$CoO$_4$ thin film anode offers a much lower initial discharge capacity of 203 mAh/g at 1 A/g suffering capacity fade upon successive cycling (Figure 4.13B). This discharge capacity is only 58% as compared to the templated mesoporous Ni$_2$CoO$_4$ anode. At higher discharge rates of 2 A/g, a lower capacity of 88 mAh/g is obtained and this value drops to 68 mAh/g after 10 additional cycles. Even after galvanostatically cycling at higher rates of 3 A/g and 4 A/g, the templated mesoporous Ni$_2$CoO$_4$ thin film anode offers higher capacity illustrating the ease of electrolyte diffusion in porous media at high rates and higher electro-active surface area afforded by the mesoporous anode. On reducing the current density back to 1 A/g, a reversible capacity of 131 mAh/g (639 mAh/cm$^3$) is obtained in case of the templated mesoporous Ni$_2$CoO$_4$ anode, while only 83 mAh/g capacity is obtained from the non-porous film. The templated mesoporous Ni$_2$CoO$_4$ thin film anode
architecture allows for strain accommodation during Na\(^+\) ion insertion and improved transport through the material in comparison to the non-porous, dense Ni\(_2\)CoO\(_4\) anode.

Figure 4.14 (A) Enhancement in electronic conductivity of MMO thin films with varying nickel content in the composite determined using 4-point probe measurements (B) X-ray diffraction profiles of MMO thin film anodes subjected to galvanostatic cycling.

The comparatively poor cycling stability of MMO anodes with lower nickel content might be due to the formation of surface-active carbonate ions on exposure of MMO anodes to ambient atmosphere, prior to the transfer to the glove-box for testing.\(^{276}\) Similar carbonate formation has been reported in case of sodium layered transition metal oxide cathodes leading to much lower discharge capacity as compared to air-protected electrodes. However, with higher nickel content in the MMO (Ni\(_2\)CoO\(_4\)), enhanced stability towards carbonate formation\(^{276}\) leads to significantly better cycling stability and charge storage performance,\(^{277}\) as in observed in case of Ni\(_2\)CoO\(_4\) anodes. Similarly, the larger lattice spacing between the crystal planes in Ni\(_2\)CoO\(_4\) and enhanced electronic conductivity (Figure 4.14A) compared to other MMOs can assist with the reversible insertion-deinsertion of sodium ions at high current densities, enhancing the cycling
stability in the process. Although the specific capacities and reversible cycling capabilities of MMO anodes obtained here are not the highest reported for metal oxide based sodium battery anodes, these materials are not optimized into composites (carbon black + binder) associated with anodes for coin cells. The performance of these materials nonetheless are comparable or slightly higher than those obtained for TiO$_2$ based anodes $^{18,66,67}$ (one of the most studied anode material). The primary aim of this study was to develop simple fabrication strategies that allow for initial screening of MMO compositions and their electrochemical behavior, for potential use as sodium ion battery anodes. Further optimization of electrolytes accompanied by addition of carbon black and binder likely will lead to improved overall battery performance.

The metal nitrate-citric acid route offers a simple strategy to fabricate mixed-metal oxide anodes that are templated by block copolymers. This generalized fabrication method should be readily extendable to various complex metal oxides for high performance sodium ion battery anodes as well as hosts of other applications.

4.4 Conclusion

In this work, we have extended a simple strategy based on metal nitrate-citric acid complex as a precursor in order to fabricate block copolymer micelle-templated mesoporous mixed-metal carbonates (MMCs) and mixed-metal oxides (MMOs) of nickel and cobalt. With no aging requirements, this method provides scalable generalized route to fabricate variety of mesoporous carbonates and/or oxides of mixed transition metals. The mesoporous nickel-cobalt MMO thin films are found to maintain an ordered porous structure through the film thickness direction with pore width around 14 nm. This porous structure provides high surface area and interconnecting pathways for electrolyte
diffusion, due to which the MMOs act as efficient high-rate sodium ion battery anodes. These mesoporous Ni$_x$Co$_{(3-x)}$O$_4$ thin film anodes are found to provide superior charge storage and enhanced cycling stability as compared to their bulk analogs. Mesoporous Ni$_2$CoO$_4$ provides initial discharge capacity of 352 mAh/g with good capacity retention when galvanostatically cycled at constant current density of 1 A/g.
CHAPTER V
HIERARCHICAL ELECTROSPUN AND COOPERATIVELY ASSEMBLED
NANOPOROUS NI/NIO/MNOₓ/CARBON NANOFIBER COMPOSITES FOR
LITHIUM ION BATTERY ANODES

5.1 Introduction

One challenge to the realization of the promise of renewable energy is the limited
capacity of standard commercial graphitic carbon anodes for lithium ion batteries.⁴²,⁴³ As
such, there has been significant interest in high theoretical capacity materials, but these
materials generally are limited by mechanical robustness from volumetric cycling during
charge-discharge or the transport of Li⁺ through the active material.²⁷⁸,²⁷⁹ Nanostructured
metal oxide electrodes represent one promising class of materials for next generation Li
ion battery anodes.⁹⁵,²⁸⁰,²⁸¹ Manganese oxide (MnOₓ) and nickel oxide (NiO) are
particularly promising candidates for energy storage applications due to their high
electrochemical activity, low operation potentials and elemental availability.²⁹,⁹⁵,¹³⁵,²⁸²
Nanostructuring into 1-dimensional anodes as nanofibers²⁸³, nanotubes²⁸⁴ or nanorods²⁸⁵,
²⁸⁶ helps to accommodate the strain associated with Li⁺ intercalation and prevents metal
oxide pulverization with improved cycling stability.²⁷
Block copolymer templating provides a scalable route to fabrication of porous metal oxide electrodes for lithium ion battery anodes with well controlled nano-architectonics with advantages of high electro-active surface, enhanced pseudocapacitive charge storage and facile electrolyte diffusion. Fabrication of 1-dimensional, porous metal oxide fibers typically involves infiltration of porous anodic alumina or track etched polycarbonate with block copolymer porogen and metal oxide precursor. A major drawback associated with this templating route is the poor connectivity of the nanotubes/nanowires, which can easily lose contact with current collector during electrochemical cycling in a lithium ion battery. 3-dimensionally interconnected nanofiber morphology, on the other hand, can prevent shorts and inactive material in anode by providing continuous pathways for electron transport, making these porous nanofiber metal oxides attractive candidates for battery anodes. However, the poor electronic conductivity of most metal oxides limits the cycling stability and rate capability, which limits their use in battery applications.

Hence, significant efforts are being directed towards fabricating nanostructured composites with an electronically conductive component, typically carbon. Carbon acts as a buffer layer to provide strain relief to volume expansion during lithium insertion/de-insertion. Additionally, carbon increases the overall conductivity to improve rate capacity. More recently, strategies involving encapsulation of the active metal oxide by electronically conductive metallic Ni have been utilized to enhance C-rate performance and cycling stability of anode materials for Li ion batteries. One challenge with fabrication of nanocomposite porous nanostructures for battery electrodes is development of scalable and manufacturable routes to produce such materials. Many
high performance battery electrode materials involve long, complex or low yield syntheses strategies, which limit their potential commercial viability.

In this work, we report an alternative and potentially scalable route to nanoporous composite interconnected fibers through electrospinning of low cost cooperatively assembled composites. These soft-templated and hierarchically porous, metallic Ni encapsulated NiO/MnO$_x$/C fiber anodes offer structural advantages to enable high charge-storage performance. The high surface area and porosity from the block copolymer template enhances electrolyte diffusion and accommodates strain associated with lithiation/delithiation. The metallic nickel encapsulation of the NiO/MnO$_x$/C nanofibers enhances the electronic conductivity and improves the cycling stability to obtain near-theoretical capacities based on the electroactive metal oxides. This electrospinning methodology is easily extended to roll-to-roll fabrication of 3-dimensionally interconnected, electronically conductive metal oxide nanofibers for applications ranging from energy storage, catalysis or even drug delivery.

5.2 Experimental Section

Materials: Nickel (II) nitrate hexahydrate (puriss. p.a., ≥ 98.5%), Manganese (II) nitrate tetrahydrate (98%), citric acid (ACS reagent, ≥ 99.5%), ethanol (ACS reagent, ≥ 99.5%, 200 proof, absolute), tetrahydrofuran (THF, ACS reagent, ≥ 99.0%, containing 250 ppm BHT as inhibitor), high molecular weight poly(ethylene oxide) (PEO, average M$_v$ ~ 5,000,000 g/mol), phenol (>99%), formaldehyde (ACS reagent, 37 wt% ($aq$) with 10-15% methanol stabilizer), NaOH (ACS reagent, >97%), conc. hydrochloric acid (ACS reagent, 37wt% ($aq$)), methoxypoly(ethylene glycol) methacrylate (PMPEGMA, 475 g
mol$^{-1}$), butyl acrylate (>99%), $N, N$-Dimethylformamide (DMF) (anhydrous, 99.8%), and hexane (anhydrous, 95%) were purchased from Sigma-Aldrich and used as received. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized following prior literature reports.$^{259}$ Deuterated chloroform (CDCl$_3$, Cambridge Isotope Laboratories, Inc.) was used as received. For battery testing, lithium hexafluorophosphate (LiPF$_6$, battery grade, $\geq$ 99.99% trace metals basis) was purchased from Oakwood Chemicals. Ethylene carbonate (EC, anhydrous, 99%) and dimethyl carbonate (DMC, anhydrous, $\geq$99%) were purchased from Sigma-Aldrich. Lithium metal foil (0.25 mm thick, MTI Corporation) was used as the reference and counter electrode.

**Synthesis of phenolic resin (resol):** A low molecular weight, thermally cross-linkable phenolic resin (resol) was synthesized through base (NaOH) catalyzed condensation of phenol and formaldehyde.$^{46}$ The reaction mixture was neutralized using 1M HCl ($aq$) to pH~7. Water was removed from the synthesized resol by rotary evaporation at 46 °C under vacuum. The resulting resol was dissolved in ethanol to yield a 50 wt% solution, and precipitated NaCl(s) was removed using a 0.45 µm glass filter.

**Preparation of mesoporous nanofibers:** Electrospun nanofiber composites of Ni/NiO/MnO$_x$/Carbon were denoted as Ni$_x$-Mn$_{100-x}$/C, where $x$ refers to wt% of nickel (II) nitrate salt relative to the total salt in the spinning dope, while C represents the carbon present in the composite on carbonization of resol. Poly[methoxy poly(ethylene glycol) methacrylate]$-block$-poly(butyl acrylate), PMPEGMA-$b$-PBA was utilized as a template to introduce porosity in the nanofibers. PMPEGMA-$b$-PBA with number average molecular weight ($M_n$) of $13.5 \times 10^4$ g mol$^{-1}$ and dispersity ($D_M$) of 1.2 was synthesized
using reversible addition-fragmentation chain transfer (RAFT) polymerization\textsuperscript{260} as described previously.\textsuperscript{189} For preparing the dope for the electrospinning, a stock solution of PEO (0.5 g) in 9 g ethanol, with 2 g of de-ionized water added dropwise, was stirred for 4-5 h until a clear viscous PEO solution was obtained. In a separate container, 0.14 g of the PMPEGMA-\textit{b}-PBA was dissolved in 5.5 g THF and stirred at 350 rpm for 1 h. A third stock solution consisting of nickel (II) nitrate hexahydrate, manganese (II) nitrate tetrahydrate and citric acid was dissolved in 1.5 g ethanol solvent and stirred for 15 min. Table 5.1 lists the details of the solids composition used for each precursor spinning dope. To prepare the spinning dope, the ethanolic resol solution was added to the metal nitrate-citric acid solution and stirred for another 15 min. Subsequently, this solution was added slowly to the PMPEGMA-\textit{b}-PBA/THF solution. Once a light green colored solution was formed, the PEO stock solution was added and then stirred for another 1 h prior to use as the spinning dope.

Table 5.1 Precursor composition for fabrication of the Ni\textsubscript{x}Mn\textsubscript{100-x}/C electrospun nanofiber composites (excluding the solvents)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O (g)</th>
<th>Mn(NO\textsubscript{3})\textsubscript{2}•4H\textsubscript{2}O (g)</th>
<th>Citric acid (g)</th>
<th>PMPEGMA-\textit{b}-PBA (g)</th>
<th>Resol (g)</th>
<th>PEO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{0}-Mn\textsubscript{100}/C</td>
<td>-</td>
<td>0.632</td>
<td>0.288</td>
<td>0.145</td>
<td>0.131</td>
<td>0.065</td>
</tr>
<tr>
<td>Ni\textsubscript{33}-Mn\textsubscript{66}/C</td>
<td>0.242</td>
<td>0.393</td>
<td>0.292</td>
<td>0.142</td>
<td>0.127</td>
<td>0.066</td>
</tr>
<tr>
<td>Ni\textsubscript{50}-Mn\textsubscript{50}/C</td>
<td>0.324</td>
<td>0.308</td>
<td>0.288</td>
<td>0.151</td>
<td>0.129</td>
<td>0.068</td>
</tr>
<tr>
<td>Ni\textsubscript{66}-Mn\textsubscript{33}/C</td>
<td>0.441</td>
<td>0.206</td>
<td>0.283</td>
<td>0.139</td>
<td>0.132</td>
<td>0.067</td>
</tr>
<tr>
<td>Ni\textsubscript{100}-Mn\textsubscript{0}/C</td>
<td>0.636</td>
<td>-</td>
<td>0.295</td>
<td>0.152</td>
<td>0.132</td>
<td>0.065</td>
</tr>
</tbody>
</table>

122
The dope was electrospun at 23 kV and fixed needle-to-collector distance of 17 cm using a stainless steel foil (20 cm x 20 cm x 75 µm) collector. During the electrospinning process, the relative humidity was maintained between 15-30% to prevent melting of the fibers by water adsorption that can dissolve the salts. The spun fibers were scraped from collector and heated to 120 °C for 24 h to crosslink the resol. These composite fibers were then calcined in a tube furnace (SentroTech Corp.) under nitrogen flow (99.995% purity, Praxair, 150 ml/min) by heating to 265 °C at 1 °C/min, hold for 1 h to form metal carbonate-polymer composite, heating to 800 °C at 1 °C/min, and finally isothermal hold at 800 °C for 45 min to fabricate the mesoporous Ni<sub>x</sub>-Mn<sub>100-x</sub>/C composite nanofibers. The fibers were cooled to room temperature at 2°C/min.

**Characterization:** The molecular weights and molecular weight distribution of PMPEGMA-<i>b</i>-PBA block copolymers was determined using gel permeation chromatography (GPC, Waters) with HR4, HT2, HR1, HR0.5 styragel, and 500Å ultrastyragel columns connected in series and a light scattering detector. GPC analyses were performed at 35 °C in distilled tetrahydrofuran (THF). Block copolymer solutions (0.1 % w/v) were injected (200 µL) into the columns with an eluent flow rate of 1.0 mL•min<sup>-1</sup>. The molecular weight was determined from a calibration curve based on polystyrene (PS) standards using Omnisec software v.4.7.0.406. The composition of the PMPEGMA-<i>b</i>-PBA was determined by <sup>1</sup>H-NMR using Varian NMRS-500 nuclear magnetic resonance instrument (500 MHz) and deuterated chloroform (CDCl<sub>3</sub>) as the solvent.

The nanofiber morphology was elucidated using scanning electron microscopy (SEM, JEOL JSM5310) operating at an accelerating voltage of 5kV. The fiber diameter
was determined from at least 100 fibers from 5 different SEM micrographs using Image J (NIH, USA). Energy-dispersive x-ray spectroscopy (EDX) on the same SEM (accelerating voltage of 25kV) was used to determine the surface elemental composition. Nitrogen adsorption-desorption isotherms (Micromeritics TriStar II) were used to determine the surface area based on Brunauer–Emmett–Teller (BET) analysis and the pore size distribution from the adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method. The Niₓ-Mn₁₀₀₋ₓ/C composite nanofibers were degassed (Micromeritics VacPrep 061) at 120 °C for 8-10 h prior to measurements.

The carbon content in Niₓ-Mn₁₀₀₋ₓ/C composite nanofibers was determined from thermogravimetric analysis (TGA, TA Instruments, TGA-Q50) in air by heating at 10 °C/min to 800 °C to burn off the carbon. X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa probe II scanning XPS microprobe, ULVAC-PHI Inc.) at a take-off angle of 45° was used to determine the composition using survey scans (0.5 eV step size and pass energy of 117.4 eV) and the oxidation states using high-resolution scans (0.125 eV step size and pass energy of 29.35 eV) for binding energies associated with Ni2p. The peaks associated with Ni2p were deconvoluted using Multipeak fitting software and applying a Shirley baseline correction to quantify the composition of metallic Ni and NiO in the nanofibers. X-ray diffraction (RigakuUltima IV diffractometer) using Cu Kα radiation (1.54 Å) was used to determine the crystal structures in the nanofibers. Rietveld refinement was carried out on the diffraction spectra of the composite fibers using Rigaku PDXL Integrated X-ray powder diffraction software. The average crystal size was estimated from the Scherrer equation using the most intense diffraction peak and assuming β=0.9.
**Battery testing:** The anodes were fabricated by mixing the active material with PAA binder at 9:1 (wt:wt) ratio in NMP to generate a slurry. This slurry was cast on copper foil by a doctor blade and heated at 100 °C overnight to ensure removal of the NMP with mass loading of 0.8-1.0 mg. The composite electrode was punched into 5/16” circular discs for assembly into CR2032 coin cells (MTI Corporation). The batteries were fabricated in an Ar glovebox with O₂ and H₂O <0.5 ppm using Li-metal as the counter electrode, Celgard 3501 (Celgard, LLC.) as the separator, and 1M LiPF₆ in EC/DMC (1:1 v/v) as the electrolyte. Galvanostatic charge-discharge was measured using a battery tester (BST8-WA, MTI) with current densities varying between 0.05A/g and 1 A/g within a potential window of 0.01-3.0 V vs Li/Li⁺. Electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation CHI660D (CH Instruments) with applied amplitude of 5 mV from 10 kHz to 0.1 Hz.

5.3 Results and Discussion

Figure 5.1 illustrates the compositional dependence of the fiber morphology for these Niₓ-Mn₁₀₀₋ₓ/C composites. For all chemical compositions examined, the continuous interconnected fiber morphology is maintained after calcination at 800 °C. This result is counter to prior reports for electrospun metal oxide nanofibers where the fiber morphology is lost during thermal processing due to crystallization.³⁰ The intermediate metal carbonate¹⁸⁴, ¹⁸⁷ and interdispersed resol/carbon likely contribute towards the improved mechanical stability of the composite fibers produced here.
Figure 5.1 SEM micrographs of (A, B) Ni$_{100}$-Mn$_{100}$/C; (D, E) Ni$_{33}$-Mn$_{66}$/C; (G, H) Ni$_{50}$-Mn$_{50}$/C; (J, K) Ni$_{66}$-Mn$_{33}$/C; and (M, N) Ni$_{100}$-Mn$_0$/C composite fibers. Size distribution
of (C) Ni₀-Mn₀/C (F) Ni₃₃-Mn₆₆/C (I) Ni₅₀-Mn₅₀/C (L) Ni₆₆-Mn₃₃/C (O) Ni₁₀₀-Mn₀/C nanofiber composites

The fiber size distribution is similar for all compositions with the fiber diameters ranging from 600 nm - 1200 nm. The average fiber diameter is approximately 900 nm. This invariance is not unexpected as the solution viscosity is dominated by the polymeric components in the dope. A closer examination of the fibers illustrates a rough surface that evolves with Ni content. At low Ni content (Figure 5.1E), the fiber surface is pocked with isolated nanoparticles on the surface. As these spots are bright in SEM relative to the rest of the fiber, these nanoparticles must contain predominately high Z atoms.

Table 5.2 Energy-dispersive x-ray (EDX) spectroscopy for Niₓ-Mn₁₀₀-x/C nanofiber composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th>Ni K Wt %</th>
<th>Atomic %</th>
<th>Mn K Wt %</th>
<th>Atomic %</th>
<th>O K Wt %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₆₆-Mn₃₃/C</td>
<td></td>
<td>48.9</td>
<td>29.05</td>
<td>26.18</td>
<td>16.64</td>
<td>24.91</td>
<td>54.32</td>
</tr>
<tr>
<td>Ni₅₀-Mn₅₀/C</td>
<td></td>
<td>44.71</td>
<td>27</td>
<td>31.52</td>
<td>20.34</td>
<td>23.77</td>
<td>52.66</td>
</tr>
<tr>
<td>Ni₃₃-Mn₆₆/C</td>
<td></td>
<td>37.82</td>
<td>22.60</td>
<td>37.92</td>
<td>24.21</td>
<td>24.26</td>
<td>53.19</td>
</tr>
</tbody>
</table>

EDX elemental analysis (Figure 5.2) suggests that these are Ni nanoparticles on the surface. At high Ni content, the size of these nanoparticles on the surface increases to generate almost scale-like morphology (Figure 5.1K). The EDX analysis is consistent with this surface structure on the fibers being predominately Ni. Table 5.2 summarizes the influence of the dope composition on the surface atomic concentrations from EDX.
Although the surface Ni concentration scales with the dope content, there is an excess of Ni at the surface in all cases based on the expected formation of metal oxides.

Figure 5.2 Scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) spectroscopy for surface elemental compositional analysis of (A) Ni_{66}-Mn_{33}/C (B) Ni_{50}-Mn_{50}/C (C) Ni_{33}-Mn_{66}/C fiber composites

XPS was used to determine the nature of the excess nickel on the Ni_{x}-Mn_{100-x}/C nanofiber composites (Figure 5.3). The Ni2p peak in the XPS profile can be deconvoluted into peaks corresponding to metallic Ni\(^0\) (binding energy = 852.3 eV) and
Ni$^{2+}$ in NiO (binding energy = 855.2 eV and 873.1 eV).\textsuperscript{311} The composition of surface metallic Ni$^0$ within the composite fiber increases from 7\% in case of Ni$_{33}$-Mn$_{66}$/C to 19\% for Ni$_{66}$-Mn$_{33}$/C (Figure 5.3). This compositional change further corroborates that the Ni$_x$-Mn$_{100-x}$/C fiber surface features are metallic Ni nanoparticles.

Figure 5.3 High resolution x-ray photoelectron spectroscopy (XPS) profiles of Ni2p peaks for (A) Ni$_{33}$-Mn$_{66}$/C (B) Ni$_{50}$-Mn$_{50}$/C and (C) Ni$_{66}$-Mn$_{33}$/C fiber composites illustrating the increase in surface Ni$^0$ content (peak at binding energy 852.5 eV) for Ni$_x$-Mn$_{100-x}$/C composites with increasing initial nickel dope.

The surface enrichment of metallic Ni for these Ni$_x$-Mn$_{100-x}$/C nanofibers is similar to segregation of metallic Ni during reduction of Ni$_x$CeO$_{2+x}$.$^{312}$ The process of Ni nanoparticle segregation and growth on oxide surface appears to follow an Ostwald ripening mechanism.$^{313}$ The conversion from metal nitrate-citric acid tends to cascade
from metal carbonate to metal oxide, so carbothermal reduction of NiO at high temperature might be suspected for the formation of metallic Ni.

However, the carbon content from TGA (Figure 5.4) is invariant (~18 wt%) with Ni content, which implies carbothermal reduction is not a major pathway. The natural resistance of nickel to oxidation hints at the direct conversion to metallic Ni\(^0\) in N\(_2\) at elevated temperatures. To further understand the underlying mechanisms causing reduction of nickel nitrate to metallic Ni\(^0\) in N\(_2\), TGA profiles were recorded for metal nitrate-citric acid complex under air and N\(_2\) atmospheres. Figure 5.4F demonstrates that the calcining atmosphere (air vs. N\(_2\)) greatly impacts the evolution from the precursors to the product. The red curve in Figure 5.4F represents the evolution of mass for Ni\(_{66}\)-Mn\(_{33}\) composite subjected to furnace calcining conditions in the presence of N\(_2\) atmosphere. A pseudo-plateau region is obtained in the range of 200 °C–330 °C corresponding to a complex metal carbonate formation. A similar pseudo-plateau is also observed on air calcination (blue curve). This plateau region is followed by a fall in mass corresponding to decomposition of metal carbonate into corresponding metal oxide. At around 355 °C, NiO/MnO\(_x\) complex oxide is formed with 26 % yield on N\(_2\) calcination. However, beyond this temperature an increase in mass (~4%) is observed corresponding to partial oxidation of inorganic residue. This suggests that part of nickel nitrate is directly reduced to metallic Ni\(^0\) in N\(_2\) at elevated temperatures. Heating of the composite beyond 335 °C leads to partial oxidation of metallic Ni\(^0\), which is seen by the apparent increase in mass of Ni/NiO/MnO\(_x\) composite. In case of air calcination (red curve), no such increase in mass is observed due to the presence of constant oxidizing environment, leading to formation of only NiO/MnO\(_x\) composite. The metallic Ni formed under N\(_2\) calcination
forms a surface coating on the nanofiber and provides some mechanical reinforcement to inhibit large structural changes on crystallization of the metal oxide during the heating stage at 800 °C.

Figure 5.4 Thermogravimetric traces for (A) Ni$_{100}$-Mn$_0$/C (B) Ni$_{66}$-Mn$_{33}$/C (C) Ni$_{50}$-Mn$_{50}$/C (D) Ni$_{33}$-Mn$_{66}$/C (E) Ni$_0$-Mn$_{100}$/C composite fibers carried out in air indicating ~18 wt% carbon yield present in all Ni$_x$-Mn$_{100-x}$/C composites. (F) Evolution of Ni$_{66}$-Mn$_{33}$ mass during calcination in nitrogen (red) and air (blue) atmosphere.
Figure 5.5 shows the XRD profiles that confirm that the fibers are crystalline after heating to 800 °C. The diffraction peaks can be assigned to metallic Ni (PDF card no. 01-070-0989), trigonal NiO (PDF card no. 01-078-4367), cubic MnO (PDF card no. 01-075-0625), tetragonal Mn$_3$O$_4$ (PDF card no. 01-071-6262), and graphite (PDF card no. 03-065-6212). The composition of spun fibers determines the crystal phases present in the calcined product. For the fibers without Mn (Ni$_{100}$-Mn$_0$/C), the primary crystalline component is metallic Ni with very weak peaks associated with trigonal NiO and graphitic carbon. This prevalence of metallic Ni is consistent with Ni$^0$ from XPS. With the addition of Mn, a more complex mixture of metallic Ni, NiO, MnO and Mn$_3$O$_4$ phases form along with some graphitic carbon as expected on pyrolysis of polymers to carbon in presence of manganese and nickel.$^{316, 317}$ Without Ni present in the spinning
dope, a mixture of MnO and Mn$_3$O$_4$ phases are found, but the carbon is not appreciably graphitized.

To more quantitatively assess the composition of the fibers, the XRD profiles were fit using Rietveld refinement. Table 5.3 summarizes the results from these fits for the mixed Ni/Mn fibers. The transition metal (oxides) in these fibers appear to be mostly crystalline as the ratio of Ni-containing crystals to Mn-containing crystals nearly matches the composition in the spinning dope. With increasing nickel content in the initial spinning dope, the concentration of Mn$_3$O$_4$ progressively decreases, while MnO concentration slightly increases in the composite fibers. This suggests that Mn$^{2+}$ (MnO) formation is favored with increasing nickel content in the spinning dope.

Table 5.3 Crystalline composition from Rietveld refinement of XRD profiles of Ni$_x$-Mn$_{100-x}$/C fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni$^0$ (mol%)</th>
<th>NiO (mol%)</th>
<th>MnO (mol%)</th>
<th>Mn$_3$O$_4$ (mol%)</th>
<th>(Ni+NiO): (MnO+Mn$_3$O$_4$) (mole ratios)</th>
<th>Ni$^0$ size (nm)</th>
<th>MnO size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>0$-Mn$</em>{100}$/C</td>
<td>--</td>
<td>--</td>
<td>91</td>
<td>9</td>
<td>--</td>
<td>--</td>
<td>30.6</td>
</tr>
<tr>
<td>Ni$<em>{33}$-Mn$</em>{66}$/C</td>
<td>16</td>
<td>23</td>
<td>7</td>
<td>54</td>
<td>0.62</td>
<td>29.2</td>
<td>23.5</td>
</tr>
<tr>
<td>Ni$<em>{50}$-Mn$</em>{50}$/C</td>
<td>32</td>
<td>25</td>
<td>9</td>
<td>34</td>
<td>1.3</td>
<td>27.8</td>
<td>24.6</td>
</tr>
<tr>
<td>Ni$<em>{66}$-Mn$</em>{33}$/C</td>
<td>43</td>
<td>27</td>
<td>12</td>
<td>18</td>
<td>2.3</td>
<td>23.7</td>
<td>24.9</td>
</tr>
<tr>
<td>Ni$<em>{100}$-Mn$</em>{0}$/C</td>
<td>90</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>36.5</td>
<td>--</td>
</tr>
</tbody>
</table>

In addition to identification of the crystal structures present, the XRD profiles were used to estimate the average crystal size by applying the Scherrer equation\textsuperscript{262} to the
most intense diffraction peaks for metallic Ni (44.6°) and MnO (40.8°). From these measurements, the average crystallite size of Ni decreases as the nickel content increases (29.2 nm in case of Ni_{33}-Mn_{66}/C to 23.7 nm for Ni_{66}-Mn_{33}/C). The surface structure of the fibers from SEM shows much larger features (~ 50 nm in case of Ni_{33}-Mn_{66}/C to 145 nm for Ni_{66}-Mn_{33}/C). As the sizes from SEM and XRD are significantly different, the Ni particles coating the fibers are likely polycrystalline, although the thickness of the particles may be similar to the crystal size determined from XRD. In contrast, the average MnO crystal size (~ 24 nm) is almost independent of the nickel concentration in the fiber except for the Ni free fibers. This difference in compositional dependencies on crystal size is likely associated with the location of the crystals in the fiber. Ni on the outside of the fiber has the potential for enhanced surface diffusion as the Ni segregates to the surface, but at high concentration this surface segregation could promote nucleation. Conversely, the MnO crystals are within the fibers; the carbon/resol within the fibers may provide constraints on the crystal growth. Carbon coatings have been shown to be an effective route to constrain crystallization of TiO$_2$ to maintain ordered mesopores.

One additional attribute of these electrospun fibers is the inclusion of block copolymer as a template. The N$_2$ adsorption-desorption isotherms in Figure 5.6 illustrate that these fibers are mesoporous. All of the Ni$_x$-Mn$_{100-x}$/C composites exhibit a type-IV isotherm with H$_2$-type hysteresis loop. These characteristics are consistent with an interconnected porous mesostructure. There is a slight shift in the closing of the hysteresis loop during desorption to lower partial pressures as the Ni content in the composite increases and the pore size distribution (PSD) determined from the adsorption isotherm shown in Figure 5.6B is only modestly impacted by the composition.
Figure 5.6 (A) N\textsubscript{2} (●) adsorption and (○) desorption isotherms for the mesoporous Ni\textsubscript{x}-Mn\textsubscript{100-x}/C fiber composites. (B) Pore size distribution for the mesoporous Ni\textsubscript{x}-Mn\textsubscript{100-x}/C fibers determined from the adsorption isotherm.

The PSD is broader than typically observed for block copolymer templated mesoporous materials,\textsuperscript{318, 319} but the average pore size, \( \sim 23 \) nm, is consistent with expectations for the block copolymer template.\textsuperscript{179} The breadth of the PSD is likely associated with the deformation of the mesostructure from crystallization of the components. Crystallization of the wall material is known to degrade the ordered
structure in mesoporous materials.\textsuperscript{145} In addition to these mesopores templated by the block copolymer, the PSD also indicates the presence of smaller mesopores (~2.5 nm). This pore size is too large and too prominent to be from the PEO,\textsuperscript{320} but densification on crystallization can lead to nanoporosity if polycrystalline. The similarity to the size of the crystals (as determined from XRD) is consistent with a common size for mesopores resulting from crystallization. From these data, Ni\textsubscript{x}-Mn\textsubscript{100-x}/C nanofibers form a three-dimensionally interconnected, hierarchically porous structure with macropores from the fiber morphology, large mesopores from the PMPEGMA-\textit{b}-PBA block copolymer template and small mesopores from crystallization of the components.

Table 5.4 BET surface area and micropore volume of Ni\textsubscript{x}-Mn\textsubscript{100-x}/C fiber composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{0}-Mn\textsubscript{100}/C</td>
<td>148</td>
<td>0.135</td>
</tr>
<tr>
<td>Ni\textsubscript{33}-Mn\textsubscript{66}/C</td>
<td>137</td>
<td>0.163</td>
</tr>
<tr>
<td>Ni\textsubscript{50}-Mn\textsubscript{50}/C</td>
<td>168</td>
<td>0.195</td>
</tr>
<tr>
<td>Ni\textsubscript{66}-Mn\textsubscript{33}/C</td>
<td>149</td>
<td>0.141</td>
</tr>
<tr>
<td>Ni\textsubscript{100}-Mn\textsubscript{0}/C</td>
<td>136</td>
<td>0.156</td>
</tr>
</tbody>
</table>

This hierarchical porosity also provides significant surface area for these electrospun fibers. From the adsorption isotherms, the BET surface area for the Ni\textsubscript{x}-Mn\textsubscript{100-x}/C nanofiber composites is approximately 150 m\textsuperscript{2}/g (Table 5.4) in all cases with an average pore volume ~ 0.16 cm\textsuperscript{3}/g. In particular, the surface area of these fiber is approximately 3 times larger than previously reported for electrospun metal oxide nanofibers\textsuperscript{283, 321} or hollow nanotubes.\textsuperscript{265, 284} This high surface area combined with
interconnected hierarchical porosity are promising attributes for electrochemical energy storage applications.

Figure 5.7 Discharge capacity of Ni$_{0}$-Mn$_{100}$/C and Ni$_{100}$-Mn$_{0}$/C nanofiber anode subjected to galvanostatic cycling between 0.01-3.0 V vs Li/Li$^+$ at varying current densities.

Figure 5.7 illustrates the galvanostatic capacity of Ni$_{0}$-Mn$_{100}$/C and Ni$_{100}$-Mn$_{0}$/C nanofiber anodes as a function of rate when incorporated into a lithium ion cell. The Ni$_{0}$-Mn$_{100}$/C as expected outperforms the Ni$_{100}$-Mn$_{0}$/C with an initial discharge capacity of 494 mAh/g, but this rapidly fades to 348 mAh/g (70% capacity retention) after 10 cycles at 0.05 A/g. Moreover, the rate capabilities are quite poor with the discharge capacity dropping to 142 mAh/g at 0.5 A/g and only 65 mAh/g at 1 A/g. The capacity does recover at low rate (0.05 A/g) to 402 mAh/g (81% of its initial capacity). However, the capacity of this electrode is significantly less than theoretical for manganese oxide (MnO = 755 mAh/g and Mn$_3$O$_4$ = 937 mAh/g) even when considering that 18 wt% of the fibers are carbon. Conversely, the Ni$_{100}$-Mn$_{0}$/C nanofiber anode exhibits stable, but low
performance due to its composition of metallic nickel and the resol-derived carbon. The carbon provides limited charge storage capabilities and mainly behaves as a current collector. As such, primarily double-layer capacitance is obtained from this electrode, although the charge transfer resistance is low due to the high conductivity of the metallic Ni and carbon. Thus, the fibers containing both Ni and Mn could provide performance advantages over these fibers.

Figure 5.8 (A) Discharge capacity of Ni$_x$-Mn$_{100-x}$/C fiber anodes subjected to varying current densities between 0.01-3.0 V vs Li/Li$^+$. (B) Specific discharge capacity of Ni$_x$-Mn$_{100-x}$/C nanofiber anode normalized by the weight of electroactive material when galvanostatically cycled at varying current densities.

Figure 5.8A illustrates the capacity of the Ni$_x$-Mn$_{100-x}$/C composite fiber anodes at varying current densities. In these cases, a significant fraction (~50%) is not fully reduced and the NiO (theoretical capacity = 717 mAh/g) should also contribute to the capacity. None of the composites outperform the Ni$_0$-Mn$_{100}$/C fibers at low rates and the initial discharge performance is found to be much lower than the expectations based on the theoretical capacity. It must be noted that the capacities shown in Figure 5.7 and Figure 5.8A include the total mass of the fibers. The nickel and carbon can be envisioned as
mechanical reinforcement for the anodes to prevent pulverization of fiber morphology from lithium insertion-deinsertion during battery cycling.\textsuperscript{67, 118, 322} The fade in capacity on cycling even at the lowest rate depends on the composition of the fiber. The higher MnO\textsubscript{x} composition fibers fade more rapidly. At 0.5 A/g, the composite electrode with the lowest theoretical capacity (Ni\textsubscript{66}-Mn\textsubscript{33}/C) exhibits the highest capacity (Figure 5.8A). At 1 A/g, the Ni\textsubscript{66}-Mn\textsubscript{33}/C composite anode exhibits a higher capacity (99 mAh/g) than even the Ni\textsubscript{0}-Mn\textsubscript{100}/C anode (49 mAh/g, Figure 5.7). This higher capacity is despite including a much larger fraction of non-active material in the mass normalization of the capacity for Ni\textsubscript{66}-Mn\textsubscript{33}/C. Even more strikingly, the performance of the Ni\textsubscript{66}-Mn\textsubscript{33}/C anode on decreasing the rate to 0.05 A/g exceeds the initial capacity of the electrode. A similar increase in capacity has been reported for Ni encapsulated MnO nanowires, where the increase in capacity is attributed to improvement in electrical contacts between the metal oxide and electronically conductive Ni upon successive cycling.\textsuperscript{298} The enhancement in capacity can also be enabled by high-rate lithiation-induced reactivation of electrode surface.\textsuperscript{323} Successive lithiation leads to a reactivation process, where the porous fiber anode structure becomes more robust to volume changes and a stable SEI layer is formed.\textsuperscript{323} These phenomena lead to an overall enhancement in charge transfer kinetics across the Ni\textsubscript{66}-Mn\textsubscript{33}/C anode and higher discharge capacities upon successive cycling.

To enable more direct comparison to the literature, the performance of these electrodes can be normalized by the mass of electrochemically active metal oxide (MO\textsubscript{x}), which includes MnO, Mn\textsubscript{3}O\textsubscript{4}, and NiO, using the composition determined from XRD (Table 5.3). Figure 5.8 illustrates the capacity of these composite fiber anodes based on the mass of MO\textsubscript{x}. In this case, mesoporous Ni\textsubscript{66}-Mn\textsubscript{33}/C fiber anode exhibits the highest
specific discharge capacity at all rates. The initial capacity is 895 mAh/g and fades to 795 mAh/g after 10 cycles at 0.05 A/g. These discharge capacities exceed or approach the theoretical value predicted (802 mAh/g) for MnO$_x$ and NiO$^{266}$ anodes. Table 5.5 shows the predicted capacities for all of the electrodes examined based on their MO$_x$ composition.

Table 5.5 Calculated theoretical capacity and obtained capacity based on MO$_x$ composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active MO$_x$ components (wt % of fiber anode)</th>
<th>Theoretical capacity (mAh/g MO$_x$)</th>
<th>Capacity at highest rate (1 A/g) (mAh/g MO$_x$)</th>
<th>Capacity after rate cycling (0.05 A/g) (mAh/g MO$_x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{10}$-Mn$</em>{100}$/C</td>
<td>81</td>
<td>798</td>
<td>89</td>
<td>539</td>
</tr>
<tr>
<td>Ni$<em>{33}$-Mn$</em>{66}$/C</td>
<td>70</td>
<td>858</td>
<td>37</td>
<td>239</td>
</tr>
<tr>
<td>Ni$<em>{50}$-Mn$</em>{50}$/C</td>
<td>58</td>
<td>830</td>
<td>107</td>
<td>498</td>
</tr>
<tr>
<td>Ni$<em>{66}$-Mn$</em>{33}$/C</td>
<td>35</td>
<td>802</td>
<td>317</td>
<td>983</td>
</tr>
</tbody>
</table>

After cycling and returning the current density to 0.05 A/g, the specific discharge capacity is found to progressively increase to 983 mAh/g after 10 cycles. This capacity is 22% higher than the theoretical performance, which is due to the contribution of the Ni and carbon to the capacity through the double layer (as shown in Figure 5.7). However, the mesoporous Ni$_{50}$-Mn$_{50}$/C and Ni$_{33}$-Mn$_{66}$/C fiber anodes exhibit significantly lower specific discharge capacities especially at high rate. This suggests that metallic Ni encapsulation of Ni$_x$-Mn$_{100-x}$/C nanofiber anode plays a crucial role in enhancing the
electronic conductivity of the composite anode while also contributing towards the enhancement in performance on cycling of the electrode.

Figure 5.9 Electrochemical impedance spectroscopy (EIS) of Ni\textsubscript{x}-Mn\textsubscript{100-x}/C fiber anodes at 0.1 - 10\textsuperscript{5} Hz prior to galvanostatic cycling. The overall impedance of composite anode is reduced with increasing Ni content.

To corroborate the enhancement in electronic conductivity of mesoporous Ni\textsubscript{x}-Mn\textsubscript{100-x}/C anodes through nickel doping, EIS was used as shown in Figure 5.9. The electrolyte solution resistance (R\textsubscript{s}) and contact resistance between the active material and current collector are almost invariant with the chemical composition of the fiber anodes. However, the charge transfer resistance (R\textsubscript{CT})\textsuperscript{28,135}, which is associated with the diameter of the semi-circle in low-frequency region, is significantly reduced as the nickel content is increased. The solid electrolyte interface (SEI) layer resistance (R\textsubscript{SEI}) and capacitance (C\textsubscript{SEI}) at high frequency is only modestly impacted.
Figure 5.10 Electrochemical impedance spectroscopy (EIS) and the simulated fits (A) Ni$_{100}$-Mn$_{0}$/C (B) Ni$_{66}$-Mn$_{33}$/C (C) Ni$_{50}$-Mn$_{50}$/C (D) Ni$_{33}$-Mn$_{66}$/C and (E) Ni$_{0}$-Mn$_{100}$/C composite fibers at 0.1 - 10$^5$ Hz prior to galvanostatic cycling. (F) Equivalent circuit used to model the impedance data (Rs = solution resistance, R$_{SEI}$ = SEI resistance, C$_{SEI}$ = SEI capacitance, R$_{CT}$ = charge transfer resistance, W = Warburg impedance, Q = constant phase element, FD = finite length diffusion impedance)
To more quantitatively compare the charge transfer resistance in Ni$_x$-Mn$_{100-x}$/C composite fiber anodes, the EIS data were fit with an equivalent circuit model, with the best fits shown as the lines in Figure 5.10. $R_{CT}$ significantly reduces from 459 Ω for Ni$_{33}$-Mn$_{66}$/C to 238 Ω for Ni$_{66}$-Mn$_{33}$/C nanofiber anode. This reduction in the overall impedance of Ni$_x$-Mn$_{100-x}$/C composite anodes is attributed to fiber encapsulation by metallic nickel, which also leads to enhancement in charge storage capabilities at high C-rates. The superior high C-rate performance of electronically conductive mesoporous Ni$_{66}$-Mn$_{33}$/C anode demonstrates the critical role of conductive additives and the development of well-defined charge transfer pathways in metal oxide anodes for Li ion batteries.

![Figure 5.11 Cyclic voltammetry curves for mesoporous (A) Ni$_{33}$-Mn$_{66}$/C (B) Ni$_{50}$-Mn$_{50}$/C (C) Ni$_{66}$-Mn$_{33}$/C fiber anodes carried out at a scan rate 0.5 mV/s.](image-url)
Finally, to gain some insights into the electrochemical charge transfer processes taking place in the Ni_x-Mn_y/C composite fiber anodes, cyclic voltammetry curves were recorded on the composite anodes at a slow scan rate of 0.5 mVs^{-1} (Figure 5.11). As can be seen in Figure 5.11, redox peaks centered around 1.05 V and 0.2 V can be associated with reduction of Mn^{2+} to Mn^{0}, Ni^{2+} to Ni^{0} along with SEI formation to electrolyte decomposition irrespective of the chemical composition. A shift in the cathodic reduction peak to 0.25 V in subsequent cycles occurs due to reversible phase transformation of Li_{2}O and metallic manganese.\textsuperscript{135, 324} Reversible oxidation peaks are observed in the anodic segment around 1.31 V due to oxidation of Mn^{0} towards higher oxidation state Mn^{2+} and Mn^{3+}. Oxidation peaks corresponding to Ni^{0} to Ni^{2+} is evidenced by the small peak centered around 2.2 V.\textsuperscript{266} A very weak and broad anodic peak associated with decomposition of polymer gel layer and partial oxidation of Mn^{0} to even higher oxidation state Mn^{4+} is also visible at 2.25 V.\textsuperscript{286, 324} Manganese oxides in the form of MnO_{2}, Mn_{3}O_{4} and MnO can often undergo reversible conversion reactions between MnO and metallic Mn.

The presence of redox peaks at such high potential in the anodic segment indicates the enhanced kinetics of charge transfer in the nickel and carbon doped Ni_x-Mn_y/C fiber anodes.\textsuperscript{324} An important point to note is that the intensity of the redox peaks significantly reduces with decrease in electroactive NiO/MnO_x content in the composite fibers. Also the CV curves for Ni_{66}-Mn_{33}/C fiber anode almost overlap with negligible reduction in redox peak intensities on successive cycling as against the CV curves obtained for Ni_{33}-Mn_{66}/C anodes. This further demonstrates the enhanced cycling efficiency in mesoporous Ni_x-Mn_{100-x}/C anodes containing higher Ni content.
Figure 5.12 Galvanostatic charge-discharge cycling of Ni$_x$-Mn$_{100-x}$/C fiber anodes at a constant current density of 0.1A/g. A current density of 0.05A/g was used for the first 5 charge-discharge cycles.

Figure 5.12 illustrates the long-term charge-discharge cycling of the mesoporous Ni$_x$-Mn$_{100-x}$/C fiber anodes. Both Ni$_{50}$-Mn$_{50}$/C and Ni$_{33}$-Mn$_{66}$/C exhibit an initial large capacity fade over the first 8 cycles and then a slow continuous capacity fade on subsequent cycling. For Ni$_{33}$-Mn$_{66}$/C, the specific discharge capacity decreases from 361 mAh/g to 188 mAh/g after 200 cycles (52 % capacity retention). However for the mesoporous Ni$_{50}$-Mn$_{50}$/C and Ni$_{66}$-Mn$_{33}$/C fiber anodes, the discharge capacity initially decreases during the first 5 cycles at the slow rate of 0.05 A/g to a minimum of 520 mAh/g and 457mAh/g, respectively. The capacity in case of Ni$_{50}$-Mn$_{50}$/C fiber anode increases upon successive cycling to a plateau value of approximately 620 mAh/g after 200 cycles. A significant increase in capacity is observed with Ni$_{66}$-Mn$_{33}$/C fiber anode with the discharge capacity increasing to 1360 mAh/g after 200 cycles. Such an increase in specific capacity can be attributed to the high-rate lithiation induced reactivation of
Ni\textsubscript{66}-Mn\textsubscript{33}/C fiber anode surface that leads to improvement in charge transfer kinetics upon successive cycling through formation of a stable SEI.\textsuperscript{323} This is translated into progressively higher discharge capacities of Ni\textsubscript{66}-Mn\textsubscript{33}/C fiber anode upon galvanostatic cycling. The cycling stability and reversible capacities exhibited by mesoporous Ni\textsubscript{66}-Mn\textsubscript{33}/C fiber anode are significantly higher than previously reported capacities for carbon-manganese oxide composite fiber anodes,\textsuperscript{28, 134, 325} but the fraction of active material is significantly lower than these prior studies. The deterioration in charge storage performance of mesoporous Ni\textsubscript{33}-Mn\textsubscript{66}/C and Ni\textsubscript{50}-Mn\textsubscript{50}/C fiber anode on successive cycling can be attributed to inefficient encapsulation of fiber surface by metallic Ni. Isolated metallic Ni particles lead to inefficient electronic transport paths and poor cycling stability.\textsuperscript{298} Thus, metallic nickel coatings can significantly enhance performance through reducing the charge transfer resistance and providing strain relief during cycling process, but continuous pathways are critical to its overall efficacy.

5.4 Conclusion

In this work, we demonstrate a simple technique to fabricate electronically conductive and interconnected porous metal oxide fiber composites (Ni\textsubscript{x}-Mn\textsubscript{100-x}/C) using electrospinning and cooperative assembly. The membrane-like fiber morphology offers several advantages over isolated nanotubes and nanowire-based lithium ion battery anodes. The chemical composition of Ni\textsubscript{x}-Mn\textsubscript{100-x}/C fiber composites and well defined contacts between the fibers enable low charge transfer resistance and enhanced cycling stability. Highest discharge capacity on the basis of active material is obtained for the mesoporous Ni\textsubscript{66}-Mn\textsubscript{33}/C fiber anode with a capacity of 1360 mAh/g after 200 cycles. This anode also exhibits good cycling stability and low impedance (238 $\Omega$) due to
effective encapsulation of fiber surface with electronically conductive metallic Ni. High-rate lithiation induced reactivation of nanofiber surface significantly contributes to towards enhancement in discharge capacities during long-term cycling studies. This study illustrates the importance of electronic conductivity and continuous charge transfer pathways necessary for high performance lithium ion battery anodes.
CHAPTER VI

IN-OPERANDO GISAXS/GIXD OF ORDERED MESOPOROUS NICKEL COBALTITE ANODES TO UNDERSTAND NANOSTRUCTURE CHANGES DURING LITHIUM ION BATTERY OPERATION

6.1 Introduction

Lithium ion batteries (LIB) are an important class of rechargeable energy storage devices possessing high energy density, long cycle life, low toxicity and relatively low cost.\textsuperscript{35, 38} However, the use of low theoretical capacity graphite based anodes (372 mAh/g)\textsuperscript{105} in LIBs is considered a major bottleneck in the advancement of battery technology. Hence, significant efforts have been directed towards developing alternate anode materials in the form of metal oxides\textsuperscript{94} or mixed-metal oxides,\textsuperscript{187, 326} which possess significantly higher discharge capacities. Another effective strategy to improve electrode capacity and cycling stability involves fabrication of porous and high surface area, nanostructured metal oxide anodes utilizing templating strategies.\textsuperscript{147, 155, 327}

Block copolymer templating offers a convenient strategy to fabricate highly ordered mesoporous metal oxides with precise control over pore geometry and porosity. Such templated metal oxide anodes possess high electro-active surface area, short Li\textsuperscript{+} ion diffusion length and provide efficient electrolyte transport paths, making them ideal materials for anodes for LIBs.\textsuperscript{155}
Various reports on block copolymer templated mesoporous metal oxides have illustrated the importance of nanoporous morphology on enhancement in charge storage capabilities of metal oxide anodes.\textsuperscript{21, 32, 143, 328} Previous studies have also focused on the effect of mesopore wall thickness,\textsuperscript{23} mesopore geometry\textsuperscript{329} and pore length\textsuperscript{146, 330} on the capacity behavior and improved rate capabilities of porous oxide anodes. However, the critical role of mesopore dimensions and porosity contributing towards enhanced charge storage performance is still not clearly understood. Similarly, the underlying mechanisms contributing towards improved capacity retention and cycling stability in ordered mesoporous metal oxide anodes are still not understood. Hence, there is a need to identify the dynamic changes occurring in ordered mesoporous metal oxide anodes during battery operation to gain insights into electrochemical charge storage processes.

A recent \textit{in-operando} SAXS study revealed that mesostructure of metal oxide anodes evolves significantly during the lithiation and de-lithiation process.\textsuperscript{31} Such evolution of anode mesostructure during battery operation can contribute towards capacity fade on long-term cycling. In case of mesoporous metal oxide anodes which follow conversion-type charge storage mechanism, only partial distortion of ordered mesostructure was observed due to limited volume expansion associated with Li\textsuperscript{+} ion insertion/de-insertion.\textsuperscript{31} However, the effect of mesopore dimensions, porosity and oxide wall thickness on the evolution of mesostructure and crystal structure during battery operation was not elucidated. Similarly, the effect of mesostructure distortion on long-term capacity retention of anode was not addressed.

To bridge the gap between these loopholes and develop design heuristics for fabrication of high energy density and stable mesoporous metal oxide anodes, we
demonstrate a complimentary *in-operando* grazing incidence small angle x-ray scattering (GISAXS) and grazing incidence x-ray diffraction (GIXD) study on block copolymer templated mesoporous NiCo$_2$O$_4$ anode. Nickel cobaltite (NiCo$_2$O$_4$) is a conversion-type metal oxide anode that stores charge primarily through redox conversion reactions$^{247,331}$ and is chosen as a model system in our study. Based on this *in-operando* study, we attempt to develop a mechanistic understanding of the effect of mesopore dimensions and oxide wall thickness on capacity retention and cycling stability of mesostructured metal oxide anodes exhibiting conversion-type charge storage mechanism.

*In-operando* GISAXS allows investigating real-time evolution of NiCo$_2$O$_4$ anode mesostructure, while GIXD tracks the changes in crystal structure of NiCo$_2$O$_4$ during battery operation. By coupling these two *in-operando* techniques, we demonstrate that the distortion of ordered mesostructure significantly depends on the initial mesopore dimensions. In case of nanostructured NiCo$_2$O$_4$ anodes possessing mesopores smaller than ~10 nm, the ordered porous structure is completely lost within the first 2 cycles due to volume expansion/contraction of oxide framework, while anodes with pore size greater than 10 nm suffer only partial distortion of mesostructure in the first 2 cycles. The initial mesopore dimensions also play an important role in the efficiency of Li$^{+}$ ion insertion/de-insertion from the mesoporous oxide framework. When the mesopore size is smaller than ~10 nm, collapse of NiCo$_2$O$_4$ anode mesostructure is accompanied by irreversible electrochemical reactions and Li$^{+}$ ions getting stuck in the oxide framework. The loss of ordered mesostructure along with irreversible chemical reactions leads to significant capacity fade in mesoporous NiCo$_2$O$_4$ anodes possessing pore dimensions smaller than 10 nm. Mesoporous NiCo$_2$O$_4$ anodes possessing mesopores larger than 10 nm suffer only
partial distortion in the mesostructure during cycling and exhibit improved cycling stability and charge storage capabilities. This study thus provides insights into capacity fade exhibited by hard-templated or Pluronictemplated metal oxide anodes (d_{pore}~5 nm) as against KLE or PEO-b-PB-b-PEO templated metal oxide anodes (d_{pore}>10 nm). Based on the findings of this complimentary in-operando study, we can develop design principles for fabrication of block copolymer templated metal oxide anodes that exhibit enhanced discharge capacity and excellent cycling stability at high C-rates.

6.2 Materials and methods

**Materials:** Nickel (II) nitrate hexahydrate (puriss. p.a., ≥98.5%), cobalt (II) nitrate tetrahydrate (reagent grade, 98 %), citric acid (ACS reagent, ≥99.5%), ethanol (ACS reagent, ≥99.5% (200 proof), absolute), tetrahydrofuran (THF) (ACS reagent, ≥99.0%, containing 250 ppm BHT as inhibitor), mercaptosuccinic acid (97%), methoxy poly(ethylene glycol) methacrylate (PMPEGMA 475 g mol^{-1}), butyl acrylate (>99%), N, N-Dimethylformamide (DMF) (anhydrous, 99.8%), hexane (anhydrous, 95%) were purchased from Sigma-Aldrich and used as received. 2,2’-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to the literature. Deuterated chloroform (CDCl₃) (Cambridge Isotope Laboratories, Inc.) were used as received.
For battery testing, lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate: dimethyl carbonate (EC: DMC) 1:1 (v/v) was purchased from BASF Battery Materials. Lithium metal foil (0.25 mm thickness) was used as the reference and counter electrode.

**Preparation of mesoporous NiCo$_2$O$_4$ thin film anodes:** Prior to mesoporous NiCo$_2$O$_4$ thin film fabrication, a thin gold layer (~ 50 nm) was initially sputter-coated on sapphire substrate (0.375” diameter, 0.02” thickness, Esco Optics) to form a conductive current collector. The gold coated sapphire substrates were treated with 10 mM ethanoic mercaptosuccinic acid for 24 h to form a hydrophilic surface. After 24 h, the substrates were rinsed by ethanol multiple times and dried using a nitrogen purge.

Mesoporous NiCo$_2$O$_4$ thin film anodes with pore size varying between 10 nm and 30 nm were prepared using block copolymer micelle templating protocols described elsewhere.$^{179, 184, 187}$ Poly[methoxy poly(ethylene glycol)methacrylate]-block-poly(butyl acrylate), PMPEGMA-b-PBA, served as the structure directing and templating agent. PMPEGMA-b-PBA block copolymer templates with molecular weights 37 kg•mol$^{-1}$, 59 kg•mol$^{-1}$ and 101 kg•mol$^{-1}$ were synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization$^{260}$ following protocols mentioned elsewhere.$^{189}$

Nomenclature used for mesoporous NiCo$_2$O$_4$ thin film anodes was m-NCx, where “m” stands for mesoporous, “NC” relates to nickel-cobalt mixed metal oxide while “x” denotes the approximate pore width of the templated oxide thin film. In a typical synthesis protocol, m-NC9 thin films were fabricated by first mixing 0.147 g of Ni(NO$_3$)$_2$.6H$_2$O and 0.285 g of Co(NO$_3$)$_2$.6H$_2$O with 0.143 g of citric acid in 0.77 g ethanol solvent. This mixture was stirred in a vortex mixer for 1h at 22 °C. In a separate
vial, 0.254 g of PMPEGMA-b-PBA with molecular weight 37 kg•mol⁻¹ was dissolved in 2.28 g of THF and stirred at 400 rpm for 1 h. The ethanoic solution of metal nitrates and citric acid was then added dropwise to the PMPEGMA-b-PBA/THF solution and stirred for another 1 h to obtain a dark red colored solution. The exact chemical compositions utilized to fabricate m-NC16 and m-NC28 thin film samples are given in the table below.

Table 6.1 Chemical composition utilized for fabrication of m-NCx thin film anodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni(NO₃)₂.6H₂O (g)</th>
<th>Co(NO₃)₂.6H₂O (g)</th>
<th>Citric acid (g)</th>
<th>PMPEGMA-b-PBA (g)</th>
<th>Ethanol (g)</th>
<th>THF (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-NC9</td>
<td>0.147</td>
<td>0.285</td>
<td>0.143</td>
<td>0.254</td>
<td>0.77</td>
<td>2.28</td>
</tr>
<tr>
<td>m-NC16</td>
<td>0.172</td>
<td>0.345</td>
<td>0.176</td>
<td>0.275</td>
<td>0.86</td>
<td>2.46</td>
</tr>
<tr>
<td>m-NC28</td>
<td>0.137</td>
<td>0.266</td>
<td>0.134</td>
<td>0.257</td>
<td>0.79</td>
<td>2.27</td>
</tr>
</tbody>
</table>

The m-NCx thin film anodes were fabricated by dip coating at 1 mm.s⁻¹ at relative humidity 30%-40%. The cast thin films were dried at room temperature for 15 min followed by calcination in preheated muffle furnace (Ney Vulcan 3-130) at 225 °C for 1 h to fabricate the micelle templated carbonates. These templated NiCo₂(CO₃)y carbonate thin films were passively cooled down to room temperature followed by another heating stage at 365 °C for 30 min to fabricate m-NCx film anodes.

**Mesoporous NiCo₂O₄ thin film morphology characterization:** Thermogravimetric analysis (Thermal Analysis Q50) was used to determine the decomposition temperature of PMPEGMA-b-BA templates, along with onset temperatures for NiCo₂(CO₃)y and NiCo₂O₄ formation. Crushed powders of the nickel nitrate, cobalt nitrate and citric acid were prepared by first mixing metal nitrate and citric acid in ethanol / THF mixture at 22 °C. This solution was dried by heating under vacuum at 50 °C for 10 h and the obtained
powders were crushed to perform TGA using a constant air purge and heating rate of 5 °C/min. Spectroscopic ellipsometry (M-2000, J. A. Woollam) was utilized to determine the thickness of the m-NCx thin film anodes. The optical properties of the porous oxide films were modelled in the wavelength range of 350–1100 nm using Gaussian and Lorentz oscillators (GenOsc model) in WVase software (J. A. Woollam). The porosity and pore size distribution of m-NCx thin film anodes was estimated from ellipsometric porosimetry (EP) using ethanol as the probe solvent. The Kelvin equation was applied to the adsorption isotherm to determine the pore size distribution in the porous thin films. Based on EP data, the volume of solvent adsorbed at saturation corresponds to quantity of ethanol filled within voids; this value at saturation pressure was used to estimate the porosity of m-NCx anodes. The mesoporous surface morphology of the m-NCx thin film anodes was investigated prior to and after galvanostatic cycling using atomic force microscopy (AFM, Dimension ICON, Veeco). Complementary real space images were obtained by transmission electron microscopy (TEM) using a JEOL JEM2100F microscope in both bright- and dark-field imaging modes. The TEM samples were prepared using the focused ion beam (FIB) in situ lift-out specimen technique.

**In-operando synchrotron GISAXS/GIXD characterization:** Grazing incidence small angle X-ray scattering (GISAXS) was performed at the 12-ID-B beamline of Advanced Photon Source (APS) at Argonne National Laboratory (ANL) to *in-operando* monitor changes in m-NCx mesostructure during battery operation. Galvanostatic cycling was carried out in a custom-designed lithium ion cell consisting of a polyimide tube window to allow x-rays to penetrate onto the thin film anodes (Figure 6.1). An incident X-ray beam of energy 14 keV (0.0918 nm) and beam size 250 µm was used and the scattering
data were collected using a Pilatus detector with sample to detector distance (SDD) fixed at 1922 mm. All samples were measured at incident angle of 0.18°, which is above the critical angle of the NiCo$_2$O$_4$ thin film sample. The 2-dimensional scattering patterns obtained through GISAXS were scanned using the Irena software package$^{337}$ to obtain the one-dimensional (1D) line-cuts profiles in the form of the Intensity vs $q_x$. For m-NCx thin film anodes, NiCo$_2$O$_4$ nanoparticle size analysis was carried out assuming a dilute system form factor and spheroid structure factor to account for the shape for NiCo$_2$O$_4$ nanoparticles.

Figure 6.1 Custom-designed lithium ion cell and outer body to carry out in-operando GISAXS/GIXD and galvanostatic cycling of m-NCx anodes

Grazing incidence X-ray diffraction (GIXD) was also performed at the 12-ID-B beamline of APS at ANL to determine changes in m-NCx crystal structure during battery charging-discharging process. Incident X-ray energy of 14 keV was utilized and the scattered intensity was collected on a charged couple device (CCD) WAXS detector. The SDD in case of GIXD was fixed at 176 mm. The background scattering contributions from LiPF$_6$ in EC/DMC electrolyte and gold coated sapphire substrate was subtracted from the diffraction patterns of m-NCx. The average crystal size of m-NCx was estimated
applying the Scherrer equation\textsuperscript{262} to the most intense diffraction peak and assuming $\beta = 0.9$.

**Electrochemical characterization of m-NCx thin film anodes:** The fabricated m-NCx thin films were directly tested as binder-free anodes in the custom-designed lithium ion cell. The average NiCo$_2$O$_4$ mass loading in the m-NCx film anodes was ~500 mg/m$^2$. Galvanostatic measurements were carried out using 1M LiPF$_6$ in EC/DMC (1:1 v/v) as the electrolyte with Li metal foil acting as the counter and reference electrode. Constant current density charge-discharge runs were carried out with a battery tester (BST8-WA, MTI) within a potential window of 0.2V-3.0V vs Li/Li$^+$. All thin film anodes were subjected to initial galvanostatic discharge at a current density of 300 mA/g, while a current density of 600 mA/g was utilized in the following cycles. A constant Ar gas flow was maintained across the custom-designed cell during battery operation to prevent oxidation of Li metal. *Ex-situ* long-term cycling tests were performed in an Ar glovebox with O$_2$ and H$_2$O <0.5 ppm, with initial discharge current density fixed at 300 mA/g, while a current density of 600 mA/g was utilized in the following cycles.

6.3 Results and discussion

To study the effect of metal oxide mesopore geometry on charge storage performance and cycling stability of lithium ion battery electrodes, templated NiCo$_2$O$_4$ thin film anodes (m-NCx) with varying pore diameter were fabricated utilizing micelle templating strategy.\textsuperscript{179, 184, 187} Figure 6.2 illustrates the surface morphology of PMPEGMA-$b$-PBA templated porous m-NCx thin films prior to galvanostatic cycling the anodes in custom-designed lithium ion cell. The average m-NCx film thickness
determined using ellipsometer is 90 nm. A well-ordered porous structure with spherical mesopores is obtained in case of m-NC28 and m-NC16 thin film anodes. Fast fourier transform (FFT) micrographs indicate an average pore center-to-center distance of 48.5 nm for m-NC28 and 26.5 nm in case of m-NC16 thin film.

The surface morphology of m-NC9 film, on the other hand, primarily appears to be made up of tiny NiCo$_2$O$_4$ nanoparticles (~5 nm). Nonetheless, the broad ring obtained from the FFT image indicates formation of an poorly ordered structure with average spacing between mesopores ~ 15 nm. Based on the AFM micrographs, the average pore width of the templated m-NCx anodes is found to significantly vary from 28 nm (m-NC28) to 9 nm (m-NC9) depending on the molecular weight of PMPEGMA-b-PBA template used. Mesopore dimensions of m-NC9 anode (d$_{pore}$~9 nm) are close to the pore size commonly observed in KIT-6, SBA-15, SBA-15 or Pluronic® (PEO-PPO-PEO) surfactant templated mesoporous metal oxide anodes. Mesoporous m-NC16 and m-NC28, on the other hand, exhibit larger pore dimensions similar to those observed in KLE, PI-b-PEO or PEO-b-PB-b-PEO templated mesoporous metal
oxides. The scaling of mesopore dimension with the total degree of polymerization to the power $\frac{1}{2}$, is similar to previous reports on block copolymer self-assembly and micelle templated of mesoporous Co$_3$O$_4$ thin films.\textsuperscript{179, 340, 341} Taking into account the average pore width and average center-to-center distance between pores, the wall thickness of m-NCx matrix is found to decrease from 20.5 nm (m-NC28) to 6 nm (m-NC9). By precisely controlling NiCo$_2$O$_4$ pore geometry and porosity, block copolymer micelle templating strategy provides a simple route to develop a mechanistic understanding of the effect of pore geometry on charge storage performance in battery electrodes.

Figure 6.3 (A) \textit{In-operando} GISAXS-galvanostatic cycling runs on m-NC9 thin film anode (B) Quantitative analysis of change in $d$-spacing of m-NC9 anode during successive lithiation and de-lithiation segments
To investigate \textit{in-operando} changes in NiCo$_2$O$_4$ anode mesostructure and crystal structure during battery operation, a custom-designed lithium ion cell (Figure 6.1) containing kapton tube window was used. Initially m-NC9 thin film anode was subjected to \textit{in-operando} grazing incidence small angle x-ray scattering (GISAXS) measurements while galvanostatically cycling the thin film anode between 0.2-3V vs Li/Li$^+$, to observe mesostructural changes in the anode (Figure 6.3). Nickel cobaltite (NiCo$_2$O$_4$) electrode follows conversion-type charge storage mechanism when tested as anode in lithium ion battery.$^{247, 295}$ On initially discharging m-NC9 anode, multiple plateaus are observed in the voltage profile around 2.1 V, 1.5 V and 0.92 V corresponding to the multi-step reduction of NiCo$_2$O$_4$ accompanied by electrolyte decomposition. These redox plateaus are also observed in the successive charge-discharge segments illustrating the reversible nature of the electrochemical reactions in these templated anodes.

To better understand the pore dynamics during the charge transfer process, the primary scattering peak obtained from \textit{in-operando} GISAXS was tracked during galvanostatic cycling of m-NC9 anode. Prior to galvanostatic cycling, m-NC9 anode indicates a primary peak centered around $q_x \approx 0.044$ Å$^{-1}$ ($d$-spacings = 14.19 nm) and a weak second order peak ($q_x \approx 0.068$ Å$^{-1}$; $d$-spacings = 9.2 nm). The $d$-spacing of primary scattering peak (14.19 nm) matches well with the average center-to-center distance (15 nm) between mesopores determined from AFM micrographs (Figure 6.2). The weak 2$^{\text{nd}}$ order peak corresponds to correlations between mesopore walls and is found to be a close match with the average pore width of m-NC9 anode ($d_{\text{pore}} \sim 9$ nm). Quantitative analysis of the primary diffraction peak indicates that $d$-spacing changes reversibly during the lithiation and de-lithiation process (Figure 6.3B). During the initial discharge cycle
(lithiation segment), $d$-spacing is found to increase from 14.19 nm to 14.52 nm. It has been well documented that metal oxide anodes undergo volume expansion during redox conversion reactions.\textsuperscript{94,331} The increase in $d$-spacing in case of mesoporous m-NC9 can be attributed to insertion of Li\textsuperscript{+} ions in the oxide matrix accompanied by volume expansion of NiCo$_2$O$_4$ framework during the conversion reactions.\textsuperscript{31} During the 1\textsuperscript{st} charge cycle (de-lithiation segment), the $d$-spacing reduces back to 14.18 nm as the Li\textsuperscript{+} ions de-insert the mesoporous NiCo$_2$O$_4$ framework. However, the weak second order peak associated with mesopore geometry almost completely disappears by the end of this segment indicating loss of correlations between mesopore walls, or significant distortion of spherical mesopore geometry. On subsequent lithiation of m-NC9 anode (1\textsuperscript{st} discharge cycle), the $d$-spacing based on primary diffraction peak again increases and reaches a value of 14.5 nm, indicating the reversible volume expansion-contraction experienced by m-NC9 framework. Surprisingly, by the end of 2\textsuperscript{nd} charge (de-lithiation) segment, the primary scattering peak originating from m-NC9 mesostructure almost disappears. This suggests collapse of mesoporous morphology by the end of 2\textsuperscript{nd} charge (de-lithiation) segment in m-NC9 anode. Quantitative analysis of the primary peak after 2\textsuperscript{nd} de-lithiation segment indicates almost 8.5\% volume expansion of m-NC9 framework.

During these successive lithiation and de-lithiation segments, intensity of primary scattering peak is found to significantly reduce (Figure 6.4A). The decrease in scattered peak intensity can be attributed to solid electrolyte interface (SEI) formation on the mesopore walls, which leads to decrease in contrast between the mesopore voids and inorganic NiCo$_2$O$_4$ matrix. However, loss of primary peak observed in 1-D GISAXS profile of m-NC9 anode indicates loss of correlations between mesopores and collapse of
mesostructure by the end of 2\textsuperscript{nd} de-lithiation segment. The full width half maximum (FWHM) of the primary scattering peak also significantly increases during the 2\textsuperscript{nd} de-lithiation segment, corroborating loss of mesostructure by the end of 2\textsuperscript{nd} de-lithiation segment (Figure 6.4B).

Figure 6.4 Quantitative mapping of (A) peak intensity and (B) full width-half max (FWHM) of primary scattering peak observed from 1-D GISAXS profiles of m-NC9 anode subjected to galvanostatic cycling vs Li/Li\textsuperscript{+}.

This is contrary to previous report on pore dynamics of ordered mesoporous Co\textsubscript{3}O\textsubscript{4} anode, which suggested only partial loss of porous mesostructure in anode materials following conversion-type charge storage mechanism.\textsuperscript{31} Collapse of mesoporous m-NC9 anode morphology suggests that small mesopores (~9 nm) and thin mesopore walls (~6 nm) cannot sustain the stresses formed during volume expansion-
contraction of metal oxide framework. This leads to collapse of m-NC9 ordered mesostructure by the end of 2nd de-lithiation segment. Based on these results, one can expect KIT-6 or Pluronic® surfactant templated ordered mesoporous oxides with pore dimensions (~5 nm) much smaller than m-NC9 anode to suffer similar loss of porous morphology during battery operation due to stresses developed in the oxide framework.

To corroborate loss of ordered porous structure on galvanostatic cycling m-NC9 anode, cross-sectional transmission electron microscopy (TEM) micrographs were obtained after 2 cycles. As can be seen in Figure 6.5A, m-NC9 anode possesses some distorted mesopores after 2 charge-discharge cycles, but the ordered porous structure as whole is completely lost. This matches with the 1-D GISAXS (Figure 6.3) profiles which suggested distortion of spherical mesopores accompanied by complete loss of ordered porous structure upon successive cycling. High resolution TEM micrographs of m-NC9 thin film (Figure 6.5C) indicate that the oxide framework is made up of 3.4 nm NiCo$_2$O$_4$ nanoparticles in the non-porous electrode after the 2nd de-lithiation segment. Elemental mapping of m-NC9 anode (Figure 6.5F-I) indicates Ni, Co and O are uniformly distributed in the NiCo$_2$O$_4$ framework. As there is no macrophase separation of metallic Ni or Co following the 2nd de-lithiation segment, loss of mesostructure during electrochemical formation of metallic Ni or Co can be eliminated. A large amount of elemental C is also detected that can be associated with solid electrolyte interface (SEI) formation on the mesopore voids. However, the presence of fewer voids corroborates the relatively non-porous morphology of m-NC9 anode after 2 lithiation/de-lithiation segments.
Figure 6.5 (A-C) Bright-field cross-sectional TEM images of m-NC9 thin film anode subjected to galvanostatic cycling for 2 cycles. (D, E) Scanning tunneling electron micrograph of m-NC9 and (F-I) elemental (Ni, Co, O and C) color map of corresponding region indicating relatively non-porous morphology and uniform distribution of Ni and Co elements.

To study the effect of mesopore dimensions on mesostructure evolution during battery operation, templated m-NC16 and m-NC28 anodes possessing larger pore...
dimensions were also subjected to *in-operando* grazing incidence small angle x-ray scattering (GISAXS) measurements while galvanostatically cycling the thin film anodes (Figure 6.6).

![Figure 6.6 In-operando GISAXS-galvanostatic cycling runs of (A) m-NC16 and (B) m-NC28 thin film anode. (C) Quantitative mapping of change in d-spacing of m-NC16 and m-NC28 anodes based on analysis of primary scattering peak.](image)

Prior to the initial discharge segment, 1-D GISAXS profiles of m-NC16 and m-NC28 anodes indicate a primary peak at $q_x \approx 0.0236 \text{ Å}^{-1}$ (d-spacing = 26.6 nm) and $q_x \approx 0.0128 \text{ Å}^{-1}$ (d-spacing = 49.1 nm) respectively. A second order peak, corresponding to correlations between mesopore walls, is also observed at $q_x \approx 0.0394 \text{ Å}^{-1}$ (d-spacing =...
15.9 nm) and \( q_x \approx 0.0216 \text{ Å}^{-1} \) (d-spacing = 29.1 nm) in case of m-NC16 and m-NC28 anodes respectively. These mesopore wall correlations are found to match well with the average mesopore width of m-NC9 (\( d_{\text{pore}} \approx 9 \text{ nm} \)) and m-NC28 (\( d_{\text{pore}} \approx 28 \text{ nm} \)) thin film anodes determined from AFM micrographs (Figure 6.2).

Figure 6.7 Galvanostatic charge-discharge curves of (A) m-NC16 and (B) m-NC28 thin film anodes illustrating the multi-step electrochemical reduction process. Quantitative mapping of primary scattering peak intensity observed from 1-D GISAXS profiles of (C) m-NC16 and (D) m-NC28 anode during galvanostatic cycling
Galvanostatic cycling of m-NC16 and m-NC28 anode in the custom-designed lithium ion cell exhibits multiple plateaus at voltages 2.46 V, 1.45 V and 0.91 V, characteristic of multi-step reduction of NiCo$_2$O$_4$ anode (Figure 6.7A,B). *In-operando* GISAXS analysis of primary diffraction peak again indicates significant reduction in primary peak intensity during the initial discharge segment due to SEI formation on mesopore walls (Figure 6.7C,D). Similar to m-NC9 anode, primary diffraction peak obtained in GISAXS profiles of m-NC16 and m-NC28 indicates reversible increase and decrease in $d$-spacing upon successive lithiation/de-lithiation (Figure 6.6C). At the end of initial discharge cycle (lithiation segment), the $d$-spacing is found to increase from 26.6 nm to 27.1 nm (m-NC16) and from 49.1 nm 49.8 nm (m-NC28) respectively due to Li$^+$ ion incorporation and volume expansion of oxide framework. Subsequent cycling leads to reversible change in $d$-spacing during lithiation and de-lithiation segments. However, unlike m-NC9 anode, the mesoporous structure is retained in each case even after 2 cycles (Figure 6.6A,B). The primary diffraction peak arising from mesopore correlations is clearly visible even upon multiple lithiation and de-lithiation segments indicating the presence of an ordered porous structure in m-NC16 and m-NC28 anodes. The intensity of the 2$^{nd}$ order peak reduces during the cycling process for m-NC16 and m-NC28 anode, indicating distortion of spherical mesopore geometry upon successive cycling. Nonetheless, the porous structure is maintained during the cycling process.
Figure 6.8 (A,B) Cross-sectional TEM micrographs of m-NC16 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling. (C) Scanning tunneling electron microscopy (STEM) micrograph of m-NC16 anode and corresponding area elemental color maps of (D) C (E) Ni (F) Co and (G) O elements in NiCo$_2$O$_4$ framework cross-sectional TEM micrographs of (A,B) m-NC16 and (C,D) m-NC28 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling.

Figure 6.8 and Figure 6.9 illustrates the cross-sectional TEM micrographs of m-NC16 and m-NC28 anodes subjected to galvanostatic cycling. Both m-NC16 and m-NC28 anodes exhibit a porous matrix primarily consisting of NiCo$_2$O$_4$ nanoparticles (6 nm-12 nm) separated by distorted spherical mesopores.
Figure 6.9 (A-C) Cross-sectional TEM micrographs of m-NC28 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling. (D) Scanning tunneling electron microscopy (STEM) micrograph of m-NC28 anode and corresponding area elemental color maps of (E) Ni (F) Co (G) O and (H) C. (I) Merged elemental color map indicating C element primarily present on mesopore walls.

A broad distribution of mesopore size is observed with the pore width varying from 6 nm to 21 nm. This matches well with the *in-operando* GISAXS spectra which indicated significant distortion and shrinkage of mesopores during the cycling process.
The significant shrinkage of mesopores is consistent with considerable volume expansion of metal oxide framework occurring during the lithiation process. As can be seen in Figure 6.8B and Figure 6.9C, the organic solid electrolyte interface (SEI) layer is primarily formed on the mesopore walls. This organic interface leads to decrease in x-ray contrast between the mesopore voids and inorganic NiCo$_2$O$_4$ matrix during the cycling process, resulting in reduction in GISAXS scattering peak intensity (Figure 6.7C,D). However, the porous structure in case of m-NC16 and m-NC28 is retained to a great extent even after successive lithiation/de-lithiation segments.

Based on the in-operando GISAXS study and ex-situ TEM micrographs, we find that m-NC16 and m-NC28 anodes undergo partial distortion in nanoporous morphology during the cycling process; but the sturdy mesopore walls accompanied by larger mesopores in case of m-NC16 and m-NC28 anodes provide strain relief during volume expansion-contraction of NiCo$_2$O$_4$ matrix and retain the porous structure during the cycling process. This suggests that below a critical pore dimension (~10 nm) and pore wall thickness (~6 nm), the stresses developed in NiCo$_2$O$_4$ framework due to lithium insertion/de-insertion leads to collapse of the ordered mesoporous structure during battery cycling operation.

To gain further insights into factors causing loss of ordered porous structure in m-NC9 anode as against m-NC16 and m-NC28 anodes, high-q region of GISAXS spectra was fit to a spheroid structure factor to determine size distribution of NiCo$_2$O$_4$ nanoparticles making up the porous framework of m-NCx anodes. Accordingly, in-operando changes in NiCo$_2$O$_4$ nanoparticle size was tracked during the initial lithiation/de-lithiation segments.
As can be seen in Figure 6.10A, NiCo$_2$O$_4$ nanoparticle diameter in m-NC9 anode prior to galvanostatic cycling is found to be approximately 3.3 nm. During the 1$^{st}$ lithiation segment (initial discharge cycle), NiCo$_2$O$_4$ nanoparticles grow in size due to Li$^+$ ion insertion and redox conversion reactions. After multiple Li$^+$ ions insertion up to 0.96 V, NiCo$_2$O$_4$ nanoparticles in the oxide framework grow in size to 3.8 nm, corresponding to size change of about 45% increase in volume (Figure 6.10B). Upon completion of redox reactions and Li$^+$ ion insertion, nanoparticle grows to 85% initial volume and finally reaches a value of 4.05 nm by the end of initial discharge cycle (lithiation
NiCo$_2$O$_4$ nanoparticles making up the framework of m-NC16 and m-NC28 anodes are found to possess larger initial dimension of 4.9 nm and 7.1 nm respectively (Figure 6.10A). Nonetheless, these anodes exhibit a similar volume expansion (~85%) due to growth in nanoparticle size at the end of initial lithiation segment. *In-situ* transmission electron microscopy (TEM) studies have revealed similar volume expansion of metal oxide anodes during the initial lithiation process.$^{342, 343, 344}$ The volume expansion (85%) experienced by NiCo$_2$O$_4$ nanoparticles in m-NCx anodes is close to the molar volume expansion (~100%) expected during electrochemical insertion of 8Li$^+$ ions.$^{345}$ Such expansion of NiCo$_2$O$_4$ nanoparticles leads to swelling of the mesoporous framework and progressive increase in $d$-spacing, as observed in 1-D GISAXS profiles (Figure 6.7). This phenomenon also contributes towards significant distortion of mesopore geometry, leading to decrease in intensity of 2$^\text{nd}$ order GISAXS peak.

On reversing the electrochemical redox reactions, Li$^+$ ion de-insertion leads to successive contraction in nanoparticle size during the 1$^\text{st}$ charge cycle. However, NiCo$_2$O$_4$ nanoparticle size in all m-NCx anodes does not reduce back to the original dimension. In case of m-NC28 and m-NC16 anodes, NiCo$_2$O$_4$ nanoparticle volume is found to be 23% and 37% larger greater the original size. On the other hand, NiCo$_2$O$_4$ nanoparticle size in case of m-NC9 framework volume expansion is found to be much larger (45%) than original dimension. This indicates that larger number of Li$^+$ ions get irreversibly stuck within the m-NC9 framework as compared to m-NC16 and m-NC28 matrix during the cycling process. Thus, the larger mesopores in case of m-NC28 and m-NC16 anode not only provide strain relief to volume expansion of framework, but also allow efficient Li$^+$ ion de-insertion from the oxide framework. However, in case of m-
NC9 anode, the smaller mesopores (~9 nm) do not provide sufficient room for volume expansion/contraction of oxide framework leading to collapse of mesostructure. The loss of mesoporous morphology is accompanied by large number of Li$^+$ ions getting irreversibly stuck within the m-NC9 framework.

Figure 6.11 Azimuthally averaged in-operando 1D-GIXD profiles of m-NCx anodes subjected to galvanostatic cycling in custom-designed lithium ion battery (●-initial discharge, ●-1st charge, ●-1st discharge, ●-2nd charge segment)

To investigate whether mesostructural changes occurring in m-NCx anodes influence changes in m-NCx crystal structure during battery operation, in-operando grazing incidence x-ray diffraction (GIXD) was carried out during galvanostatic cycling (Figure 6.11). The GIXD profiles of m-NCx anodes prior to battery operation exhibit distinct NiCo$_2$O$_4$ peaks that can be indexed to (220), (311), (222), (400), (422), (511) and (440) crystal planes. The scattering profiles are consistent with the formation of Fd-3m
spinel phase of NiCo$_2$O$_4$ (PDF card no. 01-073-1702). Applying Scherrer equation$^{262}$ to
the most intense diffraction peak ($q = 2.56$ Å$^{-1}$), the average NiCo$_2$O$_4$ crystal size is found
to ~ 3 nm, irrespective of m-NCx pore size. The larger NiCo$_2$O$_4$ nanoparticle dimension
as compared to average crystal size suggests presence of a semi-crystalline NiCo$_2$O$_4$
framework prior to galvanostatic cycling. The redox conversion reactions occurring in
NiCo$_2$O$_4$ anode during the cycling process can be explained based on the following
electrochemical reactions$^{247, 269}$

$$
\text{NiCo}_2\text{O}_4 + 8\text{Li}^+ + 8e^- \rightarrow \text{Ni} + 2\text{Co} + 4\text{Li}_2\text{O} \\
\text{Ni} + \text{Li}_2\text{O} \leftrightarrow \text{NiO} + 2\text{Li}^+ + 2e^- \\
\text{Co} + \text{Li}_2\text{O} \leftrightarrow \text{CoO} + 2\text{Li}^+ + 2e^- \\
\text{CoO} + \frac{1}{3}\text{Li}_2\text{O} \leftrightarrow \frac{1}{3}\text{Co}_3\text{O}_4 + \frac{2}{3}\text{Li}^+ + \frac{2}{3}e^- 
$$

During initial discharge process, Li$^+$ ion insertion and conversion reactions take
place in m-NCx anodes. As a result, the distance between NiCo$_2$O$_4$ crystal planes
increases causing shift in (400) and (440) diffraction peaks towards lower $q$. At the same
time, the intensity of (311) diffraction peak decreases indicating the reduction of
NiCo$_2$O$_4$ to metallic Ni and Co. At around 0.81 V, the spinel crystal structure of NiCo$_2$O$_4$
is almost completely destroyed as evidenced by the disappearance of (311), (400) and
(440) scattering planes. At this stage, formation of metallic Ni (PDF card no. 01-070-
0989) and Co (PDF card no. 00-001-1259) gives rise to diffraction peak at $q = 3.12$ Å$^{-1}$
corresponding to (111) plane, while Li$_2$O formation give rise to a peak at $q = 4.42$ Å$^{-1}$.

On re-oxidation of m-NCx anodes (de-lithiation segment), diffraction peaks
associated with metallic Ni, Co and Li$_2$O do not disappear, indicating irreversibility of
electrochemical reaction. This matches with the nanoparticle size analysis (Figure 6.10A), which suggested some Li$^+$ ions getting stuck within the oxide framework during the cycling process. Similar reports on irreversible formation of Li$_2$O upon complete de-lithiation have been reported earlier, due to irreversible reactions occurring at the electrochemical interface.$^{343}$ At this stage, very weak diffraction peaks associated with (400) and (440) planes of Co$_3$O$_4$ and NiO are observed, suggesting formation of primarily amorphous products upon de-lithiation. This result is in agreement with previous reports on conversion-type metal oxide anodes, where pulverization and loss of crystal structure due to Li$^+$ ion insertion is indicated.$^{95, 346}$ No other changes are observed in the crystal structure of m-NC16 and m-NC28 anodes upon successive cycling indicating formation of amorphous NiCo$_2$O$_4$ anode. However, in case of m-NC9 anode, at the end of 2$^{nd}$ charge cycle (de-lithiation), distinct diffraction peaks arising from (111) and (220) planes of Li$_2$O (PDF card no. 01-080-4679) are visible at $q = 2.28$ Å$^{-1}$ and $q = 3.71$ Å$^{-1}$. This indicates that large number of Li$^+$ ions get stuck within the oxide framework of m-NC9 anode, leading to 15 % larger NiCo$_2$O$_4$ particle size after 2 cycles of operation (Figure 6.10B). Thus, m-NC9 anode suffers severe distortion of porous morphology upon cycling, and the loss of mesoporous structure is accompanied by irreversible trapping of Li$^+$ ions in the oxide framework.

To finally correlate the effect of mesopore dynamics and crystal structure change on long-term charge storage performance, m-NCx anodes were subjected to galvanostatic cycling at a constant current density of 600 mA/g (Figure 6.12). Mesoporous m-NC28 and m-NC9 anodes provide high discharge capacities of 1170 mAh/g and 772 mAh/g in the first cycle.
However, upon successive cycling, m-NC9 drastically loses its charge storage capabilities exhibiting specific capacities of 245 mAh/g, 222 mAh/g, 210 mAh/g and 201 mAh/g in the 2nd, 3rd, 4th and 5th cycle. This corresponds to capacity retention of only 26% after the 5th cycle. The severe capacity fade of m-NC9 anode in the first few cycles can be explained based on the complete loss of ordered porous structure accompanied by irreversible electrochemical reactions occurring in the film anode (Figure 6.3). Since m-NC9 essentially behaves as a non-porous bulk NiCo$_2$O$_4$ anode after the 2nd cycle, a significant drop in specific capacity is observed after the 1st cycle. The specific discharge capacity continues to fade upon successive cycling reaching a value of 115 mAh/g at the end of 30 cycles (15% capacity retention).

Thin film anode m-NC28, on the other hand, also suffers from capacity fade, but the fade is found to be much gradual. Specific capacities of 754 mAh/g, 601 mAh/g, 517
mAh/g and 482 mAh/g are obtained in the 2nd, 3rd, 4th and 5th cycle, which are significantly higher than m-NC9 anode. This mesoporous anode exhibits capacity retention of 41% following 5 charge-discharge cycles. The relatively gradual fade in capacity of m-NC28 anode can be attributed to retention of mesoporous morphology and reversible Li\(^+\) ion shuttling in m-NC28 during the first few lithiation/de-lithiation segments (Figure 6.6B). Even after 30 cycles, high discharge capacity of 182 mAh/g is obtained in case of m-NC28 anode. This clearly demonstrates the importance of mesopore dimensions on capacity retention and improving cycling stability. Through careful mesostructure engineering, we believe that the cycling stability of m-NCx anodes can be further improved. To the author’s best knowledge, for the first time in-operando GISAXS/GIXD measurements have been used to correlate evolution of metal oxide anode mesostructure and charge storage performance in a lithium ion battery. This study paves way for developing metal oxide anode design principles for fabrication of next-generation lithium ion battery electrodes possessing high energy density and improved cycling stability.

6.4 Conclusion

In this in-operando study, we demonstrate that the evolution of metal oxide anode mesostructure during battery operation is greatly affected by initial mesopore dimensions. Complimentary GISAXS and GIXD probing of mesostructural and crystal structure changes illustrates that NiCo\(_2\)O\(_4\) anodes possessing mesopores smaller than 10 nm completely collapse during the first 2 cycles of operation, leading to irreversible trapping of Li\(^+\) ions in the oxide framework. The loss of mesostructure is accompanied by substantial capacity fade (85%) on long-term cycling of these anodes. These drawbacks
can be overcome by fabrication of ordered mesoporous oxide anodes possessing larger pore dimensions, which suffer only partial loss of mesostructure and exhibit improved cycling performance in a lithium ion battery. Such a complimentary GISAXS and GIXD in-operando study provides a mechanistic understanding of charge storage mechanisms in mesoporous metal oxide anodes and provides a platform to develop design principles for fabrication of high energy density oxide anodes exhibiting improved cycling stability in lithium ion batteries. We believe this study can be further extended to gain insights into reinforcement provided by carbon in mesostructured carbon-metal oxide composite anodes, and its contribution towards improved cycling stability in lithium ion battery.
CHAPTER VII

OVERALL SUMMARY AND FUTURE STUDIES

The broad objective of this research was to develop a simple fabrication strategy for synthesis of block copolymer templated ordered mesoporous metal oxide composites and correlate the effect of nanoporous morphology with charge storage properties of these materials in super-capacitors and lithium/sodium ion batteries. First we combined block copolymer self-assembly with sol-gel processing to fabricate mesoporous carbon-vanadia composite electrodes, as vanadium oxide is an ideal, high specific capacitance material. However, since block copolymer self-assembly and sol-gel processing requires precise control over relative rates of surfactant self-assembly as well as hydrolysis and condensation of metal oxide precursors, we utilized block copolymer micelle templating to fabricate highly porous, semi-crystalline mixed-metal oxide composites, by de-convoluting the self-assembly and sol-gel processing steps. This synthesis strategy could be used to fabricate variety of ordered mesoporous mixed-metal oxide composites in the form of thin film coatings or nanofiber membranes. Finally to correlate the effect of mesostructure on charge storage properties of mesoporous metal oxide anodes in lithium/sodium ion battery, we designed a custom-designed lithium/sodium ion cell that allowed simultaneous \textit{in-operando} GISAXS/GIXD investigation of mesostructural changes and crystal phase changes during battery operation.
Through these studies, we studied the critical effect of anode mesopore dimensions on cycling stability of ordered mesoporous metal oxide anodes for lithium battery applications.

In the first part of the dissertation, we demonstrated the fabrication of mesoporous carbon-vanadia composite thin films by combining evaporation-induced block copolymer self assembly and sol-gel processing. Previous work has demonstrated loss of surfactant-templated mesostructure on calcination of vanadia-based systems due to crystallization of vanadium oxide. We demonstrated that through incorporation of carbon, vanadia crystallization can be suppressed, to maintain an ordered mesostructure even after calcination at 800 °C. By careful investigation of the effect of calcining environment on final mesostructure, we demonstrated that carbothermal reduction in presence of inert Ar gas led to collapse of ordered carbon-vanadia mesostructure. Calcining under nitrogen blanketing on the other hand could help maintain the porous morphology through formation of an intermediate metal nitride, without affecting the carbon content. This study emphasized the importance of inert calcining environment during fabrication of mesoporous carbon-metal oxide composites. The fabricated mesoporous carbon-vanadia composites served as promising super-capacitor electrodes, exhibiting 7 times higher capacitance as compared to a non-porous analog.

The second part of the dissertation involved utilizing block copolymer micelle templating strategy to fabricate ordered mesoporous mixed-metal oxide composites for use as high-rate battery anodes. Utilizing this strategy, hydrolysis and condensation steps of individual metal precursors required in sol-gel processing could be eliminated, making this an easier synthesis methodology. We developed a simple strategy to fabricate variety
of Ni-Co mixed-metal oxide (Ni$_x$Co$_{(3-x)}$O$_4$) composites with tunable chemical and electrical properties by varying the chemical composition of the materials. The Ni$_x$Co$_{(3-x)}$O$_4$ thin films exhibited nanoporous morphology irrespective of chemical composition and a uniform pore size that could be tuned by simply varying the molecular weight of the templating agent. These composite mesoporous thin film anodes exhibited improved high-rate performance as compared to their bulk analogs, when tested as anodes in sodium ion battery owing to their high electro-active surface area, short diffusion paths for Na$^+$ ions and ease of transport of electrolyte ions. The electronic conductivity of these composites could also be easily by varying the nickel content in the composites. Mesoporous Ni$_2$CoO$_4$ anode demonstrated the highest electronic conductivity (~0.23 S.cm$^{-1}$) and good cycling stability when cycled at high current densities of 1 A.g$^{-1}$.

To illustrate that the block copolymer micelle templating strategy could be further extended to industrially relevant roll-to-roll fabrication processes, we designed electrospun mesoporous composite nanofibers of electronically conductive Ni/NiO/MnO$_x$/C in the third part of this thesis. We demonstrated that the micelle templating strategy allowed fabrication of high surface area (~150 m$^2$/g) composite fibers that could maintain the nanofiber morphology through processing temperatures as high as 800 °C. The properties of these composite anodes could be easily tuned by varying the nickel and manganese content in the nanofibers. Similarly, through incorporation of higher nickel content in the nanofiber composites, efficient coating of nanofiber surface with metallic nickel could be obtained. This led to significantly lower impedance and charge transfer resistance in these composite fiber anodes. The metallic Ni coating on the
nanofiber surface also led to enhancement in cycling efficiency and discharge capacities close to the theoretical capacity of Mn₃O₄ based anodes in lithium ion battery.

Utilizing the micelle templating strategy to fabricate mesoporous metal oxide anodes, we that demonstrated the importance of nanoporous morphology and chemical composition on the enhanced charge storage capabilities of ordered mesoporous composites in energy storage applications. However, the effect of mesopore dimension contributing towards improved charge storage in mesoporous metal oxide composites was not clearly understood at this point of time. Similarly the factors causing capacity fade on long-term cycling of mesoporous metal oxides remained unclear. To identify the causes of enhancement in discharge capacity of mesoporous metal oxide anodes but poor cycling stability, and develop design heuristics in terms of mesopore dimensions, geometry and wall thickness for fabrication of next-generation, high energy density battery electrodes, we designed a custom-built lithium/sodium ion cell. This custom-built cell allowed in-operando monitoring of mesopore morphology and crystal structure during battery operation. Based on such an in-operando study, we demonstrated that mesopores smaller than 10 nm significantly shrink and collapse during the first 2 cycles of operation due to volume expansion of oxide framework. The collapse of porous structure is accompanied by Li⁺ ions getting stuck irreversibly in the framework as the volume changes can no longer be accommodated by the non-porous oxide structure. This contributes towards significant capacity fade observed in mesoporous metal oxide anodes possessing pores smaller than 10 nm. However, mesopores larger than 15 nm can effectively accommodate the volume expansion of oxide framework during Li⁺ ion insertion/de-insertion improve Li⁺ ion transport across the porous metal oxide electrode.
and improve cycling efficiency of the templated anode. Based on these studies, we could correlate the effect of mesopore dimensions on long-term cycling efficiency of ordered mesoporous metal oxide composites in energy storage applications.

Following are some recommendations for future work:

- Utilizing the block copolymer micelle templating strategy, we demonstrated that templated Ni$_x$Co$_{(3-x)}$O$_4$ mixed-metal oxides exhibited excellent high-rate performance when tested as anodes in sodium ion battery. However, the significant capacity fade and poor cycling efficiency of these nanostructured anodes remained an issue to be solved. A possible strategy to improve cycling efficiency involves fabricating mixed-metal oxides containing an alloying element within the oxide matrix (example: ZnCo$_2$O$_4$ or ZnMn$_2$O$_4$). Zinc component in the mixed-metal oxide crystal provides high discharge capacities through lithium-alloying mechanism. The larger spacing between the crystal planes of ZnCo$_2$O$_4$ can also allow efficient Li$^+$ insertion/de-insertion, thereby improving the cycling efficiency of the anodes. We have demonstrated that metallic Ni coating can help improve high-rate charge storage performance of battery anodes. Since zinc is a semi-conducting material with poor electronic conductivity, it will be interesting to study the effect of highly conductive metallic silver nanoparticle doping in these nanostructured, porous ZnCo$_2$O$_4$ anodes.

- Electrospinning provides a convenient processing technique to fabricate large quantities of mesoporous metal oxide electrodes in the form of interconnected nanofibers. The present study did not focus on the effect of nanofiber diameter on charge storage performance of metal oxide anodes. By fabricating smaller diameter nanofiber anodes (< 500 nm), the diffusion path of Li$^+$/Na$^+$ ions can be further
reduced to allow battery cycling at significantly higher current densities. Similarly, the interconnected morphology can also help accommodate the stresses formed during Li⁺/Na⁺ ion insertion due to volume expansion/contraction. Hence, the effect of nanofiber morphology on charge storage performance of alloying-type materials such as silicon, germanium or aluminum, which exhibit large volume changes, needs to be performed.

- The present study on electospun composite nanofiber anodes did not focus on the fabrication of different nanofiber morphologies such as core-shell morphology or hollow nanofibers. Since charge storage performance is greatly affected by anode nano-architecture, the effect of nanofiber morphology on discharge capacities and cycling stabilities of nanofiber anodes needs to be studied. Specifically, the core-shell metal oxide nanofiber morphology represents an important nanostructure for use as anode in battery applications. Using concentric needles for electrospinning solutions, host of metal oxide-carbon composites can be fabricated containing carbon shell (electron transport paths) and metal oxide core (electroactive surface). The carbon coating on nanofiber surface can restrict volume expansion of metal oxide during Li⁺/Na⁺ ion insertion and help improve cycling stability of anode. The thickness of each component in the composite nanofiber can have a significant effect on the final charge storage performance of such composite anodes and needs to be studied. Similarly, in case of hollow nanofiber anodes, the effect of porosity on cycling stability also needs to be studied in a systematic manner.

- Based on the *in-operando* GISAXS/GIXD study, we concluded that mesoporous mixed-metal oxide anodes possessing pore dimensions smaller than 10 nm collapse
during the first 2 cycles of operation, leading to significant capacity fade. On the other hand, fabricating templated metal oxide anodes with larger mesopores (> 10 nm) could retain the mesoporous morphology after 2 cycles and exhibit enhanced charge-storage performance when tested in a lithium ion battery. However, these anodes ($d_{\text{pore}} \sim 30$ nm) also exhibited a gradual capacity fade, suggesting loss of mesoporous morphology on long-term cycling. Hence, there is a need to further optimize the mesopore dimensions and oxide wall thickness to develop mesoporous mixed-metal oxide anodes that suffer minimal capacity fade upon long-term cycling.
REFERENCES


28. Park, S. H.; Lee, W. J. Hierarchically mesoporous carbon nanofiber/Mn₃O₄ coaxial nanocables as anodes in lithium ion batteries. *J. Power Sources* 2015, 281, 301-309.


77. Hu, L. B.; Chen, W.; Xie, X.; Liu, N. A.; Yang, Y.; Wu, H.; Yao, Y.; Pasta, M.; Alshareef, H. N.; Cui, Y. Symmetrical MnO$_2$-Carbon Nanotube-Textile Nanostructures


100. Bruce, P. G. Energy storage beyond the horizon: Rechargeable lithium batteries. *Solid State Ionics* **2008**, *179* (21-26), 752-760.


194


276. Duffort, V.; Talaie, E.; Black, R.; Nazar, L. F. Uptake of CO_{2} in Layered P2-Na_{0.67}Mn_{0.5}Fe_{0.5}O_{2}: Insertion of Carbonate Anions. *Chem. Mater.* 2015, 27 (7), 2515-2524.

277. Yuan, D. D.; Hu, X. H.; Qian, J. F.; Pei, F.; Wu, F. Y.; Mao, R. J.; Ai, X. P.; Yang, H. X.; Cao, Y. L. P2-type Na_{0.67}Mn_{0.65}Fe_{0.2}Ni_{0.15}O_{2} Cathode Material with High-capacity for Sodium-ion Battery. *Electrochim. Acta* 2014, 116, 300-305.


APPENDIX

LIST OF PUBLICATIONS

This section enlists all current and proposed future publications that form a part of this dissertation as well as based on several other aspects covered during this PhD.


†Equal contribution