ELECTROCHEMICAL STUDIES OF LITHIUM-ION BATTERY ANODE MATERIALS IN LITHIUM-ION BATTERY ELECTROLYTES

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ELECTROCHEMICAL STUDIES OF LITHIUM-ION BATTERY ANODE
MATERIALS IN LITHIUM-ION BATTERY ELECTROLYTES

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The stability of uncoated copper (Cu) foils and graphite-coated copper (Cu-C) foils in lithium-ion battery electrolytes were extensively studied in this dissertation.

At first, the electrochemical behavior and stability of the Cu foils and Cu-C foils were studied. Cyclic voltammetry was used to study the redox behavior of the foils in the electrolyte solutions. The reduction of electrolyte and its effect on the oxidation of copper was also studied. Bulk electrolysis was used to quantitatively study the dissolution of the foils in dry electrolytes and in electrolytes doped with impurities of H$_2$O or HF. It was found that the graphite coating greatly influenced the redox behavior of the copper substrate and provided some protection to the copper from oxidation. Impurities increased the oxidation tendency of both Cu foils and Cu-C foils and may influence the integrity of the Cu-C foil electrode.

During these studies, the open-circuit voltage (OCV) of Cu foil and Cu-C foil electrodes in Li-ion battery electrolytes was found to be a variable value over time. A detailed study showed that the OCV first rapidly decreased until reaching a minimum, and then gradually increased until reaching a meta-steady or steady state. These results were compared with OCV studies of Al foil, Pt wire, glassy carbon and Cu disk and wire electrodes. The OCV variation appeared to correlate to a surface change on the electrode after being immersed into the electrolyte solutions. The influence of aging of
the reference electrode, the surface condition and edge effect of the copper foil, and solution impurities on the stability of the OCV was also studied.

Atomic absorption spectroscopy (AAS) was used to quantitatively evaluate the stability of Cu and Cu-C foils in lithium-ion battery electrolytes at open-circuit. Results showed that the stability of Cu and Cu-C foils was different in “fresh” electrolytes whereas it was similar in “aged” electrolytes. For Cu foils, in the “fresh” electrolyte, the copper foils showed a small amount of dissolution (up to ~ 50 ppm) during their storage in electrolyte for up to 20 weeks. On the contrary, only trace amounts (less than 1 ppm) of dissolution of Cu-C foils were found in the same “fresh” electrolyte. However, in “aged” electrolyte, large amounts of copper dissolution (up to several hundred ppm) were found in both Cu foils and Cu-C foils. The study showed that the condition of the electrolytes was critical to the stability of the copper foils.

Finally, FTIR reflectance and IR microscopy surface analyses of these foils after storage in electrolyte solution were performed to further study the causative factor of the copper dissolution in “aged” electrolytes. It was found that a carboxylic copper salt (ROCO₂Cu) and other possible copper salts existed in the composition of the surface films of both foils.

Approved ___________________________

Professor of Chemistry
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Abbreviations

AAS ................................. flame atomic absorption spectroscopy

AE ................................. auxiliary electrode

AFM ................................. atomic force microscopy

Al-C ................................. aluminum foil coated with graphite and binder

BE ................................. bulk electrolysis

Cu-C ................................. copper foil coated with graphite and binder

CV ................................. cyclic voltammetry

DEC ................................. diethyl carbonate

DMC ................................. dimethyl carbonate

EC ................................. ethylene carbonate

FTIR ................................. Fourier transform infrared spectroscopy

GC ................................. glassy carbon

LOD ................................. limit of detection

LOQ ................................. limit of quantitation

MCMB ............................... mesocarbon microbeads

MEC ................................. methyl ethyl carbonate

OCV ................................. open-circuit voltage

PC ................................. propylene carbonate

ppm ................................. parts per million (mg L⁻¹)

PVDF ............................... polyvinylidene fluoride
RE ......................................... reference electrode
SEI ......................................... solid electrolyte interface
SPE ......................................... solid polymer electrolyte
WE ......................................... working electrode
Chapter 1 – A Brief Review of Lithium-Ion Cells and the Motivation for this Work

The demand for energy storage sources of high energy density has been growing rapidly recently as a result of the impetus of portable consumer electronics prevalence. Currently, more stringent requirements exist both in energy density and power density of energy storage devices in the large applications, such as zero emission electric vehicles and satellites. Also, there is high demand for high performance batteries. The secondary lithium-ion battery is a promising option to meet such demands because of its inherent outstanding characteristics. Li-ion batteries have become prevalent in small cell applications, such as cellular phones and notebook computers since their first introduction into the market in 1991 by Sony Energetic Inc.¹

The proposal of the Li-ion battery for large applications appears to be a logical choice considering its characteristics. Many companies and government agencies are currently investigating Li-ion cells. However, there are still many problems to solve before their successful utility in such applications. For instance, long-term stability of cell components, heat control and safety issues, along with the better quality and cost-performance requirements, are among the concerns. Research in this field has been very active and resulted in hundreds of publications and regular symposia at national and international conferences, such as the semi-annual meetings of the Electrochemical Society (ECS) and the annual meeting of the International Meeting on
Lithium Batteries (IMLB).

In this introduction, some general concepts concerning Li-ion cells are presented. Then a brief technical review of Li-ion cells is given. Finally, the motivation for the work in this dissertation is discussed.

1.1 General Concepts

A battery consists of one or more cells, which are interconnected in parallel or serial, or the combination of the two, depending on the specific application requirements. The simplest electrochemical cell, which is the element of a battery, is composed of an anode (negative electrode), a cathode (positive electrode), and electrolyte.

The Li-ion cell refers to a cell whose active anode material is carbon-based, and which Li ions can intercalate into and deintercalate from during charge and discharge processes. The carbon commonly used is either coke type or graphite, or the combination of the two, depending on the specific application. The active cathode material is a lithiated transition metal oxide, also which Li ions deintercalate from and intercalate into during charge and discharge processes, respectively. The most widely studied cathode materials include LiCoO$_2$, LiNiO$_2$, and LiMn$_2$O$_4$. The electrolyte can be either a solid polymer electrolyte (SPE) or a nonaqueous liquid electrolyte. Liquid electrolyte is usually comprised of a Li salt and various solvents from the ester, ether or carbonate families.
The schematic of the Li-ion cell is shown in Fig. 1-1. The reactions at the electrodes and the overall cell reaction are as follows:

\[
\text{Cathode: } \text{LiMO}_2 \xrightarrow{\text{Charge}} \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \quad (1-1)
\]

\[
\text{Anode: } C + x\text{Li}^+ + xe^- \xrightarrow{\text{Discharge}} \text{Li}_x C \quad (1-2)
\]

\[
\text{Overall: } \text{LiMO}_2 + C \xrightarrow{\text{Charge}} \text{Li}_x C + \text{Li}_{1-x}\text{MO}_2 \quad (1-3)
\]

Where LiMO\(_2\) represents the lithiated transition metal oxide.

The basic parameters in the evaluation of the performance of a rechargeable battery include energy density, power density, cell voltage, charge retention life and cycle life. The comparison (Table 1-1) of the performance of Lithium and Li-ion cells with that of traditional batteries shows that Li-ion cells have superior advantage. These outstanding characteristics have resulted in the Li-ion batteries’ prevalence in small cell applications and also made them suitable for large applications, which have high requirements in energy density and power density.

1.2 A Brief Technical Review of the Li-ion Cells

1.2.1 The History of Li-ion cells

The search for high energy density cells inevitably lead to lithium, which is the lightest and the most electropositive of the alkali metals.\(^2\) The theoretical energy density of Li metal is 3.86 Ah/g, which is the highest.\(^2\) However, there are many difficulties associated with the use of Li metal, which took about forty years of
Figure 1-1. Schematic of the electrochemical process of a lithium-ion cell. [Reproduced from: B. Scrosati, in Lithium Ion Batteries, M. Wakihara, O. Yamamoto, Editors, p. 219, Kodansha Ltd., Tokyo, Japan (1998).] Shown in charging mode.
Table 1-1. Comparison of performance characteristics of different batteries.

<table>
<thead>
<tr>
<th>Battery System</th>
<th>Energy Density(^a)</th>
<th>Battery Voltage</th>
<th>Self Discharge</th>
<th>Cycle Life(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wh/kg</td>
<td>Wh/L</td>
<td>V</td>
<td>%/month</td>
</tr>
<tr>
<td>Lead Acid</td>
<td>30-35</td>
<td>80-90</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Ni/Cd</td>
<td>30-40</td>
<td>70-100</td>
<td>1.2</td>
<td>10-20</td>
</tr>
<tr>
<td>NiMH</td>
<td>60-80</td>
<td>140-180</td>
<td>1.2</td>
<td>10-20</td>
</tr>
<tr>
<td>Lithium Metal</td>
<td>150-200</td>
<td>300-400</td>
<td>3.6</td>
<td>2-3</td>
</tr>
<tr>
<td>Lithium Ion</td>
<td>100-125</td>
<td>260</td>
<td>3.6</td>
<td>9-12</td>
</tr>
</tbody>
</table>

\(^a\) Energy density (both gravimetric and volumetric) delivered by typical cells.

\(^b\) Cycle life - to 80% capacity, 100% depth of discharge.
extensive study to overcome before its introduction to the market.

The first difficulty of Li metal is its high reactivity with electrolyte, which made aqueous electrolyte impossible. Therefore, the first attempt was to find a stable electrolyte media and an appropriate cathode in order to use Li metal as the anode. The materials studied among the early prototype cells used halides, such as AgCl, CuCl₂, CuCl, CuF₂, or NiF₂, as the cathode, which forms LiX (X = Cl or F) and the corresponding metallic phase during the discharge process.³ A typical nonaqueous electrolyte as proposed by Chilton and Cook was LiCl-AlCl₃ dissolved in propylene carbonate (PC).³ The main problem of this battery system was the high self-discharge rate as the result of the formation of soluble complexes of the cathode.

The problem of the appropriate cathode was solved in the early 1970’s from the development of the “topotactical” electrochemical reaction of the insertion transition metals⁴, in which Li ions can insert into the crystalline structure and thus reduce the metals from a higher oxidation state.³ This success led to the currently used cathode materials.

After success with the cathode material, the problem in the Li metal anode was revealed. It was found that Li forms a dendrite structure during cycling, which creates a high volume change of the anode and resulted in poor cycling efficiency and safety problems.¹⁻³ The safety issue caused the short, unsuccessful market endeavor of the first introduction of Li batteries into the market in the mid-1980’s, which ended with a recall of the products.² Extensive studies have been performed to solve the problem, which mainly have been aimed at appropriate electrolytes. However, the safety
problem of lithium batteries was not completely solved until the introduction of the concept of Li ion cells, which use insertion carbon material as the anode instead of Li metal.

The unexpected discovery of the Li insertion property of carbon in mid-1980’s brought the breakthrough needed for the new battery system based on Li-ion concept.\(^1\) Sony was the first company to commercialize such a battery and introduced it into the market in 1991. Since then, Li-ion batteries have prevailed in the portable cell market. The sale volume of portable Li-ion batteries exceeded the total sale volume of all other types of batteries, such NiCd and NiMH in 1999.\(^3\) This market is still expanding rapidly. According to the market research report “World Lithium Battery Markets” by Frost & Sullivan (an international marketing consulting company), this industry is projected to produce 2.75 million units annually, which equals $4.94 billion in revenue by 2005.\(^5\)

1.2.2 The Active Cathode Material

The current extensively studied cathode candidate materials include LiCoO\(_2\) and LiNiO\(_2\) (both of layered structure), and LiMn\(_2\)O\(_4\) (spinel framework structure). LiCoO\(_2\) was the easiest to prepare and was the first commercialized cathode material for Li-ion cells. LiNiO\(_2\) was later found to be more stable and has a lower self-discharge rate than LiCoO\(_2\). Both of them are expensive compared to LiMn\(_2\)O\(_4\) as the result of the natural abundance of manganese. LiMn\(_2\)O\(_4\) is more “environmentally friendly” as well. Therefore, it is the most promising material. The layered structure of
LiCoO$_2$ and LiNiO$_2$ can be obtained through the reaction between LiOH and the corresponding metal oxide in air at 700 °C. The spinel LiMn$_2$O$_4$ is obtained through the reaction between Li$_2$CO$_3$ and MnO$_2$ in air at 800 °C. The average voltages of LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$ vs. Li at low discharge rate are 3.7 V, 3.5 V and 3.8 V, respectively.

### 1.2.3 The Carbon Anode

That a carbonaceous material can be used as the anode for Li-ion cells is based on the fact that the potential of lithiated carbon is very close to that of Li metal. (The voltage of lithiated graphite vs. Li metal is from 0.0 to 0.5 V.) As a result, the whole cell voltage of Li-ion cells is similar to those using Li metal as the anode. In addition, during charge and discharge processes, Li ion can intercalate into and deintercalate from carbon without significant volume, mechanical and electrical property changes. A variety of carbonaceous materials were studied as the intercalation anode materials, such as graphite, petroleum coke, carbon fibers and mesocarbons. The morphologic difference in different carbon materials has great impact on their lithium intercalation behavior. Carbon with sp$^2$ bonding between carbon atoms can be roughly classified into three categories: graphite, soft carbon and hard carbon. Soft carbon refers to highly oriented carbon but having less crystallinity than graphite, which includes mesocarbon microbeads (MCMB), some types of cokes, etc. Hard carbon refers to highly disorder carbon materials, which is usually prepared from organic polymers and resins, such as glassy carbon, some types of carbon fibers, etc. Graphite and soft
carbon are currently more widely used even though the first commercialized Li-ion cell used a hard carbon material. Graphite can intercalate Li up to the ratio of 1:6 (LiC$_6$).\textsuperscript{1-3} Compared with highly ordered graphite and soft carbon, hard carbon has relatively higher initial specific capacity because the hard carbon can form a Li rich phase after deep charge.\textsuperscript{9} However, such a Li rich phase is highly reactive and results in high irreversible specific capacity during cycling.\textsuperscript{1-3} Graphite and soft carbon, on the contrary, have more improved cyclability as the result of the more defined structure.\textsuperscript{1-3} In the work performed in this dissertation, the carbon used is a mixture of graphite and mesocarbon microbeads (MCMB).

1.2.4 The Electrolytes

There are mainly two types of electrolytes for Li-ion cells: polymer electrolytes and liquid electrolytes.\textsuperscript{6} The most commonly used electrolytes are liquid electrolytes, which are composed of Li salts dissolved in nonaqueous organic solvents. The candidates of Li salts include LiClO$_4$, LiAsF$_6$, LiPF$_6$, LiSO$_3$CF$_3$, LiN(SO$_2$CF$_3$)$_2$, etc.\textsuperscript{6} LiClO$_4$ was the mostly studied in the initial works and it was found to be subject to violent decomposition, which might cause safety problems. LiAsF$_6$ had drawbacks of thermal and electrochemical instability and it is also hazardous to the environment from the As. LiSO$_3$CF$_3$ tends to be subject to association in electrolyte solution, which results in lower conductivity. LiN(SO$_2$CF$_3$)$_2$ has the tendency to corrode aluminum, which is the cathode current collector of the Li-ion cell. LiPF$_6$ currently is the most widely used salt. However, it reacts with trace amounts of water in solution to produce
HF, which is shown in this dissertation to have a detrimental effect on the stability of the anode materials.

The nonaqueous aprotic organic solvents commonly selected include ester, ether or carbonate families. The molecular structures of some typical solvents are shown in Table 1-2. The current most widely used solvents for Li-ion cells are based on organic carbonates, such as propylene carbonate, ethylene carbonate, etc. These solvents have good conductivity and electrochemical stability towards the highly oxidizing cathode.

The quality of the electrolytes is very important to a Li-ion cell. During the charging process, when Li ions intercalate into the carbon material, electrolyte solution is reduced to form a passivation film on the anode, which was named as the solid electrolyte interface (SEI) by Peled. Even though the mechanism of the SEI formation has not been fully understood, such an SEI is believed to be an electron insulator while allowing Li ions to penetrate freely. Thus the SEI stabilizes the lithiated carbon anode, which is the main factor of the success of Li-ion cells.

1.3 Motivation

Li-ion cells have achieved great commercial success in small cell applications, such as cellular phones and camcorders. Their outstanding characteristics of high energy and power density are very suitable for large applications, such as electric vehicles and satellites. However, many further requirements are necessary for these applications. For instance, in electric vehicle application, abuse and over-discharge of the batteries are expected. In satellite applications, long-term stability of the battery is
<table>
<thead>
<tr>
<th>Name</th>
<th>Structural</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-butyrolactone (γBL)</td>
<td>H₂C—CH₂</td>
</tr>
<tr>
<td></td>
<td>H₂C—O—C=O</td>
</tr>
<tr>
<td>tetrahydrofuran (THF)</td>
<td>H₂C—CH₂</td>
</tr>
<tr>
<td></td>
<td>H₂C—O—CH₂</td>
</tr>
<tr>
<td>propylene carbonate (PC)</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>H₂C—CH—CH₃</td>
</tr>
<tr>
<td>ethylene carbonate (EC)</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>H₂C—CH₂</td>
</tr>
<tr>
<td>dimethyl carbonate (DMC)</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>CH₃—CH₃</td>
</tr>
<tr>
<td>diethyl carbonate (DEC)</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>C₂H₅—C₂H₅</td>
</tr>
<tr>
<td>diethoxyethane (DEE)</td>
<td>H₂C—O—C₂H₅</td>
</tr>
<tr>
<td></td>
<td>H₂C—O—C₂H₅</td>
</tr>
<tr>
<td>dioxolane</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O=C=O</td>
</tr>
<tr>
<td></td>
<td>H₂C—CH₂</td>
</tr>
</tbody>
</table>
needed. One of the many additional requirements for large applications is the long-term stability of anode materials.

The anode of a Li-ion cell is a carbonaceous material applied on a copper foil current collector, which is fabricated from a slurry of carbon, binder and an appropriate solvent by a casting or pressing procedure. According to previous findings, the anode is expected to be stable after lithium is intercalated into the carbon material and a high quality of SEI passivation film is formed. However, because lithiated carbon is air-sensitive, the Li-ion cell is fabricated in a totally discharged state (i.e., un lithiated carbon anode and fully lithiated cathode) and the lithiation of carbon is later performed by the charge process of the cell. After the assembly of the Li-ion cell, whether the cell needs immediate activation (charge process) depends on the answer of the intrinsic stability of the anode materials. In applications subject to over-discharge of the cells, the electrochemical stability of the anode under polarized conditions needs to be evaluated. For long-term applications, the stability of the anode materials at open circuit should be answered. In addition, the effects of possible electrolyte impurities and atmospheric contaminants towards the stability of the anode materials also need to be addressed.

Aurbach and Cohen found by in situ atomic force microscopy (AFM) that copper foil is not completely inert in LiAsF₆/propylene carbonate and suggested that contaminants may oxidize the copper.¹¹ Aurbach and Weissman also classified copper as one of the nonactive/slightly active metals in nonaqueous polar aprotic electrolytes.¹²
The intrinsic stability of the anode materials is crucial to a Li-ion cell since it might cause degraded cell performance. This work aimed at finding an answer to the intrinsic stability of the anode materials in the electrolyte solution by quantitative evaluation of the stability of the anode materials under various conditions. The research on this issue not only has fundamental meaning but also has practical purpose. This work fills some of the void in the research of copper stability in nonaqueous media. In addition, the results from this work can be used to assist engineers in the design of batteries for appropriate applications.
Chapter 2 - Electrochemical Stability of Copper in Lithium-ion Battery

Electrolytes

2.1 Introduction

All Li-ion cells currently in production use a carbonaceous coating applied to a copper foil substrate as the negative electrode, a lithium metal oxide cathode (LiCoO$_2$, LiNiO$_2$, or LiMn$_2$O$_4$) and liquid electrolyte comprised of a Li salt and various solvents from the ester, ether or carbonate families. As assembled, a Li-ion cell is unformed and the cell potential is $\sim 0$ V (a typical unformed graphite/Li$_x$NiO$_2$ cell is 0.2 V). This implies that the cathode is 0.2 V more positive (more oxidizing) than the anode (electrolyte-graphite-Cu half cell). Shifting the potential of the anode negatively (during the charging formation) has been extensively studied and leads to reduction of solvent, atmospheric contaminants and salt anions, the exact reaction depending on specific species in solution. Ultimately, the intercalation of Li into graphitic carbon occurs between 0.25 and 0.01 V and a practical battery anode is formed. However, if the formation process does not occur immediately after electrolyte filling, what is the intrinsic stability of the carbonaceous-coated copper electrode which does not have the protective films of electrolyte reduction?

Aurbach and Cohen in a study of Li deposition suggested that copper at open-circuit in LiAsF$_6$-PC is not completely inert and contaminants may oxidize the copper. Dissolution of copper should be avoided because it will plate on the carbon anode surface during the first charge and could lead to degraded battery performance.
Preliminary work suggested the oxidation of copper occurs near 3.5 V \textit{vs.} Li^+/Li which is less than 0.5 V positive of the open-circuit of the electrode. This chapter is focused on quantifying the oxidation of copper (without a graphite coating) at potentials near and positive of the OCV potential \textit{vs.} Li^+/Li.

2.2 Experimental Section

The electrochemical stability characteristics of copper were studied in a homemade three-electrode cell. The cell (Fig. 2-1) was manufactured from an end-sealed 25 mm Ace-thread glass connector and an O-ring sealed threaded Teflon plug that had been machined with electrode ports and a rubber septum port. The working electrodes (WE) were battery grade copper foil that were prepared as “flags” with a working area of 1×1 cm$^2$ and connected to a 22-gauge nickel wire. The 12 µm copper foil, grade LP1/LP3, was used as received from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at = 130 ppm. The flag of a WE was rinsed with acetone and air-dried before use. The reference electrodes (RE) were prepared by rolling and pressing an approximately 1×1 cm$^2$ lithium foil (Cyprus Foote Mineral Company) onto the tip of a nickel wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diameter porous Vycor tip (Bioanalytical Systems, BAS, MF-2042). The auxiliary electrode (AE) was either a 0.5 mm diameter platinum wire (7.5 cm length, BAS MW-1032, for Cyclic Voltammetry) or a 0.5 mm diameter platinum wire coil (23 cm length, BAS MW-
Figure 2-1. The schematic of the homemade cell. Electrolyte solutions flooded just above the 1×1 cm² portion of Cu foil when the cell was assembled in a dry box.
isolated in a glass tube containing a porous Vycor\textsuperscript{TM} tip for Controlled Potential Electrolysis).

The electrolytes used in this study were 1 M LiPF\textsubscript{6} in ternary mixtures of (I) PC:EC:DMC (propylene carbonate:ethylene carbonate:dimethyl carbonate) [1:1:3 vol.], (II) EC:DMC:MEC (EC:DMC:methyl ethyl carbonate) [1:1:1 vol.] and (III) EC:DMC:DEC (EC:DMC:diethyl carbonate) [2:2:1 vol.]. The electrolytes were obtained from EM Industries/Merck K.G.a.A and were prepared from 99.98% purity solvents (< 20 ppm H\textsubscript{2}O, as determined by a Karl Fischer titration) and Stella LiPF\textsubscript{6}. The electrolytes were guaranteed at < 80 ppm HF and were analyzed at Saft as < 50 ppm using an acid-base titration. The electrolytes were shipped to Ohio University in glass bottles and then stored in a dry box. Inspection of the bottles with time revealed no etching of the glass surface. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times.

Cell assembly was performed in a dry box. The moisture and oxygen contents of the dry box were both less than 1 ppm. For the study of electrolytes doped with impurities (deionized H\textsubscript{2}O and HF), a 10 µL GC syringe (Hamilton) was used to add the impurities to the cell through the rubber septum on the cell cap after the assembled cells were removed from the dry box, and the solution in the cell was stirred for 25 min before the analysis to ensure solution homogeneity. All experiments were performed with the Cypress Instruments CS-2000 computer-controlled electrochemical system potentiostat/galvanostat.
2.3 Results and Discussion

2.3.1 Cyclic Voltammetry.

Cyclic Voltammetry (CV) was first performed to investigate the oxidation-reduction of copper in the electrolytes. Cyclic voltammograms in Fig. 2-2 showed that when the potential scan was initiated at OCV of each cell in the positive direction to 3.6 V, a sharp rise in current for the oxidation of copper was observed followed by reduction of copper ion on the reverse scan as seen by the peak at ~ 3.4 V. The CV signals were so reproducible that five consecutive runs in each CV could hardly be differentiated. Cyclic voltammograms (Fig. 2-3) at different scan rates (20, 60 and 100 mV/s) initiated from OCV to 3.6 V and then back to the OCV were obtained in solution I and II. The results in Fig.2-3 show that the oxidation-reduction of copper was not diffusion-limited. CVs were also performed with different forward potential limits in the two solutions. Figure 2-4 shows that the oxidation current of copper increases rapidly with the increase of the forward potential.

CV was also run to investigate the reduction of electrolyte and its influence on the oxidation-reduction of copper foil. In the CV of the copper electrode in the electrolytes of 1 M LiPF$_6$ in solvent I and III (Fig. 2-5), the potential scan was initiated at 3.06 V and swept negative to (a) 2.0 V, (b) 1.7 V, (c) 1.4 V, (d) 1.0 V, and (e) 0.0 V successively on the same electrode. In solvent I on the first run from 3.06 V to 2.0 V, two small reduction peaks were observed at 2.8 V (broad) and 2.5 (sharp) and a large peak at 2.0 V was seen. In the run to 1.7 V, the small peaks are not observed and the
Figure 2-2. Five consecutive cyclic voltammograms of Cu foil electrode in (a) 1 M LiPF$_6$/PC:EC:DMC(1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:MEC(1:1:1 vol.). $E_{\text{initial}} =$ OCV, $E_+ = 3.6$ V, $E_- = 2.95$ V, $E_{\text{final}} =$ OCV. Scan rate = 20 mV/s.
Figure 2-3. Cyclic voltammograms of Cu foil electrode at different scan rates (20, 60 and 100 mV/s) in (a) 1 M LiPF$_6$/PC:EC:DMC(1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.). $E_{\text{initial}} = E_{\text{final}} = 3.15$ V (a) and 3.35 V (b). $E_c = 3.6$ V.
Figure 2-4. Cyclic voltammograms of Cu foil electrode with different forward potential limits (3.6 V, 3.65 V and 3.7 V) in (a) 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.). $E_{\text{initial}} = \text{OCV}$, $E_\text{f} = 2.95$ V, $E_{\text{final}} = \text{OCV}$. Scan rate = 20 mV/s.
Figure 2-5. Successive cyclic voltammograms of the reduction of electrolyte solutions on the same Cu foil with different reversal potentials (2.0 V, 1.7 V, 1.4 V, 1.0 V and 0.0 V) in (a) 1 M LiPF$_6$/PC:EC:DMC(1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:DEC (2:2:1 vol.). $E_{\text{initial}} = $ OCV. Scan rate = 20 mV/s.
large peak is greatly diminished in size and shifted negatively. The other runs to 1.4 V and 1.0 V did not result in any reduction peaks being observed. In solvent III on the first CV run from 3.06 V to 2.0 V, a sharp reduction peak at ca. 2.8 V is observed followed by another sharp, broad peak at ca. 2.1 V. The other runs are similar to those observed in solvent I. The large reduction peaks at or near 2.0 V are attributed to reduction of the PF$_6^-$ anion$^{13}$ while the smaller peaks at 2.5 and 2.8 V are not assigned.

In the first run, the electrolytes were reduced to foul the copper electrode and formed a passivating film on the copper foil surface, this diminished the reduction current in subsequent scans. It was also found that in both electrolyte solutions, if the potential was scanned to –0.1 V there was a very sharp reduction peak, which would signal reduction of lithium ion (Fig.2-6). A sharp oxidation peak followed on the reverse scan at 0.12 V signifying the oxidation (anodic stripping) of deposited lithium. The influence of the electrolyte reduction on the oxidation-reduction of copper was found to be rather direct. Figure 2-7 shows three successive CVs in which the potential scan was initiated at OCV, swept positive to 3.6 V, negative to 0.0 V, and then positive again ending at the OCV. It can be seen that the reduction of electrolyte at ~ 2.0 V caused the oxidation-reduction currents of copper to diminish remarkably in solvent I and II. This denotes that the passivating film formed by the reduction of electrolyte gave some protection to the copper foil against oxidation. Further studies (Fig. 2-8) show that the oxidation-reduction current of copper can be regenerated to some extent by stirring the solution for a while (~25 min). This means that the passivating film could dissolve in the bulk solution.
Figure 2-6. Cyclic voltammograms of the lithium deposition/oxidation on the Cu foil electrode in (a) 1 M LiPF$_6$/PC:EC:DMC(1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:DEC (2:2:1 vol.). $E_{\text{initial}} = E_{\text{final}} = \text{OCV}$, $E_\text{c} = 2.0 \text{ V}$ (A) and $-0.1 \text{ V}$ (B). Scan rate = 20 mV/s.
Figure 2-7. Three consecutive cyclic voltammograms of Cu foil electrode in (a) 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.). $E_{\text{initial}}$ = OCV, $E_+$ = 3.6 V, $E_-$ = 0.0 V, $E_{\text{final}}$ = OCV. Scan rate = 20 mV/s.
Figure 2-8. Initial cyclic voltammogram and the first run after stirring of Cu foil electrode in (a) 1 M LiPF$_6$/PC:EC:DMC(1:1:3 vol.) and (b) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.). $E_{\text{initial}} = \text{OCV}$, $E_+ = 3.6$ V, $E_- = 0.0$ V, $E_{\text{final}} = \text{OCV}$. Scan rate = 20 mV/s.
Electrolytes doped with impurities of 500 ppm water or 1000 ppm concentrated aqueous HF (49%, wt%, Fisher) were also studied using CV. The results are similar to those without such impurities, which means CV is not an effective way to investigate the effect of the impurities on the electrochemical characteristics of copper foil.

2.3.2 Chronocoulometry and Controlled-Potential Electrolysis (Bulk Electrolysis).

Chronocoulometry and bulk electrolysis (BE) were utilized to study the effect of oxidation of the copper electrode over time. BE was shown to be an effective way to quantify the oxidation of the copper foil electrode at different electrolysis potentials and to investigate the influence of impurities on the dissolution of copper.

Chronocoulometry in solution III was performed under quiescent conditions with a 10 s potential step. It was determined that no significant oxidation occurred until the potential reached between 3.5 V and 3.6 V for a potential step from 3.06 to 3.1 V through 3.6 V (made in 0.1 V increments).

Bulk electrolysis in solution III was performed under a fixed convective-diffusion condition with a long duration of 5400 s (1.5 hr) at different potential steps from OCV to 3.4 V through 3.7 V (made in 0.1 V increments). These results are shown in Fig. 2-9 and Table 2-1. At 3.4 V and 1.5 hr duration, the accumulated charge of 26 mC represents a theoretical dissolution of $8.5 \times 10^{-3}$ mg Cu or 0.054% of the copper electrode. Based on the chronocoulometric data, it can be estimated that the oxidation of the copper at 3.2 V vs. Li$^+$/Li would be comparatively two to three orders
Figure 2-9. Bulk electrolysis of Cu foil electrode: (a) i-t; (b) Q-t in 1 M LiPF$_6$/EC: DMC:DEC (2:2:1 vol.). Time duration = 5400 s (1.5 hr).
Table 2-1. Bulk electrolysis results of Cu foil electrode in 1 M LiPF₆/EC:DMC:DEC(2:2:1). The average mass of a Cu electrode was 15.8 ± 0.2 mg.

<table>
<thead>
<tr>
<th>Electrolysis Potential (mV)</th>
<th>Observed Mass Loss of Cu (± 0.1 mg)</th>
<th>Accumulated Charge (mC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>0.1</td>
<td>26</td>
</tr>
<tr>
<td>3500</td>
<td>0.7</td>
<td>609</td>
</tr>
<tr>
<td>3600</td>
<td>1.3</td>
<td>2,740</td>
</tr>
<tr>
<td>3700</td>
<td>2.1</td>
<td>5,008</td>
</tr>
</tbody>
</table>
of magnitude lower, while at 3.1 V the extent of copper dissolution cannot be quantitatively estimated. At high potentials, the oxidation current (~ 170 µA) began at 3.5 V, grew rapidly (~600 µA) at 3.6 V, and reached ~ 1000 µA at 3.7 V which represented a 14% mass loss of copper after 1.5 hr.

Bulk electrolysis was also performed on copper electrodes in the other two supporting electrolyte solutions I and II. Copper electrodes in the dry electrolytes were studied first. Then the electrolytes were doped with impurities of 500 ppm H₂O or concentrated aqueous HF (49%, wt%) to the level of 1000 ppm. The electrolyte solutions are hygroscopic and undergo hydrolysis as the following:

\[
H_2O + LiPF_6 \rightarrow LiF + 2HF + POF_3
\]

BE in these studies was performed with the same duration (5400 s) but at potential steps from OCV to 3.45 V through 3.65 V (made in 0.05 V increments). Figure 2-10 shows the BE signals of copper electrodes in solution I and Fig. 2-11 is the results obtained in solution II. The dissolution of copper was characterized by two ways: weighing the copper foil before and after the electrolysis and recording the total charge exhausted during the electrolysis. These results are summarized in Table 2-2. From the results it can be seen that the oxidation current of copper substrate increases with the increase of electrolysis potential in all cases. Also, the current is rather stable during the electrolysis when the electrolysis potential is below 3600 mV, but it drops dramatically after a period of time during the electrolysis at 3650 mV. This is because the area of the copper electrode diminishes due to extensive oxidation during the electrolysis, hence the current drops. In Fig. 2-10a,b,c and Fig. 2-11c, the copper
Figure 2-10. Bulk electrolysis of Cu foil electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H$_2$O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potentials step from OCV to 3450 mV through 3650 mV (made in 50 mV increments). Time duration is 5400 s (1.5 hr). (The abrupt current drop around 4800 s at 3650 mV in (a) resulted from breaking of the Cu electrode.)
Figure 2-11. Bulk electrolysis of Cu foil electrode in 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H$_2$O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potentials step from OCV to 3450 mV through 3500 mV (made in 50 mV increments). Time duration is 5400 s (1.5 hr).
Table 2-2. Bulk electrolysis results of Cu foil electrode, H$_2$O was doped to 500 ppm. HF was doped to 1000 ppm. The average mass of a 1×1 cm$^2$ Cu electrode was 15.0 ± 0.4 mg.

* Complete (100%) electrolysis.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Observed Mass Loss (± 0.1 mg)</th>
<th>Accumulated Charge (mC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3450 mV</td>
<td>3500 mV</td>
</tr>
<tr>
<td>PC:EC:DMC(1:1:3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dry)</td>
<td>0.3</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>547</td>
<td>1,777</td>
</tr>
<tr>
<td>(Doped with H$_2$O)</td>
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</tr>
<tr>
<td></td>
<td>143</td>
<td>5,528</td>
</tr>
<tr>
<td>(Doped with HF)</td>
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<td>5,092</td>
</tr>
<tr>
<td>PC:EC:DMC:MEC(1:1:1)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.3</td>
</tr>
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<td></td>
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<td>1,478</td>
</tr>
<tr>
<td>(Doped with H$_2$O)</td>
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<td>1.7</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>3,269</td>
</tr>
<tr>
<td>(Doped with HF)</td>
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</tr>
<tr>
<td></td>
<td>1,225</td>
<td>6,917</td>
</tr>
</tbody>
</table>
electrodes were completely oxidized at 3650 mV by the end of the electrolysis period. BE results also show that the oxidation of copper depends on the composition of the solvents. The results show that copper electrode had a higher tendency to be oxidized in solvent I than in solvent II and III. The results in Table 2-2 and Figs. 2-10 and 2-11 also clearly showed the influence of impurities on the dissolution of copper. It can be seen that even small amounts of impurities (H₂O or HF) enhanced the extent of copper oxidation considerably. The effect of HF seemed to be higher compared to that of H₂O.

The effect of electrolyte reduction on the oxidation of a copper electrode was also investigated. BE with a duration of 5400 s and a potential step from OCV to 3650 mV was performed on a copper electrode after it was passivated by the reduction of electrolyte solution I (through negative CV scan). The result was compared with the BE result from a “fresh” copper electrode performed under the same conditions (Fig. 2-12). The results showed that the oxidation current of the passivated copper electrode started from less than 0.4 mA and it took ca. 1000 s to resume a limiting current (~ 5.2 mA). This denoted that the passivating film gave the copper foil electrode some protection from oxidation. Only after this protective film was destroyed, was the limiting current achieved. Similar results were also found in the other solvents.

2.4 Conclusions

The results in this chapter showed that the oxidation-reduction of copper in the lithium-ion battery electrolytes occurs at a potential positive of the OCV of copper
Figure 2-12. Bulk electrolysis of Cu foil electrode (one is “fresh”; the other is fouled by reduction of electrolyte using CV) in 1 M LiPF₆/PC:EC:DMC(1:1:3 vol.).
electrode vs. Li⁺/Li. It was found that the reduction of electrolyte solutions fouled the copper electrode and markedly reduced the oxidation of the copper electrode, which is believed to give the copper electrode some protection to oxidation. It was also seen that the stability characteristics of copper vary in different electrolyte solutions. The oxidation current of the copper electrode was found to be higher in solution I than in electrolytes II and III at the same electrolysis potential. Bulk electrolysis was found to be an effective way to investigate the effects of impurities on the dissolution of copper. It was found that the impurities greatly influence the stability of copper electrode. A small amount of impurity of H₂O (500 ppm) or HF (1000 ppm) considerably enhanced the extent of copper oxidation.

The finding that the oxidation of copper starts at 3.4 V vs. Li⁺/Li has relevancy to a practical Li ion cell. If a Li ion cell containing LiCoO₂ is overdischarged to ~ 0.4 V, it can be seen that copper oxidation would commence because the OCV of fully discharged LiₓCoO₂ is ~ 3.8 V vs. Li⁺/Li.¹⁵ Knowing E_{cell} = 0.4, then E_{anode} = 3.8 V – 0.4 V = 3.4 V vs. Li⁺/Li. As assembled, copper shows a potential of 3.06 V vs. Li⁺/Li and the chronocoulometry results suggested essentially no oxidation of copper at this potential.
Chapter 3 - Electrochemical Stability of Graphite-coated Copper in Lithium-ion Battery Electrolytes

3.1 Introduction

Rechargeable Li-ion batteries operating at ambient temperature are under extensive study because they have outstanding characteristics and fewer safety concerns compared to conventional technologies.\(^1\,\,2\) Applications of Li-ion cells in portable electronic devices, such as cellular phones and laptop computers, have achieved considerable commercial success in recent years.\(^3\) Large Li-ion cells also are being investigated for military and commercial applications, such as satellites, underwater propulsion and electric vehicles because the properties of high energy density and specific energy make the Li-ion cells very suitable in such applications.\(^1\,\,3\) In these latter applications, long-term chemical stability of each component in the Li-ion cells is required, which includes the electrochemical stability of the electrode current collectors.

Some efforts have been made to investigate the electrochemical stability of the aluminum positive-electrode substrates which is commonly used as the positive current collector in rechargeable Li-ion batteries, because it may undergo severe corrosion at potentials above 3.5 V vs. Li\(^+\)/Li during cell charging.\(^16,\,17\) On the contrary, few electrochemical studies have been undertaken to investigate the stability of the negative-electrode current collector in Li-ion battery electrolytes. The negative-electrode current collector is a thin copper foil onto which graphite is coated with a
binder for the active material. It is expected that the graphite-coated copper is electrochemically stable when Li-ion cells are in the charged state because the open-circuit voltage (OCV) of the copper substrate is above 3.0 V vs. Li⁺/Li in most electrolytes and the actual negative-electrode potential in the cell charged state varies from 0 to 1.5 V vs. Li⁺/Li (which is actually the potential of lithiated carbon vs. Li⁺/Li).² In other words, the negative electrode is cathodically protected when the cell is in a charged state. In practice, the Li-ion cell is manufactured in a discharged state because the positive materials are typically synthesized in the lithiated form. The electrochemical stability of graphite-coated copper is crucial because dissolved copper will plate on the carbon anode surface during the first charge and could lead to degraded battery performance. Aurbach and Cohen in a study of Li deposition by in situ atomic force microscopy suggested that copper at open-circuit in LiAsF₆/propylene carbonate (PC) is not completely inert and contaminants may oxidize the copper.¹¹ During the period after electrolyte is impregnated into the cell, does the negative electrode require protections and what is the intrinsic electrochemical stability of graphite-coated copper in Li-ion battery electrolytes?

In order to study the electrochemical stability of the negative-electrode current collector in Li-ion battery electrolytes, the oxidation-reduction characteristics of copper foil electrodes (without a graphite coating) were previously studied in different electrolyte solutions. The results were reported in Chapter 2.¹⁸ In this chapter, the electrochemical stability of graphite-coated copper was investigated in two different electrolytes using the techniques of cyclic voltammetry (CV) and controlled-potential
coulometry (bulk electrolysis). CV was used to study the oxidation-reduction of graphite-coated copper and to investigate the influence of the graphite coating on the electrochemical stability characteristics of the copper substrate. Bulk electrolysis was used to quantitatively investigate the dissolution of graphite-coated copper. The effect of H$_2$O and HF impurities on the dissolution of graphite-coated copper was also quantitatively studied using this method. The results were compared with those obtained from uncoated copper foil electrodes in Chapter 2.

3.2 Experimental Section

The electrolytes used in this study were 1 M LiPF$_6$ in ternary mixtures of (I) propylene carbonate (PC)-ethylene carbonate (EC)-dimethyl carbonate (DMC) [1:1:3 vol.] and (II) EC-DMC-methyl ethyl carbonate (MEC) [1:1:1 vol.]. The electrolyte solutions were obtained from EM Industries/Merck K. G. a. A. and were prepared from 99.98% purity solvents (<20 ppm H$_2$O, as determined by a Karl Fischer titration) and Stella LiPF$_6$. The electrolytes were guaranteed at <80 ppm HF and were analyzed at Saft as <50 ppm using an acid-base titration. The electrolytes were shipped to Ohio University in glass bottles where they were stored in a dry box. Inspection of the bottles with time revealed no etching of the glass surface. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times. Lithium foil (Cyprus Foote Mineral Company) and battery-grade copper foil coated with graphite and binder were supplied by Saft. The copper foil (12 µm thick) grade LP1/LP3, was obtained from Fukuda Metal Foil and Powder Co. The
The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at ≤ 130 ppm. The coating consisted of a blend of 50 wt.% mesocarbon micro beads (MCMB 10-28) and 50 wt.% Timcal SFG-44 graphites using polyvinylidene fluoride (PVDF) as a binder. The carbon loading per electrode face was ~ 13 mg/cm$^2$ or 26 mg/cm$^2$ (double side coated).

All experiments were performed using a homemade three-electrode cell. The schematic and the details of the cell were described in Chapter 2. The working electrode (WE) was a copper foil coated with graphite and binder, which was cut into a 1×1 cm$^2$ flag. The flag was then connected to a 22-gauge nickel wire by pressing the tip of the nickel wire onto the flag pole (with the graphite coating removed from this part of the foil). The reference electrode (RE) was made by rolling and pressing a 1×1 cm$^2$ lithium foil onto the tip of a nickel wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diameter porous Vycor$^{TM}$ tip (Bioanalytical Systems, BAS, MF-2042). The auxiliary electrode (AE) was a 0.5 mm diameter platinum wire coil (23 cm length, BAS MW-1033, isolated in a glass tube containing a porous Vycor$^{TM}$ tip).

All cells were assembled and sealed in a dry box filled with argon. The water and oxygen contents inside the dry box were both less than 1 ppm. A 10 µL GC syringe (Hamilton) was used to add H$_2$O and HF impurities to the cell through a rubber septum on the cell cap after the assembled cells were removed from the dry box, and the solution in the cell was stirred for 25 min before the analysis to ensure
solution homogeneity. All experiments were performed with a Cypress Instruments CS-2000 computer-controlled electrochemical system potentiostat/galvanostat.

### 3.3 Results and Discussion

#### 3.3.1 Cyclic Voltammetry

CV was used to investigate the oxidation-reduction of the graphite-coated copper electrode in the electrolyte solutions at a potential scan rate of 20 mV/s. CVs were initiated at the OCV and scanned positive to a variable forward potential limit, reversed back to 2.95 V, and then forward ending at the OCV. Similar results were obtained in both solutions. Figure 3-1a-c shows the CVs of the graphite-coated copper in EC:DMC:MEC (1:1:1 vol.) with different forward potential limits of 3.60 V, 3.65 V and 3.70 V, respectively. In these CVs, five consecutive scans were recorded each using a “fresh” intact graphite-coated copper electrode. Figure 3-1d shows the five consecutive CVs of the copper foil electrode (without graphite coating) with the forward potential limit of 3.60 V for comparison. It can be seen that there was almost no oxidation-reduction signal at graphite-coated copper until the forward potential limit reached 3.65 V. This behavior is different from that of the uncoated copper foil electrode shown in Fig. 3-1d, where the oxidation-reduction current peaks were quite large with the forward potential limit of 3.60 V. It appeared that the graphite coating shifted the copper oxidation by 50 mV positive of the uncoated copper. Contrary to the reproducible CV signals of the uncoated copper foil electrode, the CV current of the graphite-coated copper differed greatly between each scan when the forward potential
Figure 3-1. Cyclic voltammograms (five consecutive scans) of a graphite-coated copper electrode in 1 M LiPF₆/EC:DMC:MEC (1:1:1 vol.) with potential limits of (a) 3.60 V; (b) 3.65 V; and (c) 3.70 V. (d) is the CV of Cu foil electrode (without graphite coating) with a potential limit of 3.60 V for comparison. $E_{\text{initial}} = \text{OCV}$. Scan rate = 20 mV/s.
limit reached 3.65 to 3.70 V. It can be seen in Fig. 3-1b and 3-1c that the characteristic of the initial CV differed greatly from subsequent CVs and the oxidation and reduction peaks grew larger and larger in the consecutive CVs. A probable explanation is that the increase in the CV current in consecutive scans was influenced by the graphite coating during the CVs. In the initial CV, the copper ions formed during the positive scan pass through the intact graphite coating, diffuse into the bulk solution, and are then reduced to copper which plates on the graphite coating during the negative-going scan. In the subsequent CVs, the copper plated on the graphite coating will join the oxidation processes, however at a lower potential, and then additional copper will plate on the coating during the reduction processes. Thus both the oxidation and reduction currents were larger in the subsequent CVs.

Similar CVs of the graphite-coated copper electrode were obtained in PC:EC:DMC (1:1:3 vol.), as shown in Fig. 3-2a-c. The CV of the uncoated copper foil electrode in the same electrolyte is shown in Fig. 3-2d for comparison. It can be seen that the CV results showed similar characteristics to those obtained in EC:DMC:MEC (1:1:1 vol.) except that the graphite coating appeared to give the copper substrate more protection in this electrolyte solution, as evidenced by comparing currents in Fig. 3-2b to Fig. 3-1b.

CVs in which the potential scan was initiated at 3.00 V and swept negatively to 0.00 V and then back to 3.00 V for the graphite-coated copper electrode in both electrolyte solutions are shown in Fig. 3-3. It can be seen that the intercalation and de-intercalation of lithium into/from the graphite coating occurred in the potential
Figure 3-2. Cyclic voltammograms (five consecutive scans) of a graphite-coated copper electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.) with potential limits of (a) 3.60 V; (b) 3.65 V; and (c) 3.70 V. (d) is the CV of Cu foil electrode (without graphite coating) with a potential limit of 3.60 V for comparison. $E_{\text{initial}} = \text{OCV}$. Scan rate = 20 mV/s.
Figure 3-3. Cyclic voltammograms (10 consecutive scans) of a graphite-coated copper electrode with the potential range of 3.00 to 0.00 V in (a) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.) and (b) 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Scan rate = 20 mV/s.
window of 1.5 to 0.0 V (vs. Li⁺/Li) in both electrolyte solutions. As shown in Fig. 3-3, Li insertion in EC:DMC:MEC (1:1:1 vol.) has a higher efficiency than in PC:EC:DMC (1:1:3 vol.) because the currents of Li intercalation and de-intercalation are higher in the former electrolyte. It is believed that the capacity of the Li intercalation process is influenced primarily by reduction of the electrolyte solution. In order to obtain a satisfactory capacity, the reduction of an electrolyte solution should provide a compact, protective and effectively passivating solid electrolyte interface (SEI) on the graphite surface which enables only Li⁺ ion migration. Our results indicated that EC:DMC:MEC (1:1:1 vol.) provided a better SEI on the graphite surface and ensured better Li intercalation performance than PC:EC:DMC (1:1:3 vol.) under the conditions of these laboratory glass cells.

All CVs shown above were performed in dry electrolytes. However, the electrolyte solutions are hygroscopic and undergo a slow hydrolysis following:

\[ H_2O + LiPF_6 \rightarrow LiF + 2HF + POF_3 \] (3-1)

Electrolytes doped with impurities of 500 ppm deionized H₂O or concentrated aqueous HF (49, wt%, Fisher) to the level of 1000 ppm were studied, and the results are shown in Fig. 3-4 (doped with H₂O) and Fig. 3-5 (doped with HF). It can be seen that the addition of a small amount H₂O or HF impurity to the electrolyte solution considerably influenced the Li insertion process. As shown in Figs. 3-4 and 3-5, the capacity of the Li insertion process deteriorated markedly, and the effect of HF appeared to be greater than that of H₂O. This means the current generated during the negative scans is almost entirely and repetitively associated with inefficient reduction.
Figure 3-4. Cyclic voltammograms of graphite-coated copper electrode with the potential range of 3.00 to 0.00 V in electrolyte solutions (doped with 500 ppm H_2O) of (a) 1 M LiPF_6/EC:DMC:MEC (1:1:1 vol.) and (b) 1 M LiPF_6/PC:EC:DMC (1:1:3 vol.). Scan rate = 20 mV/s.
Figure 3-5. Cyclic voltammograms (5 consecutive scans) of graphite-coated copper electrode with the potential range of 3.00 to 0.00 V in electrolyte solutions (doped with 1000 ppm HF) of (a) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.) and (b) 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Scan rate = 20 mV/s.
processes on the graphite, with less lithium intercalation.

3.3.2 Controlled-Potential Electrolysis (Bulk Electrolysis).

Bulk electrolysis (BE) was utilized to study the effect of oxidation of the graphite-coated copper electrode over time. BE was shown to be an effective way to quantify the oxidation of the graphite-coated copper electrode at different potentials and to investigate the influence of impurities on the dissolution of copper.

BE in the electrolyte solutions was performed under a fixed convective-diffusion condition with a long duration of 5400 s (1.5 hr) at different potential steps from OCV to 3450 mV through 3700 mV (in 50 mV increments). The graphite-coated copper electrodes in the dry electrolytes were studied first. Then the electrolytes were doped with impurities of 500 ppm H₂O or concentrated aqueous HF (49 wt%) to the level of 1000 ppm. Figure 3-6 shows BE results for the graphite-coated copper electrodes in EC:DMC:MEC (1:1:1 vol.), and Fig. 3-7 shows results obtained in PC:EC:DMC (1:1:3 vol.). The percent oxidation of copper was calculated from the charge passed during BE, and the values are presented in Table 3-1. From the BE results it can be seen that the response of the graphite-coated copper electrodes shared some common characteristics in both electrolytes: the oxidation current increased with increased potential in all cases; small amounts of impurities (H₂O or HF) considerably enhanced the extent of copper oxidation in both electrolyte solutions; and the effect of HF appeared to be higher compared to that of H₂O in both electrolyte solutions. However, the response of the graphite-coated copper electrodes also showed different
Figure 3-6. Bulk electrolysis of graphite-coated copper electrode in 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H$_2$O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potential stepped from OCV to 3500 through 3700 mV (made in 50 mV increments). Time duration is 5400 s (1.5 hr).
Figure 3-7. Bulk electrolysis of graphite-coated copper electrode in 1 M LiPF$_6$/PC: EC:DMC (1:1:3 vol.): (a) dry electrolyte; (b) electrolyte doped with 500 ppm H$_2$O; (c) electrolyte doped with 1000 ppm HF. Electrolysis potential stepped from OCV to 3500 mV through 3700 mV in (a) and from OCV to 3450 mV through 3650 mV in (b) and (c) (all made in 50 mV increments). Time duration is 5400 s (1.5 hr).
Table 3-1. Bulk electrolysis results of the graphite-coated copper electrode. H$_2$O is doped to 500 ppm. HF is doped to 1000 ppm.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>3450 mV</th>
<th>3500 mV</th>
<th>3550 mV</th>
<th>3600 mV</th>
<th>3650 mV</th>
<th>3700 mV</th>
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<td>&lt; 1</td>
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<td>60</td>
</tr>
<tr>
<td>(Dry)</td>
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<td></td>
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</tr>
<tr>
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<td>&lt; 1</td>
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<td>41</td>
<td>57</td>
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<tr>
<td>(Doped with H$_2$O)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>EC:DMC:MEC(1:1:1)</td>
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<td>2</td>
<td>9</td>
<td>14</td>
<td>42</td>
<td>94</td>
</tr>
<tr>
<td>(Doped with HF)</td>
<td></td>
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</tr>
<tr>
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<td>1</td>
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</table>

*a* Not measured.
characteristics in different electrolyte solutions. As shown in Fig. 3-6, the oxidation current for graphite-coated copper in EC:DMC:MEC (1:1:1 vol.) was rather stable in all BE experiments, even when the potential reached as high as 3700 mV. However, in PC:EC:DMC (1:1:3 vol.) (Fig. 3-7), the oxidation current changed greatly during the electrolysis. It can be seen in Fig. 3-7a (dry electrolyte) that when the potential reached 3600 mV, the oxidation current of the graphite-coated copper grew abruptly at ~ 5000 s and then reached a steady state. When the potential was increased to 3650 mV and 3700 mV, abrupt growths in current occurred at ~ 4000 s and at ~ 1600 s, respectively. The abrupt growth in the oxidation current was found to be the result of peeling or detachment of the graphite coating from the copper foil surface as a result of massive dissolution of the copper at the coating interface. This phenomenon indicated that the graphite coating gave the copper foil some protection from oxidation because the oxidation current increased greatly after the graphite coating peeled off the copper foil. Similar phenomena were also observed in the same electrolyte doped with impurities. The oxidation current grew abruptly resulting from the peeling of the graphite coating at ~ 1200 s (at 3700 mV) in the electrolyte doped with 500 ppm H$_2$O (Fig. 3-7b); the oxidation currents grew abruptly at ~ 4200 s (3550 mV), ~ 1900 s (3600 mV) and ~ 800 s (3650 mV) in the electrolyte doped with HF (Fig. 3-7c). As shown in Fig. 3-7, H$_2$O appeared to diminish the peeling effect, and HF appeared to accelerate it. Also, in Figs. 3-7b and 3-7c, it can be seen that the oxidation current at a potential of 3650 mV dropped dramatically after the current grew abruptly resulting from the peeling of the graphite coating. This is because the area of the exposed
copper foil diminished quickly due to extensive oxidation during the electrolysis, hence the current decreased. In Fig. 3-7c, the exposed copper foil (1×1 cm\(^2\)) was completely oxidized at 3650 mV by the end of the electrolysis period, and the oxidation current dropped to ~ 0 at 4800 s. Finally, by comparison with the BE results for the uncoated copper foil electrodes,\(^{18}\) it was found that the oxidation current of graphite-coated copper was markedly smaller. This also indicates that the graphite coating gave the copper foil some protection and decreased the oxidation tendency of the copper substrate.

### 3.4 Conclusions

Cyclic voltammetry of graphite-coated battery-grade copper foil electrodes in two electrolyte solutions showed similar results. The results showed that the graphite coating greatly influenced the oxidation-reduction of the copper substrate and significantly altered the CV currents in consecutive CVs. The graphite coating was also shown to give some protection to the copper foil substrate against oxidation, which was confirmed in a BE study. BE was used to quantitatively study the oxidation tendency of graphite-coated copper electrodes in the electrolyte solutions. It was found that the graphite coating tended to peel off the copper foil in PC:EC:DMC (1:1:3 vol.), which incurred a higher oxidation current, whereas the graphite coating was rather stable in EC:DMC:MEC (1:1:1 vol.). With the shield of the graphite coating, the oxidation tendency of the graphite-coated copper electrode was much smaller compared to that of an uncoated copper foil electrode. A small amount of H\(_2\)O (500
ppm) or HF (1000 ppm) impurity was also shown to considerably enhance the oxidation tendency of the graphite-coated copper electrode, as was the case for the copper foil electrode.
Chapter 4 - Open-Circuit Voltage Study of Copper Foil Electrodes in Lithium-Ion Battery Electrolytes

4.1 Introduction

Ambient temperature Li-ion batteries have been under extensive study because of their outstanding characteristics, such as high energy density, high cell voltage and fewer safety concerns. Application of small Li-ion cells in portable electronic devices, such as cellular telephones and notebook computers, has achieved great success. The sale value of Li-ion cells has exceeded that of NiMH and NiCd among portable cells and the market for Li-ion cells is expected to continue to expand. More recently, large Li-ion cells have been investigated for commercial and military applications, such as electrical vehicles and satellites. In these applications, long-term stability of each component in the cell is required; one concern is the electrochemical stability of the current collectors.

Aluminum foil, as the positive current collector, has to endure a high oxidizing potential when a Li-ion cell is fully charged and it may also undergo severe corrosion during the charge operation. Therefore, some efforts have been directed to study the corrosion behavior of the aluminum substrate. On the other hand, less effort has been made in investigating the electrochemical stability of the copper negative current collector. Actually, copper is expected to be stable when the Li-ion cell is in charged state because copper is cathodically protected when Li is intercalated onto the carbon material. However, in practice, the Li-ion cell is manufactured in a fully discharged
state. Aurbach and Cohen found by *in situ* atomic force microscopy (AFM) that copper foil at open-circuit in LiAsF$_6$/propylene carbonate (PC) is not completely inert and contaminants may oxidize the copper.$^{11}$ Aurbach and Weissman also classified copper as one of the nonactive/slightly reactive metal electrodes in nonaqueous polar aprotic electrolyte solutions, such as Li salts in various solvents from the ester, ether or carbonate families, which are typical electrolyte solutions for Li-ion cells.$^{12}$ In addition, in some applications, such as electrical vehicles, over-discharge of Li-ion cells is expected.

In order to understand the intrinsic stability of copper in Li-ion battery electrolytes, we have studied previously the electrochemical stability of copper foil electrodes and graphite coated copper foil electrodes in Chapter 2 and Chapter 3, respectively, in different Li-ion battery electrolyte solutions using the techniques of cyclic voltammetry (CV) and controlled-potential electrolysis (bulk electrolysis) in half-cell reactions.$^{18, 19}$ During those studies, the open-circuit voltage (OCV) of the half-cell was found to be a variable value over time. Therefore, detailed studies on the OCV of the cell over time have been performed. The OCV of cells comprised of inert materials as the working electrode, such as aluminum, platinum wire, and glassy carbon, were studied for comparison. Then, the effect of some pertinent cell factors, such as aging of the reference electrode, surface conditions, edge effect of the copper foil electrodes and impurities on the OCV were studied.
4.2 Experimental Section

All of the OCV studies were performed using a homemade three-electrode cell as described in Chapter 2. The working electrode (WE) was copper foil, which was cut into a 1×1 cm² flag. The flag was then connected to a 22-gauge nickel wire by pressing the tip of the nickel wire onto the flag pole. In the studies of inert materials, the WE of aluminum foil was prepared in the same way. Glassy carbon electrodes were used by connection to their metal pin. The reference electrode (RE) was made by rolling and pressing a 1×1 cm² lithium foil onto the tip of a nickel wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diameter porous Vycor™ tip (Bioanalytical Systems, BAS, MF-2042). The auxiliary electrode (AE) was a 0.5 mm diameter platinum wire coil (23 cm length, BAS, MW-1033).

The electrolytes used in the OCV studies were 1 M LiPF₆ in ternary mixtures of (I) propylene carbonate (PC)-ethylene carbonate (EC)-dimethyl carbonate (DMC) [1:1:3 vol.] and (II) EC-DMC-methyl ethyl carbonate (MEC) [1:1:1 vol.]. The electrolyte solutions were obtained from EM Industries/Merck K. G. a. A. and were prepared from 99.98% purity solvents (< 20 ppm H₂O, as determined by a Karl Fischer titration) and Stella LiPF₆. The electrolytes were guaranteed at < 80 ppm HF and were analyzed at Saft as < 50 ppm using an acid-base titration. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times before the electrolytes were stored in a dry box.

The lithium metallic foil (Cyprus Foote Mineral Company), the battery-grade copper foil, and the aluminum foil were supplied by Saft. The copper foil (12 µm
thick) grade LP1/LP3, was obtained from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at \( \leq 130 \) ppm. The aluminum foil (20 µm thick) grade H18 Temper, was obtained from Nippon Foil Mfg. Co. The foil (both sides shiny) had a purity of 99.85% with the major trace element being Cu at 0.03%.

The glassy carbon electrode (3.0 mm diameter, BAS, MF-2012) is embedded in a 55 mm long by 6 mm o.d. plastic rod. Electrical connection was made through a metal (brass) rod permanently mounted in the electrode. The glassy carbon was polished with a slurry of 0.05 µm \( \gamma \)-alumina on a Microcloth® polishing cloth (Buehler). The electrode was then rinsed with dilute nitric acid, and deionized, double-distilled water, and dried with a laboratory tissue. Platinum wire working electrodes were 0.65 mm diameter.

A copper rod electrode was embedded in a 56 mm long by 6.5 mm o.d. plastic rod with only the tip surface (2.0 mm diameter) exposed to air. The copper rod electrode surface was polished in the same way as the glassy carbon electrode and rinsed with deionized, double-distilled water and dried with a laboratory tissue. A copper wire (0.5 mm o.d.) electrode was polished with silicon carbide sandpaper (1500 grit), rinsed with deionized, double-distilled water and dried with a lab tissue.

All of the cells were assembled and sealed in a dry box filled with argon. The water and oxygen contents inside the dry box were both less than 1 ppm. All OCV experiments were performed with the Cypress Systems CS-2000 computer-controlled
electrochemical system potentiostat/galvanostat, which has an input impedance of ~ $10^{11}$ ohms.

The OCV studies in this chapter can be classified into several sets of experiments. In the first set, OCV studies of Cu foil electrodes were performed in two different electrolyte solutions: (I) 1 M LiPF$_6$/PC:EC:DMC (1:1:3); and (II) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1). All of the REs were made fresh in these cells. The Cu foils were rinsed with acetone and air-dried before assembly of the cell. In the second set, OCV of cells consisting of inert materials (Al foil, Pt wire, or glassy carbon) as the WE was studied for comparison. The REs were also made fresh and the electrolyte was 1 M LiPF$_6$/PC:EC:DMC (1:1:3). In the third set of the experiments, the effect of aging of the REs on the OCV of Cu foil electrodes in 1 M LiPF$_6$/PC:EC:DMC (1:1:3) was studied. The REs were stored in the dry box for 48 h and 96 h for aging before cell assembly. In the fourth set, in order to study the effect of the surface condition (oxide film, fingerprints, etc.) of the copper foil on the OCV, the copper foil electrodes were polished with 1500 grit silicon carbide sandpaper before cell assembly. Next, an oxide film was grown artificially on the copper foil surface by placing an electrode in a Fisher Isotemp® 500 series laboratory oven for 48 h and 96 h at 100 °C before cell assembly. In the fifth set of experiments, the possible edge effect of copper foil was studied by OCV studies with a copper rod electrode and a copper wire electrode. The REs were made fresh and the electrolyte was 1 M LiPF$_6$/PC:EC:DMC (1:1:3) in the last two sets.
Next, in order to study the impurities influence on the OCV variation, an experiment of a cell comprised of two Cu foil electrodes, which were consecutively introduced into the same electrolyte, was designed to address the origin of the OCV variation. Finally, different amounts of HF were added into the electrolyte solution to further study the effect of HF on the OCV variation.

4.3 Results and Discussion

Open-circuit voltage (OCV) is an important parameter of a cell. OCV should be a stable value over time if none of the components (electrodes, electrolyte, etc.) of the cell change over time. On the other hand, variation of OCV of a cell can provide information about the stability of the cell components. In unpublished studies at our laboratory, the OCV of the cell (assembled in the same way as described in the experimental section) was found to have a larger than expected change over time. The OCV of each cell in this work was recorded continuously for an extensive period of time (up to two days) when the WE was immersed into electrolyte.

In the first set of the OCV experiments, two separate cells were made as described above and the reference electrodes (RE) were freshly made before the OCV measurement. (Cell assembly in the dry box took about 30 min to complete.) During assembly of the cell, the WEs were kept above the electrolyte solution surface. Just before the OCV measurement, the WEs were lowered into the electrolyte solution. This ensured that the OCV measurements had the same starting time conditions. The results (Fig. 4-1) show that the OCV signals in both electrolyte solutions showed
Figure 4-1. OCV vs. time of copper foil electrode in (a) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1 vol.); and (b) 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.); Reference electrode was made fresh.
similar behavior. Both OCVs decreased at first until reaching a minimum, then increased with some fluctuations until reaching a meta-steady state. The decreasing period ranged from 30 to 60 min and the increasing period ranged from 600 to 1000 min in the two different cells. In both experiments, whether the electrolyte solution was stirred or not during the experiment did not influence the results. Repeat experiments all showed similar OCV behavior with an exception of the whole OCV signal shifting ± 80 mV, which probably resulted from variation of junction potentials in different cells.

In the second set of experiments, the OCV measurement of Al foil, Pt wire, and glassy carbon electrodes in 1 M LiPF$_6$/PC:EC:DMC (1:1:3) was obtained for comparison and the results are shown in Figs. 4-2 to 4-4. It can be seen that these results were quite different from those in the first set. As shown in Fig. 4-2, the OCV of Al foil initiated at a voltage of 2.58 V and increased continuously to a steady state (~ 3.16 V), which resulted from the formation of a passivation film on the surface of Al foil.\textsuperscript{16} Such a stable and thin anodic passivation film formed on the Al foil protects Al foil from further corrosion,\textsuperscript{12} hence the OCV reached a steady state as shown in Fig. 4-2. By comparison, the OCV of a Pt wire electrode was continuously stable at 3.50 V for 20 hours when immersed in the electrolyte as shown in Fig. 4-3.

The OCV results of a “non-activated” and an “activated” glassy carbon (GC) electrode are shown in Fig. 4-4a and 4-4b, respectively. The activation of the GC electrode was performed by scanning the electrode between 4.00 to 5.00 V vs. Li at 50 mV/s for 10 min. As seen in Fig. 4-4a, the OCV of the “non-activated” GC electrode
Figure 4-2. OCV vs. time of an aluminum foil electrode in 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
Figure 4-3. OCV vs. time of a platinum wire electrode in 1 M LiPF6/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
Figure 4-4. OCV vs. time of (a) a non-activated glassy carbon electrode and (b) an activated glassy carbon electrode; in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
initiated at 3.49 V and increased continuously to ~ 3.99 V, whereas the OCV of the “activated” GC electrode initiated at 3.55 V, quickly increased to a plateau and reached a steady state of ~ 3.86 V. The electrochemical pretreatment of the GC electrode with constant or cycled potentials is a well-established process to improve the activity of the GC electrode. The pretreatment is believed to be able to remove debris, impurities, and even microparticulate carbon, which results from the polishing process, from the GC surface.\textsuperscript{20} As shown in Fig. 4-4, compared with the “non-activated” GC electrode, the OCV of the “activated” GC reached the steady state faster and the steady state was also more stable as a result of the electrochemical pretreatment.

The above studies confirmed that the OCV evolution on glassy carbon or Al were similar while the behavior on copper foil was quite different. However, why the OCV varied over time is still not answered. The instability of any cell component could cause the OCV variation. In the third set of experiments, the effect of aging of the RE on the OCV stability was examined.

As described above, the RE used in this work is Li metal in electrolyte solutions. As is well known, Li can induce a solid electrolyte interface (SEI) on the fresh Li surface, which has been attributed to a complicated and not fully understood reduction mechanism of the electrolyte solution. In this set of experiments, the procedures were the same as those in the first set except that the REs were stored in the dry box for 48 h and 96 h before cell assembly. The OCV study was performed on cells containing Cu foils in 1 M LiPF$_6$/PC:EC:DMC (1:1:3) and the results are shown
in Fig. 4-5. As compared with the results in Fig. 4-1, it can be seen that the aging of
the reference electrode did not change the OCV signal markedly. The OCV signals
kept the same characteristics as the cells with fresh made REs and the extent of the
initial decrease and subsequent increase of the OCV was roughly the same. Rahner, in
a study of the SEI formation on Li, reported that the OCV of fresh cut Li vs. Li⁺/Li
decreased to less than 1 mV within 10 s in 1 M LiClO₄/PC, which denotes that SEI
formation on Li is a rather fast process.²¹ Hence on the time scale of this study, aging
of the RE did not influence the OCV of the cell and we ruled out the RE as a causative
factor.

The influence of surface conditions of copper foils on the OCV was examined
in the fourth set of experiments. The copper foil was polished with silicon carbide
sandpaper (1500 grit), rinsed with acetone, dried with a lab tissue and then
immediately moved into the dry box. Then the cells were assembled in the same way
as in the first set of experiments. One electrode was polished lightly only to remove
fingerprints and other marks on the copper foil surface whereas the other electrode
was polished thoroughly for a longer time until totally shiny on both sides. The OCV
results of both electrodes are shown in Fig. 4-6. It can be seen that the characteristic
response of the OCV signal was unchanged. Next, the copper foil electrode was cured
in an oven (100 °C) for 48 h and 96 h to grow an oxide film before cell assembly. The
copper foil appeared dull after being cured in the oven. The OCV results are shown in
Fig. 4-7. It can be seen that the characteristic response of the OCV signal of Cu foil
Figure 4-5. OCV vs. time of copper foil electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Reference electrode had been aged in a dry box for 48 h in (a) and 96 h in (b).
Figure 4-6. OCV vs. time of copper foil electrode in 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.). The copper foil electrode was lightly polished in (a) and was thoroughly polished in (b). Reference electrode was made fresh.
Figure 4-7. OCV vs. time of copper foil electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). The electrodes were cured in an oven (100 °C) for 48 h in (a) and 96 h in (b). Reference electrode was made fresh.
electrode was not changed. The results in this set of experiments indicated that the initial surface condition had limited influence on the stability of the OCV.

In the fifth set of experiments, the edge effect of Cu foil on the OCV was studied by OCV studies using a copper rod electrode with only the disc surface exposed to the electrolyte solution and a copper wire electrode. The results are shown in Fig. 4-8. It can be seen that OCV of both electrodes is similar to that of the copper foil electrodes, which denotes that edge effect is not the cause of the OCV variation of copper in the electrolyte solution.

From the OCV results in the above experiments, it can be seen that none of the studied factors is the main cause of the OCV variation of Cu foil electrodes over time. The question of the origin of the OCV variation is still unanswered.

Theoretically, the OCV of an electrode is determined by the double-layer charge formed on the interface between the electrode and the solution. Variation of OCV of an electrode indicates the double-layer charge change. A negative shift of OCV denotes that the accumulated charge on the electrode decreases if the charge is positive or vice versa, increases if the charge is negative. Porter and coworkers in a study of chemisorption of thiol-derived monolayers on a gold electrode observed that OCV of the gold electrode shifted negatively about 0.2 V upon the introduction of butanethiol as the result of the transfer of negative charge from the sulfhydryl group to gold electrode in the form of chemisorption. Thiourea, which is commonly used as a leveling and brightening agent in the electrodeposition of copper, has a similar electron distribution on the thioureido group to that on the carbonate group of organic
Figure 4-8. OCV vs. time of (a) a copper rod electrode and (b) a copper wire electrode; in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
carbonates. The dipole moment of thiourea (4.89 Debyes\textsuperscript{23}) is very close to that of propylene carbonate (4.98 Debyes\textsuperscript{24}). It was found that addition of thiourea to aqueous sulphuric acid solutions caused the OCV of a copper electrode to decrease as a result of adsorption of thiourea on the copper surface\textsuperscript{25, 26}. It appears that a similar adsorption process occurred when copper foil electrode was immersed into organic carbonates electrolyte. The transfer of negative charge from the carbonate group (more specifically, the electron dense oxygen atom in the carbonate group) to the copper electrode during the adsorption process resulted in the initial drop of OCV of the copper electrode. The minimum of the OCV denotes that a complete highly oriented organic carbonates monolayer was formed on the copper foil surface.

After the OCV minimum, the increase of OCV denotes a gradual discharge of the accumulated charge. It appears that oxidation of copper by possible impurities, such as H\textsubscript{2}O, HF, etc. in the electrolyte solution, resulted in the positive shift in the OCV. It is a well studied phenomenon that thiourea can form stable complexes with copper ions in aqueous solution.\textsuperscript{25-27} Previous study using continuous wave (CW) and pulse electron paramagnetic resonance (EPR) showed that complexation of Cu\textsuperscript{2+} with carbonate ligands in aqueous solution forms mono- and bidentate copper-carbonate complexes.\textsuperscript{28} The formation of a possible complex of copper ion with organic carbonates could greatly assist the oxidation process of copper by the impurities since it shifts the reaction of copper oxidation in the favored direction. The oxidation of copper by impurities would shift the OCV positively until reaching a meta-steady state of OCV, which denotes the formation of a meta-stable copper oxide film on the copper
foil surface. (It is well known that oxide film formed on copper surface is not as stable
as that formed on other metals, such as aluminum.)

Aurbach and Cohen showed by in situ AFM images that structural changes
arose on the copper foil electrode surface owing to the introduction of the electrolyte
solution (LiAsF₆/PC) and suggested that contaminants might oxidize the copper
substrate. This result is consistent with the findings of the above OCV studies.

To further study the impurities influence on the OCV variation, an experiment
with a cell of two Cu foil electrodes consecutively introduced into the electrolyte
solution was designed. At first, the OCV of a Cu foil electrode was continuously
recorded when the electrode was immersed in the electrolyte while the other Cu foil
electrode was kept above the electrolyte solution. When the OCV of the first Cu foil
electrode reached a meta-steady state at ~ 1600 min, the second Cu foil electrode was
introduced into the electrolyte solution to replace the first Cu foil electrode and the
OCV continued to be recorded. As shown in Fig. 4-9, the OCV positive shift after the
minimum of the second Cu foil electrode is much smaller than that of the first
electrode. It denotes that trace amount of impurities in the electrolyte solution has
been decreased by reaction with the first electrode before the introduction of the
second electrode. The smaller initial OCV drop of the second electrode comparing to
that of the first electrode appears to result from the adsorption of electrolyte vapor on
the second copper foil electrode when it was kept above the electrolyte solution in the
cell.
Figure 4-9. OCV vs. time of cells with two copper foil electrodes being consecutively introduced into 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.), of which the first electrode was replaced with the second new electrode after the OCV of the first electrode reached steady state. Reference electrode was made fresh.
Next, different amounts of concentrated aqueous HF (49 wt %, Fisher) were added into the electrolyte solution to the level of 500, 1000, and 2000 ppm. The results are shown in Fig. 4-10. It can be seen that the positive OCV shift from minimum to meta-steady state increased when HF level in the electrolyte increased from 500 ppm to 1000 ppm. When 2000 ppm HF was added, the OCV kept shifting positively and did not reach a meta-steady state even after 2200 min. This suggests that HF may be a possible oxidizing species toward copper in the electrolyte. This possibility is surprising considering the well-known behavior of Cu in aqueous solvents where copper metal is unattacked by HF unless trace oxidants are present\textsuperscript{30} (carbonate electrolytes were degassed of air and the dry box was monitored at less than 1 ppm O\textsubscript{2} content). Furthermore, copper or Monel alloys are the choice for handling and transferring liquid HF.\textsuperscript{31}

We reported on copper dissolution in fresh electrolyte of 1 M LiPF\textsubscript{6}/PC:EC:DMC (1:1:3) (less than 20 ppm H\textsubscript{2}O and 50 ppm HF) in another study.\textsuperscript{32} In that study, samples of 1×1 cm\textsuperscript{2} copper foil stored in 5 mL fresh electrolyte at OCV for one week in sealed plastic containers showed copper dissolution to the level of 5 ppm in the electrolyte solution as measured by flame atomic absorption spectroscopy (AAS). The dissolution of copper appeared to stabilize at ∼50 ppm after 13 weeks storage, which equals 3.9 × 10\textsuperscript{-6} mol Cu ion in the 5 mL solution. HF in the electrolyte was calculated to be < 13.9 × 10\textsuperscript{-6} mol and H\textsubscript{2}O is < 5.6 × 10\textsuperscript{-6} mol. Considering that some oxidized copper exists on the copper foil surface without entering the electrolyte
Figure 4-10. OCV vs. time of copper foil electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.) doped with HF to the level of (a) 500 ppm; (b) 1000 ppm; (c) 2000 ppm. Reference electrode was made fresh in each of the three cells.
solution, the ratio of copper ion in the solution is close to the stoichiometric ratio of reaction between copper and such impurities. Finally, we continue Cu corrosion studies in carbonate electrolytes so that causative species and conditions can be detailed in a future publication.

4.4 Conclusion

Detailed OCV studies of Cu foil electrodes in Li-ion battery electrolytes showed that the OCV of copper foil electrodes exhibited different behavior from that of inert materials. Combined with previously published results\textsuperscript{11}, battery-grade copper foils, which are commonly used as the negative electrode current collector in Li-ion batteries, appear to show a two-step process when immersed into the electrolyte solution. In the first step, organic carbonates adsorbed on the surface of the copper foil, which caused a negative shift of OCV. Then, the copper was oxidized by impurities with the assistance of a possible complexation of copper ion with organic carbonates, until a metal-stable oxide film formed on the surface in the second process, which resulted in a positive shift of OCV to a meta-steady state. This effort was aimed at understanding the behavior of Cu foils exposed to lithium-ion carbonate electrolytes; those conditions are fundamentally different from the real Li-ion cell conditions where Cu foil is protected by intercalated Li in carbon and an S.E.I. layer. The conditions in this chapter best reflect a cell prior to electrochemical formation.
Chapter 5 - Open-Circuit Voltage Study of Graphite-Coated Copper Foil Electrodes in Lithium-Ion Battery Electrolytes

5.1 Introduction

Ambient temperature rechargeable Li-ion batteries have been under extensive study since their introduction into the market by Sony in 1991.\textsuperscript{1} Such batteries have many outstanding characteristics, such as high energy density, high cell voltage and fewer safety concerns, compared to conventional techniques.\textsuperscript{2} The active material of the negative electrode in a Li-ion cell is carbon based. Li can be intercalated into or deintercalated from the carbon during the charge or discharge process. The positive electrode active material is a lithiated transition metal oxide, such as LiNiO\textsubscript{2}, LiCoO\textsubscript{2} or LiMn\textsubscript{2}O\textsubscript{4}. Copper foil is used as the negative electrode current collector and aluminum foil is used as the positive electrode current collector in all Li-ion cells currently in production. The electrolyte can be either a solid polymer electrolyte (SPE) or a nonaqueous liquid electrolyte. Liquid electrolyte is usually comprised of a Li salt and various solvents from the ester, ether or carbonate families.

Application of small portable Li-ion cells in electronic devices, such as cellular telephones and notebook computers, has achieved great commercial success. The sale value of Li-ion cells exceeded that of NiMH and NiCd in the total portable cells market in 1999.\textsuperscript{3} More recently, large Li-ion cells have been investigated for applications requiring large power density and energy density, such as electrical vehicles and satellites.\textsuperscript{2, 3} In these applications, long-term stability of each component
in the cell is required. The electrochemical stability of the anode materials, graphite-coated copper foil (Cu-C), is one of the concerns.

In order to understand the intrinsic stability of the anode materials in Li-ion battery electrolytes, we have studied previously in Chapters 2 and 3 the electrochemical behavior of Cu foil electrodes and Cu-C foil electrodes in different nonaqueous organic carbonate Li-ion battery electrolyte solutions in half-cell reactions. Open-circuit voltage (OCV) studies on Cu foil electrodes (without graphite coating) were reported in Chapter 4. In that study, the OCV variation over time of Cu foil electrodes was observed and subsequently studied in detail. Combined with our previous findings of Cu dissolution, it was suggested that impurities, such as HF, could oxidize copper foils in nonaqueous electrolyte solutions, which resulted in the OCV variation of Cu foil electrodes over time. The OCV studies provided some insight into the intrinsic stability of uncoated Cu foil in the Li-ion electrolyte solutions. In this chapter, similar OCV studies on Cu-C foil electrodes were performed. The OCV of graphite-coated aluminum foil (Al-C) was studied for comparison. The effect of some pertinent cell factors, such as aging of the reference electrode and thermal treatment of the Cu-C foil electrodes was also studied. The results are compared with the findings on uncoated Cu foil electrodes and summarized.

5.2 Experimental Section

OCV study of Cu-C foil electrodes was performed using the same homemade
three-electrode cell as in the OCV study of Cu foil electrode.\textsuperscript{18} The working electrode (WE) was Cu-C foil, which was cut into a 1×1 cm\textsuperscript{2} flag. The flag was then connected to a 22-gauge Ni wire by pressing the tip of the Ni wire onto the flag pole. (The graphite coating was scraped from tip part of the flag pole.) In the comparison study using an Al-C foil, the electrode was prepared in the same manner. The reference electrode (RE) was made by rolling and pressing a 1×1 cm\textsuperscript{2} Li foil onto the tip of a Ni wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diameter porous Vycor\textsuperscript{TM} tip (Bioanalytical Systems, BAS, MF-2042). The auxiliary electrode (AE) was a 0.5 mm diameter Pt wire coil (23 cm length, BAS, MW-1033).

Two electrolytes were used in the OCV studies: (I) 1 M LiPF\textsubscript{6} in ternary mixtures of propylene carbonate (PC)-ethylene carbonate(EC)-dimethyl carbonate (DMC) [1:1:3 vol.], and (II) 1 M LiPF\textsubscript{6} in ternary mixtures of EC-DMC-methyl ethyl carbonate (MEC) [1:1:1 vol.]. The electrolyte solutions were obtained from EM Industries/Merck K. G. a. A. and were prepared from 99.98\% purity solvents (< 20 ppm H\textsubscript{2}O, as determined by a Karl Fischer titration) and Stella LiPF\textsubscript{6}. The electrolytes were guaranteed at < 80 ppm HF and were analyzed at Saft as < 50 ppm using an acid-base titration. The electrolytes were shipped to Ohio University and stored in a dry box. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times before it was moved into the dry box.

The Li metallic foil, the battery-grade Cu-C foil, and Al-C foil were all supplied by Saft. The Li foil was obtained from Cyprus Foote Mineral Company. The
Cu foil (12 µm thick) grade LP1/LP3, was obtained from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at ≤ 130 ppm. The coating consisted of a blend of 50 wt.% mesocarbon micro beads (MCMB 10-28) and 50 wt.% Timcal SFG-44 graphites using polyvinylidene fluoride (PVDF) as a binder. The carbon loading per electrode face is ~ 13 mg/cm$^2$ or 26 mg/cm$^2$ (double side coated). The Al foil (20 µm thick) grade H18 Temper, was obtained from Nippon Foil Mfg. Co. The foil (both sides shiny) had a purity of 99.85% with the major trace element being Cu at 0.03%. The coating was applied with a reverse comma bar coater and consisted of a blend of 47.7 wt.% mesocarbon microbeads (MCMB 10-28), 47.7 wt.% Timcal SFG-44 graphites using 4.5 wt.% polyvinylidene fluoride (PVDF) as a binder. The carbon loading per electrode face is 4.6 mg/cm$^2$.

All of the cells were assembled and sealed in a dry box filled with argon, in which water and oxygen contents were both less than 1 ppm. All OCV experiments were performed with the Cypress Systems CS-2000 computer-controlled electrochemical system potentiostat/galvanostat. The input impedance of this instrument is ~ $10^{11}$ ohms.

Several experimental parameters were tested as outlined briefly: (1) OCV studies of Cu-C foil electrodes were performed in the two electrolytes. REs were made fresh in these cells and WEs were rinsed with acetone and air-dried before assembly of the cell. (2) The effect of aging of the REs on the OCV in 1 M LiPF$_6$/PC:EC:DMC (1:1:3) was studied. The REs were stored in the dry box for 48 h and 96 h for aging
before cell assembly. (3) OCV measurement of a cell consisting of Al-C foil as the WE was performed for comparison to Cu-C. (4) In order to study the effect of impurities, OCV of a cell comprised of two Cu-C WEs, which were consecutively introduced into the same electrolyte, was measured. (5) The effect of thermal treatment of the graphite coating on the OCV was studied by placing the Cu-C foil electrodes in a Fisher Isotemp® 500 series laboratory oven for 48 h and 96 h at 100 °C before cell assembly. The REs were made fresh and the electrolyte was 1 M LiPF₆/PC:EC:DMC (1:1:3) in the last three sets of experiments. Results were compared with those obtained from uncoated Cu foil electrodes.

5.3 Results and Discussion

In Chapter 4 studies of Cu foil electrodes in Li-ion battery electrolytes, the OCV was shown to be an effective way to study the interface change of the Cu over time. This provided some insight into the intrinsic stability of the electrodes and the role of impurities in electrolyte solutions. In this chapter, similar studies were performed on Cu-C foil electrodes by continuous measurement of the OCV for an extensive period of time (up to two days) when the electrode was immersed into electrolyte solution.

At first, OCVs of two separate cells composed of a Cu-C foil electrode as the WE were studied in the two different Li-ion battery electrolytes as described above. REs in both cells were freshly made before the OCV measurement. (Cell assembly in the dry box took about 30 min to complete.) During assembly of the cell, the WEs
were kept above the electrolyte solution. Just before the OCV measurement, the WEs were immersed into the electrolyte solution, which ensured that the OCV measurements had the same starting time. The results (Fig. 5-1) show that the OCV signals in both electrolyte solutions had similar characteristics. The OCVs both appear to follow a two-step process. In the first step, the OCV decreased quickly until reaching a minimum. This was followed by increasing gradually until reaching a steady state. In electrolyte II [1 M LiPF₆/EC-DMC-MEC (1:1:1)], the initial decreasing period was 60 min and the following increasing period was ~ 1000 min. The initial OCV drop was 0.13 V and the OCV increase was ~ 0.36 V. In electrolyte I [1 M LiPF₆/PC:EC:DMC (1:1:3)], the initial OCV drop was 0.29 V and took about 35 min. The OCV increase from the minimum to the steady state was about 0.20 V and took about 1200 min. Duplicate experiments showed the same OCV versus time shape characteristics and the whole OCV showed a variation of ± 70 mV, which probably resulted from variation of junction potentials in the different cells. Whether the electrolyte solution was stirred or not during the experiment did not influence the results. For the remainder of the experiments investigating the causative factor of the OCV variation, only electrolyte I was used.

Next, the effect of aging of the reference electrode on the OCV was examined. In this experiment, the cell assembly procedures were the same as those indicated above except that the REs were stored in a dry box for 48 h and 96 h before cell assembly. The results are shown in Fig. 5-2. As compared with the result in Fig. 5-1b, it can be seen that the OCV versus time signals had the same characteristic shape as
Figure 5-1. OCV vs. time of Cu-C foil electrode in: (a) 1 M LiPF₆/EC:DMC:MEC (1:1:1 vol.) and (b) 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
Figure 5-2. OCV vs. time of Cu-C foil electrode in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.). Reference electrode had been aged in a dry box for 48 h (a) and 96 h (b).
that of the cells composed of freshly made REs. In addition, the extent of the initial
decrease and subsequent increase of the OCV was roughly the same. These results
showed that aging of the reference electrode did not change the OCV signal markedly.
This result is consistent with the Chapter 4 findings. As previously discussed, aging of
the RE (Li metal) is a rather fast process\textsuperscript{21}, so it did not influence the OCV of the cell
on the time scale of the experiment. Aging of REs is not a causative factor of OCV
variation. Therefore, the OCV variation resulted from the variation of the working
electrode (Cu-C-electrolyte half cell) over time. However, whether the OCV variation
is resulted from the Cu foil substrate or the graphite coating has not been answered.

As compared with the OCV results obtained from Cu foil electrodes, it can be
seen that the characteristic OCV signals of Cu-C electrodes is quite different from that
of Cu foil electrodes even though the OCV variation of Cu foil electrodes also showed
a two-step process over time. In the first step, the initial OCV drop of Cu-C foil
electrode was about two times larger than that of Cu foil electrode. In the second step,
the OCV of the Cu foil electrodes never achieved a real steady state, but did with the
Cu-C foil electrodes. In addition, the OCV signal of the Cu-C foil electrodes in the
second step was smooth as compared with a fluctuated increasing OCV signal of the
Cu foil electrodes.

To further study the effect of the Cu foil substrate on the OCV of a Cu-C foil
electrode, the OCV of a cell comprised of an Al-C foil as the WE in electrolyte I was
studied (Fig. 5-3). It can be seen that the OCV of an Al-C foil electrode showed a
similar two-step process over time. The OCV of the Al-C foil electrode dropped from
Figure 5-3. OCV vs. time of Al-C foil electrode in 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.). Reference electrode was made fresh.
3.44 V to a minimum (3.20 V), then increased to a steady state of 3.45 V. This result is different from the OCV signal of Al foil (without graphite coating), which was shown in Chapter 4. The OCV of an Al foil did not show the two-step process over time. Instead, it started at a voltage of 2.58 V and increased continuously to a steady state (~3.16 V), which resulted from the formation of a passivation film on the surface of the Al foil. This difference in the OCV signals between Al-C and Al denotes that the variation of Al-C originated from the graphite coating rather than the foil substrate.

Close comparison (Fig. 5-4) of the initial part of the OCVs of Al-C and Cu-C showed some differences. It can be seen that the initial drop in the OCV of the Al-C foil electrode was more gradual and lagged as compared with that of a Cu-C foil electrode while the rising portion of the OCV of Cu-C is more gradual than that of Al-C. In addition, the whole OCV curve of Al-C is ~0.15 V higher than that of Cu-C, which might result from either the difference in the OCV of different metals or the junction potential difference of Al-Ni from Cu-Ni. (Ni wire was used as the electrical connection to each foil.) This suggests that the foil substrate has some influence on the OCV variation over time. However, considering the difference in OCV variation of Cu from that of Al, the effect of the foil substrate on the OCV is limited. Yet, both Cu-C and Al-C foil electrodes have a similar characteristic two-step OCV variation. The magnitude of the initial OCV drop and the subsequent OCV increase of both electrodes are close to each other. In addition, both electrodes achieved a steady state. These results suggest that the graphite coating is the main factor causing the characteristic two-step OCV variation over time. The foil substrate has limited
Figure 5-4. Comparison of the initial part of the OCV of Al-C (Fig. 5-3) and Cu-C (Fig. 5-1b) in 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.).
influence. However, why the graphite coating (or more specifically, the graphite-electrolyte) caused the OCV variation over time is not answered.

It is a well accepted concept that the OCV of an electrode is determined by the double-layer charge formed on the interface between electrode and solution. Variation of the OCV of an electrode denotes the double-layer charge change and provides insight into the electrochemical stability of the electrode. Actually, solvent adsorption and double-layer potential drop at electrodes, as a result of solvent dipole contribution to the inner-layer potential drop, was extensively studied in the 1970s and earlier.\textsuperscript{33} The structure of the interface of both Hg/EC\textsuperscript{34} and Hg/PC\textsuperscript{35} has been investigated. It was found that the capacity of the interface changed as the result of the reorientation of the solvent molecules (PC or EC).\textsuperscript{34, 35} It appears that the adsorption of the electrolyte solvents on the graphite surface resulted in the initial OCV drop of Cu-C and Al-C electrodes due to the transfer of negative charge from the solvent molecules to the electrodes as the result of the orientation of the negative ends of the solvent dipoles towards graphite surface. After a complete, highly oriented layer was formed on the graphite surface, the OCV reached the minimum.

After the OCV minimum, the increase in the OCV denotes a gradual discharge of the accumulated charge. It appears that the specific adsorption of an impurity of HF into the graphite coating from the electrolyte solution resulted in the positive shift in the OCV.

To further study the impurity influence on the OCV variation of a Cu-C foil electrode, an experiment consisting of a cell with Cu-C foil electrodes consecutively
introduced into the electrolyte solution was performed. In this experiment, the OCV of the first Cu-C foil electrode was continuously recorded while the other Cu-C foil electrode was kept in the headspace of the cell just above the electrolyte solution.

After the OCV of the first Cu-C foil electrode reached a steady state at 1650 min, the second Cu-C foil electrode was introduced into the electrolyte solution replacing the first Cu-C foil electrode and the OCV continued to be recorded. The smaller initial OCV drop of the second electrode compared to that of the first electrode is suggested to have resulted from the adsorption of electrolyte solvent vapor on the second Cu-C foil electrode when it was kept above the electrolyte solution in the cell. During the second step of the process, if the positive OCV shift resulted from the interaction between the graphite coating and either solute or solvent of the electrolyte solution, the magnitude of the OCV positive shift of the two electrodes should be the same. However, from the results shown in Fig. 5-5, it can be seen that the magnitude of the positive OCV shift of the second Cu-C foil electrode is much smaller than that of the first electrode. It suggests that the oxidizing species (trace amount of HF in the electrolyte solution) was partially consumed through specific adsorption on the graphite coating of the first electrode before the introduction of the second electrode.

It is well known that clean carbon surfaces are reactive to form surface oxides in the form of chemisorption from the unsatisfied valences. The type of surface oxides depends on the carbon material and pretreatment history, which can be classified into acidic, basic, and neutral. On acid-adsorbing carbons, the adsorption of acid to the carbon material was ascribed to the interaction between the surface
Figure 5-5. OCV vs. time of a cell with two Cu-C foil electrodes being consecutively introduced into 1 M LiPF$_6$/PC:EC:DMC (1:1:3 vol.), of which the first electrode was replaced with the second electrode after the OCV of the first electrode reached steady state. Reference electrode was made fresh.
oxides and acid in the solution according to the following equation proposed by Panzer and Elving$^{36}$:

\[(C_xO) + H^+ + A^- \rightarrow (C_xOH)^+ + A^- \quad (5-1)\]

It appears that the accumulated positive charge, which resulted from the specific adsorption of H$^+$ to the graphite coating, caused the positive shift of OCV. Since the rate of the adsorption process is mainly controlled by the diffusion rate of H$^+$ to the graphite coating, the OCV shift is gradually increased until the adsorption saturation is achieved, which corresponds to the OCV steady state.

In Chapter 4, it was found that Cu foil (without graphite coating) could be oxidized by HF in the same electrolyte solutions. From the above studies, it can be inferred that specific adsorption of HF on the graphite coating should give protection to the Cu foil substrate from oxidation. This inference is further verified by another study discussed below.

In a comparison study of dissolution of Cu and Cu-C foils in fresh electrolyte I, samples of 1×1 cm$^2$ Cu and Cu-C foils were separately stored in 5 mL electrolyte at OCV up to 14 weeks in the Corning® 15 mL clear polypropylene centrifuge tubes. Samples were prepared in a dry box (less than 1 ppm O$_2$ and H$_2$O), then sealed and stored in the dry box until they were taken out for copper dissolution measurement, which was monitored by flame atomic absorption spectroscopy (AAS) in different week intervals. It was found that copper dissolution of the Cu foil samples reached ~50 ppm, whereas only a trace amount (< 1 ppm) of copper dissolution was found in
Cu-C foil samples after 14 weeks. It appeared that the adsorption of HF on the graphite coating protected the Cu foil beneath the coating from corrosion.

Finally, the influence of thermal treatment of the graphite coating on the OCV was examined by curing Cu-C foil electrodes in an oven at 100 °C for 48 h and 96 h before cell assembly. The OCV results are shown in Fig. 5-6. The OCV of the thermally treated Cu-C foil electrode showed complicated results. Small humps appeared after the initial OCV drop in both OCV curves. This could have resulted from a graphite oxide change by the thermal treatment. These results indicated that the thermal treatment of the graphite coating had some influence on the OCV.

5.4 Conclusion

The OCV of Cu-C foil electrodes was shown to undergo a two-step process over time, which resulted from the interaction between the graphite coating and the electrolyte solution. In the first step, the OCV dropped quickly until reaching a minimum as a result of adsorption of electrolyte solvents on the graphite coating. In the second step, the OCV gradually increased as a result of specific adsorption of HF in the graphite coating, which protected the Cu substrate from oxidation. The foil substrate was shown to have limited influence on the OCV variation whereas thermal treatment of the graphite coating markedly changed the characteristic of the OCV curve.
Figure 5-6. OCV vs. time of Cu-C foil electrode in 1 M LiPF₆/PC:EC:DMC (1:1:3 vol.). The electrodes were cured in an oven at 100 °C for 48 h (a) and 96 h (b). Reference electrode was made fresh.
Chapter 6 - Quantitation of The Dissolution of Battery-Grade Copper Foils in Lithium-Ion Battery Electrolytes by Flame Atomic Absorption Spectroscopy

6.1 Introduction

Li-ion batteries have achieved great commercial success in portable cell applications, such as cellular phones and notebook computers. They are currently under extensive study for large applications, such as electric vehicles and satellites, because their outstanding characteristics of high energy density, high power density, and high cell voltage are very suitable for such applications.\textsuperscript{1-3} In these large battery applications, long-term chemical stability of each battery component is required. The electrochemical stability of the anode materials is one of the concerns.

All Li-ion batteries currently in production use a carbonaceous coating applied on a copper foil substrate as the anode. Lithium ion can intercalate into and deintercalate from this coating during charge and discharge processes. The copper foil is the current collector. The anode (Cu-graphite-electrolyte half cell) is expected to be electrochemically stable when the Li-ion cell is in charged state because the anode is cathodically protected when Li is intercalated into the carbon material. (The open-circuit voltage (OCV) of the lithiated anode is from 0 to 1.5 V vs. Li\textsuperscript{+}/Li while the unlithiated anode is above 3.0 V vs. Li\textsuperscript{+}/Li.\textsuperscript{3,4}) However, Li-ion cells are manufactured in a fully discharged state. Preliminary results showed that the anode was susceptible to copper dissolution if the cell was not activated (charged) after assembly.\textsuperscript{18, 19} Aurbach and Cohen found by \textit{in situ} atomic force microscopy (AFM) that copper foil
at open-circuit in LiAsF$_6$/propylene carbonate (PC) is not completely inert and suggested that contaminants may oxidize the copper foil. Previous OCV studies in Chapter 4 confirmed that copper foil is not completely inert in Li-ion battery electrolytes and an impurity of HF in the electrolyte solution could oxidize the copper foil substrate. Copper dissolution should be avoided because Cu ions in the electrolyte solution might plate on the anode during the charge process, which could lead to degraded performance of the cell.

In order to quantitatively evaluate the stability of the battery-grade copper foil in Li-ion battery electrolyte at OCV, atomic absorption spectroscopy (AAS) was used to detect the copper dissolution over time. AAS is an efficient technique and extensively used to quantify trace amounts of metals and elements. AAS was at first used to study copper dissolution in fresh electrolyte solutions. Then electrolyte solutions aged for six months were studied. In addition, cyclic voltammetry (CV) was used to determine the chemical state of copper ion since AAS does not distinguish it.

6.2 Experimental Section

6.2.1 Materials

The battery-grade copper foil was supplied by Saft. The copper foil (12 µm thick) grade LP1/LP3, was obtained from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at ≤ 130 ppm.
The electrolytes used were 1 M LiPF$_6$ in ternary mixtures of (I) propylene carbonate (PC)-ethylene carbonate (EC)-dimethyl carbonate (DMC) [1:1:3 vol.] and (II) EC-DMC-methyl ethyl carbonate (MEC) [1:1:1 vol.]. The electrolyte solutions were obtained from EM Industries/Merck K. G. a. A. and were prepared from 99.98% purity solvents (< 20 ppm H$_2$O, as determined by a Karl Fischer titration) and Stella LiPF$_6$. The electrolytes were guaranteed at < 80 ppm HF and were analyzed at Saft as < 50 ppm using an acid-base titration. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times before electrolyte solutions were moved into a dry box.

6.2.2 Sample Preparation

Samples were prepared by putting 1×1 cm$^2$ Cu foils (9.5 ± 0.1 mg) in 5 mL Li-ion battery electrolyte solution. Sample preparation was performed in a dry box (less than 1 ppm O$_2$ and H$_2$O). Corning® 15 mL clear polypropylene centrifuge tubes and caps were used as sample containers since they were found not to dissolve or swell in the electrolytes. Glass tubes were avoided since trace HF was present in the electrolytes and sample storage was up to 20 weeks. Sample preparation was different between “fresh” and “aged” electrolyte solutions.

In “fresh” electrolyte I, eleven samples were prepared in 5 mL electrolyte in a dry box in one day, then sealed with Parafilm and stored in the dry box until they were taken out one at a time for AAS measurements over a twenty week period.
In “aged” electrolyte solutions, samples were prepared weekly over an 8 week period. Thus all 8 samples could be measured in one day avoiding any inter-day error of the AAS method, and only one calibration curve was needed for each electrolyte solution. Both electrolytes I and II were studied. The samples were prepared in 5 mL electrolyte solution and sealed with Parafilm in a dry box, and then removed for storage in a desiccator. The effect of impurities on copper dissolution was also studied by doping 500 ppm H₂O or 1000 ppm HF into the electrolyte solutions. In the study of the impurities, the original caps of the centrifuge tubes were replaced with rubber septa, through which the impurities were added using a GC syringe (Hamilton). In addition, in order to study any influence of the amount of electrolyte solutions on copper dissolution, samples were prepared in different volumes of electrolytes (2 mL, 5mL, 10 mL and 15 mL) during the first week of sample preparation.

6.2.3 Atomic Absorption Spectroscopy

A flame atomic absorption spectrometer (SP9 Series, Pye Unicam Ltd.) was used with a Jarrell-Ash hollow cathode lamp (type 45435) for Fe-Cu-Mn. Absorbance measurements were made at the Cu principle line at 324.8 nm and at an alternative 327.4 nm (sensitivity 2× less). The experimental conditions and instrumental settings were used as recommended by the manufacturer. The bandpass was set to 0.5 nm. The flame gases were air/acetylene. The lamp current was 5 mA. The air flow rate was 4.0 L·min⁻¹ and the acetylene flow rate was 0.8 L·min⁻¹.
6.2.4 Calibration

The calibration standard was copper (II) cyclohexanecarboxylate (Acros Organics). A 100 ppm Cu\(^{2+}\) stock solution was prepared by dissolving a weighed amount of the standard directly in the electrolyte solutions. It took about 5 hr for the salt to dissolve in the electrolyte solutions. The crystalline copper salt is blue colored while the stock solution was colorless after the salt had completely dissolved.

Calibration was performed over the range of 1 to 70 ppm Cu\(^{2+}\). A blank solution was also measured. Standard solutions were prepared by dilution of the stock solution with the appropriate electrolyte solution.

All calibration stock and standard solutions were prepared immediately before the calibration measurements and stored in polyethylene containers. In the measurement of copper dissolution samples with concentrations out of the linear range of the calibration curve, the samples were diluted with corresponding electrolyte.

6.2.5 Cyclic Voltammetry

Cyclic voltammetry (CV) was used to identify the chemical state of copper ion in the electrolyte solution. CVs were performed using a homemade three-electrode cell as described previously.\(^3\) The glassy carbon working electrode (WE) [3.0 mm diameter, Bioanalytical Systems (BAS), MF-2012] was embedded in a 55 mm long by 6 mm o.d. plastic rod. Electrical connection was made through a metal (brass) rod permanently mounted in the electrode. The glassy carbon was polished with a slurry of 0.05 μm γ-alumina on a Microcloth\textsuperscript{®} polishing cloth (Buehler). The electrode was then
rinsed with dilute nitric acid, and deionized, double-distilled water, and dried with a laboratory tissue.

The reference electrode (RE) was made by rolling and pressing a 1×1 cm² lithium foil onto the tip of a nickel wire and assembled in a dry box in electrolyte solution in a glass tube containing a 6 mm diameter porous Vycor™ tip (BAS, MF-2042). The lithium metallic foil (Cyprus Foote Mineral Company) was supplied by Saft. The auxiliary electrode (AE) was a 0.5 mm diameter platinum wire coil (23 cm length, BAS, MW-1033). CVs were recorded with the Cypress Systems CS-2000 computer-controlled electrochemical system potentiostat/galvanostat.

6.3 Results and Discussion

6.3.1 Identification of Cu ion

The Cu principle line at 324.8 nm and an alternative line at 327.4 nm (sensitivity 2× less) were used for the identification of Cu ions in the sample. The Cu principle line was used for the quantitative analysis.

6.3.2 Calibration

A weighted regression analysis method was used because analysis of the calibration results revealed that an assumption that error in the absorbances is constant was not correct, which is most likely the result of instrumental noise. Instead, the relative standard deviation was roughly the same for the absorbance. The calibration
The weighted regression analysis\textsuperscript{38, 39} yielded the following equation in the two electrolyte solutions.

For electrolyte (I) 1 M LiPF$_6$/PC:EC:DMC(1:1:3):

$$A = 0.00421 C - 0.0001, \quad r^2 = 0.9982 \quad (6-1)$$

where C is the concentration of copper ion in ppm and A is the absorption of copper ion. The linear range was 2.3 to 70 ppm. $S_{y/x} = 0.0021$, $S_m = 0.00011$, $S_a = 0.0010$. ($S_{y/x}$, $S_m$, and $S_a$ are the standard deviation of the A on C, the slope and the intercept, respectively.) The limit of detection (LOD) was 0.7 ppm and limit of quantitation (LOQ) was 2.3 ppm. LOD and LOQ were calculated using the following equation:

$$C_L = k S_B/K$$

where $S_B$ is the standard deviation of the blank response, K is the slope of the calibration graph, $k$ is a numerical factor chosen for appropriate confidence level. $k = 3$ was used for the calculation of LOD and 10 was used for LOQ.

For electrolyte (II) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1):

$$A = 0.00475 C + 0.0002, \quad r^2 = 0.9987 \quad (6-2)$$

The linear range was 2.1 to 70 ppm. $S_{y/x} = 0.0033$, $S_m = 0.00019$, $S_a = 0.0013$. The LOD was 0.6 ppm and the LOQ was 2.1 ppm.

The accuracy of the method was tested by measuring the concentrations of electrolyte spiked with the calibration standard at concentrations other than those of the standard solutions. The results (Table 6-1) showed satisfactory recovery. The stability of the calibration was checked at four points (1, 5, 20 and 70 ppm) of the
Figure 6-1. An AAS calibration curve for copper in electrolyte 1 M LiPF₆/PC:EC: DMC (1:1:3). The error bars represent the 95% confidence interval for 8 replicates at each concentration level.
Table 6-1. Accuracy study of the AAS system by measuring electrolytes spiked with the calibration standard to concentrations other than those used in the calibration curve to evaluate the % recovery.

<table>
<thead>
<tr>
<th>Spiked Conc. (ppm)</th>
<th>Obtained Conc. (ppm) (mean ± s_d) (n =5)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Spike recovery in 1 M LiPF_6/EC:DMC:MEC (1:1:1)</td>
</tr>
<tr>
<td>8.2</td>
<td>8.99 ± 0.63</td>
<td>109.6</td>
</tr>
<tr>
<td>16.4</td>
<td>16.2 ± 1.2</td>
<td>98.8</td>
</tr>
<tr>
<td>30.7</td>
<td>31.8 ± 1.5</td>
<td>103.7</td>
</tr>
<tr>
<td>51.2</td>
<td>49.4 ± 2.4</td>
<td>96.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spike recovery in 1 M LiPF_6/PC:EC:DMC (1:1:3)</td>
</tr>
<tr>
<td>8.3</td>
<td>8.94 ± 0.86</td>
<td>107.8</td>
</tr>
<tr>
<td>16.5</td>
<td>16.0 ± 0.9</td>
<td>96.7</td>
</tr>
<tr>
<td>31.0</td>
<td>31.7 ± 1.2</td>
<td>102.3</td>
</tr>
<tr>
<td>51.7</td>
<td>51.5 ± 1.8</td>
<td>99.6</td>
</tr>
</tbody>
</table>
standard solutions during the middle of the copper foil dissolution measurement and
after the measurement.

6.3.3 Determination of Copper Foil Dissolution

At first, copper dissolution was studied in “fresh” electrolyte I, which was
transferred into a dry box on the same day it was received at Ohio University from
Saft. Eleven samples were prepared in the fresh electrolyte as described earlier on the
next day and stored in the dry box. These samples were taken out one at a time for
AAS measurements over the next 20 weeks. From the AAS results (Table 6-2), it can
be seen that copper dissolution of the battery-grade copper foil in the “fresh”
electrolyte solution progressed over time until the 13th week from 5 ppm to ~ 50 ppm.
From 13 to 20 weeks storage the copper concentration appeared to level at ~ 50 ppm.
This suggests that copper dissolution slowed down or even stopped after a certain
period of storage time (~ 13 weeks). The electrolyte solution remained clear in all the
samples for the 20 week period, which indicates that copper ion is colorless in
electrolyte I solution.

During these AAS measurement, each sample in Table 6-2 was exposed to air
for ~ 30 min for measurement, then resealed with Parafilm afterwards and stored in a
desiccator. In the 20th week after the sample preparation week, all the resealed samples
were measured by AAS again, and the results are summarized in Table 6-3. The AAS
results showed that environmental exposure (O₂, moisture, etc.) had a great impact on
copper dissolution. From these resealed samples, a large amount of copper dissolution
Table 6-2. Concentrations of copper detected by AAS after 1×1 cm$^2$ Cu foils were stored in fresh 1 M LiPF$_6$/PC:EC:DMC (1:1:3) electrolyte for up to 20 weeks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Duration Since Prepared (week)</th>
<th>Concentration (ppm) of Cu (mean ± s.d) (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1$^{st}$-Week</td>
<td>1</td>
<td>5.0 ± 0.4</td>
</tr>
<tr>
<td>Cu-2$^{nd}$-Week</td>
<td>2</td>
<td>5.0 ± 0.3</td>
</tr>
<tr>
<td>Cu-4$^{th}$-Week</td>
<td>4</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>Cu-6$^{th}$-Week</td>
<td>6</td>
<td>13.9 ± 0.5</td>
</tr>
<tr>
<td>Cu-8$^{th}$-Week</td>
<td>8</td>
<td>19.3 ± 0.5</td>
</tr>
<tr>
<td>Cu-9$^{th}$-Week</td>
<td>9</td>
<td>39.0 ± 0.8</td>
</tr>
<tr>
<td>Cu-11$^{th}$-Week</td>
<td>11</td>
<td>42.3 ± 0.8</td>
</tr>
<tr>
<td>Cu-13$^{th}$-Week</td>
<td>13</td>
<td>49.9 ± 1.1</td>
</tr>
<tr>
<td>Cu-15$^{th}$-Week</td>
<td>15</td>
<td>47.6 ± 1.3</td>
</tr>
<tr>
<td>Cu-17$^{th}$-Week</td>
<td>17</td>
<td>53.0 ± 1.7</td>
</tr>
<tr>
<td>Cu-20$^{th}$-Week</td>
<td>20</td>
<td>54.3 ± 0.8</td>
</tr>
</tbody>
</table>
Table 6-3. Concentrations of copper detected by AAS after stored Cu foil samples were opened ~ 30 min for measurement (as in Table 6-2) and then resealed and stored for several additional weeks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Duration Since Resealed (week)</th>
<th>Concentration (ppm) of Cu (mean ± s_d) (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1\textsuperscript{1\textdegree} Week-Resealed</td>
<td>19</td>
<td>415.5 ± 3.7</td>
</tr>
<tr>
<td>Cu-2\textsuperscript{2\textdegree} Week-Resealed</td>
<td>18</td>
<td>354.7 ± 3.8</td>
</tr>
<tr>
<td>Cu-4\textsuperscript{4\textdegree} Week-Resealed</td>
<td>16</td>
<td>376.1 ± 4.8</td>
</tr>
<tr>
<td>Cu-6\textsuperscript{6\textdegree} Week-Resealed</td>
<td>14</td>
<td>345.9 ± 3.6</td>
</tr>
<tr>
<td>Cu-8\textsuperscript{8\textdegree} Week-Resealed</td>
<td>12</td>
<td>278.8 ± 5.9</td>
</tr>
<tr>
<td>Cu-9\textsuperscript{9\textdegree} Week-Resealed</td>
<td>11</td>
<td>*</td>
</tr>
<tr>
<td>Cu-11\textsuperscript{11\textdegree} Week-Resealed</td>
<td>9</td>
<td>224.2 ± 2.6</td>
</tr>
<tr>
<td>Cu-13\textsuperscript{13\textdegree} Week-Resealed</td>
<td>7</td>
<td>186.2 ± 3.1</td>
</tr>
<tr>
<td>Cu-15\textsuperscript{15\textdegree} Week-Resealed</td>
<td>5</td>
<td>131.6 ± 3.0</td>
</tr>
<tr>
<td>Cu-17\textsuperscript{17\textdegree} Week-Resealed</td>
<td>3</td>
<td>91.4 ± 0.8</td>
</tr>
<tr>
<td>Cu-20\textsuperscript{20\textdegree} Week-Resealed</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Sample was not kept.
was detected. Copper dissolution progressed rapidly and reached more than 400 ppm in 19 weeks. Also, visual inspection of the copper foils in the resealed tubes showed that dark spots appeared on the foil surface and the whole surface of the foils appeared dull as compared with samples that had not been opened.

In order to identify the chemical state of copper ion in the electrolyte solution, cyclic voltammetry (CV) was used. Figure 6-2 shows the CVs of (1) the calibration stock solution of 100 ppm copper (II) cyclohexanebutyrate in electrolyte I; (2) the solution of a sample of Cu foil stored in fresh electrolyte I for 20 weeks; the copper concentration was measured at ~ 50 ppm by AAS; and (3) the solution of a sample of Cu foil that had been prepared in fresh electrolyte I, exposed to the air for 30 min, resealed and stored for 19 weeks. The copper concentration of this sample was measured at ~ 400 ppm. The CV of the calibration stock solution was initiated at 3.90 V, scanned negatively to 2.80 V, and then scanned positively back to 3.90 V. In the other two sample solutions, the CVs were scanned negatively from 3.80 V to 2.80 V, and then scanned positively back to 3.80 V. The scan rate was 20 mV/s in all solutions. From Fig. 6-2, it can be seen that in the initial negative scan, two reduction peaks (Peak 1 and Peak 2) appeared in all three solutions. In the subsequent positive return scan, a sharp oxidation peak (Peak 3) appeared in all three solutions. In addition, there was a small, broad oxidation peak after this sharp oxidation peak that appeared only in the calibration stock solution. The peak potential values are listed in Table 6-4. The data in Figure 6-2 and Table 6-4 are indicative of Cu$^{2+}$ in all three solutions and suggests that copper dissolution in Li-ion battery electrolyte at OCV was
Figure 6-2. Cyclic voltammograms of: (1) (---) standard stock solution of 100 ppm copper (II) cyclohexanebutyrate in electrolyte 1 M LiPF$_6$/PC:EC:DMC (1:1:3); (2) (----) solution of Sample Cu-20th-Week in Table 6-2 (~ 50 ppm Cu ion); (3) (••••) solution of Sample Cu-1st-Week-Resealed in Table 6-3 (~ 400 ppm Cu ion). Scan rate = 20 mV/s.
Table 6-4. Identification of peak potential values as shown in Figure 6-2. Peaks are numbered according the sequence of appearance in the CV scan.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Peak 1 (Reduction)</th>
<th>Peak 2 (Reduction)</th>
<th>Peak 3 (Oxidation)</th>
<th>Peak 4 (Oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.05</td>
<td>3.32</td>
<td>3.43</td>
<td>3.73</td>
</tr>
<tr>
<td>2</td>
<td>3.06</td>
<td>3.36</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.01</td>
<td>3.33</td>
<td>3.52</td>
<td></td>
</tr>
</tbody>
</table>
in the form of Cu (II). As compared with copper potentials in aqueous solution, Peak 1 corresponds to the reduction of Cu$^{2+}$ to Cu$^{0}$; and Peak 2 corresponds to the reduction of Cu$^{2+}$ to Cu$^{+}$, [and simultaneous reduction of Cu$^{+}$ to Cu$^{0}$ afterwards]. Peak 3 corresponds to the oxidation of Cu$^{0}$ to Cu$^{2+}$. The small, broad oxidation peak, which appeared only in the calibration stock solution, is not assigned.

Next, copper dissolution in “aged” electrolyte solutions was studied. Both electrolytes (I and II) were stored in a dry box for six months before being used for sample preparation. Both electrolytes appeared light brown in color after the storage. Impurity effects were studied by doping H$_2$O or HF into the electrolyte solutions. There were three sets of samples in each electrolyte solution: (1) Cu foils in dry electrolyte, (2) Cu foils in electrolyte doped with 500 ppm H$_2$O, and (3) Cu foils in electrolyte doped with 1000 ppm HF (49 wt % aqueous solution, Fisher). The results of an eight-week copper dissolution study in the “aged” electrolyte solutions are listed in Tables 6-5 and 6-6. It can be seen that the tendency of copper dissolution was similar in both electrolyte solutions, which suggested that the composition of the electrolyte had a limited influence. The copper concentrations in all sets of samples in both electrolyte solutions increased rapidly over time. In the dry electrolyte, the copper concentration reached ~ 300 ppm in both electrolytes by eight weeks. The H$_2$O and HF impurities appeared to have lessened copper dissolution in the electrolyte solutions. Copper dissolution was only about half of that in the electrolyte solutions without doped impurities, as discussed below.
Table 6-5. Concentrations of copper detected by AAS after 1×1 cm² Cu foils were stored in 1 M LiPF₆/PC:EC:DMC (1:1:3) electrolyte for up to 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Time Duration (week)</th>
<th>Dry Electrolyte Concentration (ppm)</th>
<th>Electrolyte Doped with 500 ppm H₂O Concentration (ppm)</th>
<th>Electrolyte Doped with 1000 ppm HF Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.8 ± 0.4</td>
<td>2.4 ± 0.3</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>21.9 ± 0.8</td>
<td>3.1 ± 0.4</td>
<td>8.8 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>38.0 ± 2.0</td>
<td>17.1 ± 0.7</td>
<td>23.4 ± 0.7</td>
</tr>
<tr>
<td>4</td>
<td>44.5 ± 1.9</td>
<td>31.2 ± 1.1</td>
<td>58.0 ± 1.4</td>
</tr>
<tr>
<td>5</td>
<td>207.1 ± 6.7</td>
<td>61.9 ± 1.7</td>
<td>74.4 ± 3.2</td>
</tr>
<tr>
<td>6</td>
<td>282.9 ± 8.2</td>
<td>73.9 ± 2.6</td>
<td>80.5 ± 3.7</td>
</tr>
<tr>
<td>7</td>
<td>290.7 ± 8.1</td>
<td>99.4 ± 2.7</td>
<td>113.9 ± 4.0</td>
</tr>
<tr>
<td>8</td>
<td>338.8 ± 10.2</td>
<td>116.9 ± 3.0</td>
<td>130.5 ± 7.9</td>
</tr>
</tbody>
</table>
Table 6-6. Concentrations of copper detected by AAS after 1×1 cm² Cu foils were stored in 1 M LiPF₆/EC:DMC:MEC (1:1:1) electrolyte for up to 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Time Duration (week)</th>
<th>Concentration (ppm) of Cu (mean ± s.d) (n = 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry Electrolyte</td>
</tr>
<tr>
<td>1</td>
<td>1.6 ± 0.8</td>
</tr>
<tr>
<td>2</td>
<td>4.1 ± 1.1</td>
</tr>
<tr>
<td>3</td>
<td>87.4 ± 4.9</td>
</tr>
<tr>
<td>4</td>
<td>101.2 ± 5.1</td>
</tr>
<tr>
<td>5</td>
<td>142.1 ± 8.4</td>
</tr>
<tr>
<td>6</td>
<td>190.7 ± 11.5</td>
</tr>
<tr>
<td>7</td>
<td>247.7 ± 11.6</td>
</tr>
<tr>
<td>8</td>
<td>281.1 ± 15.9</td>
</tr>
</tbody>
</table>
Copper dissolution results for samples stored in different volumes of the “aged” electrolyte I (2, 5, 10 and 15 mL) are listed in Table 6-7. The results showed that the total amount of copper dissolution was independent of the volume of the electrolyte solution.

From the above AAS results, it can be seen that the copper dissolution behavior was different between “fresh” and “aged” electrolyte solutions. The copper dissolution was much larger in the “aged” electrolyte than it was in the “fresh” electrolyte. It appears that the copper dissolution mechanism was different between “fresh” and “aged” electrolyte solution.

In “fresh” electrolyte (less than 20 ppm H$_2$O and 50 ppm HF), copper dissolution in 5 mL electrolyte solution appeared to stabilize at ~ 50 ppm after 13 weeks storage, equalling $3.9 \times 10^{-6}$ mol Cu. HF in the electrolyte was calculated to be $< 13.9 \times 10^{-6}$ mol and H$_2$O was $< 5.6 \times 10^{-6}$ mol. Considering that some oxidized copper exists on the foil surface without entering the electrolyte solution, the copper in the solution is close to the stoichiometric ratio from a reaction between copper and these impurities. Combined with previous findings in Chapter 4, it can be suggested that copper dissolution in the “fresh” electrolyte solution was caused by the oxidation of the copper foils by the impurities.

If the reaction mechanism of copper dissolution in the “aged” electrolyte solutions was similar to that in the “fresh” electrolyte, it could infer that the dissolution tendency should be similar the dry “aged” electrolyte solutions and that doping of the impurities would increase the dissolution. However, the copper
Table 6-7. Concentrations of copper detected by AAS after 1×1 cm² Cu foils were stored in different volumes of electrolyte solution for 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Electrolyte Volume (mL)</th>
<th>Concentration (ppm) of Cu (mean ± s_d) (n = 5)</th>
<th>Total amount of Cu (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samples in 1 M LiPF₆/PC:EC:DMC (1:1:3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>854.8 ± 25.2</td>
<td>1710 ± 50</td>
</tr>
<tr>
<td>5</td>
<td>338.8 ± 10.2</td>
<td>1694 ± 51</td>
</tr>
<tr>
<td>10</td>
<td>161.0 ± 5.1</td>
<td>1610 ± 51</td>
</tr>
<tr>
<td>15</td>
<td>111.1 ± 3.4</td>
<td>1667 ± 50</td>
</tr>
<tr>
<td>Samples in 1 M LiPF₆/EC:DMC:MEC (1:1:1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>576.8 ± 29.8</td>
<td>1154 ± 56</td>
</tr>
<tr>
<td>5</td>
<td>281.1 ± 15.9</td>
<td>1406 ± 79</td>
</tr>
<tr>
<td>10</td>
<td>143.0 ± 7.3</td>
<td>1430 ± 73</td>
</tr>
<tr>
<td>15</td>
<td>71.9 ± 3.7</td>
<td>1079 ± 55</td>
</tr>
</tbody>
</table>
dissolution was more than ten times larger in the “aged” electrolyte solutions than that in the “fresh” electrolyte. The doped H$_2$O and HF impurities resulted in decreased dissolution tendency. In addition, the fact that dissolution was independent of the volume of the electrolyte solution showed that H$_2$O and HF were not the main causative factor in the dissolution. Otherwise, the total amount of dissolution would have been larger in the larger volume of electrolyte solution. All these results showed that the dissolution mechanism in the “aged” electrolyte solutions was different from that in the “fresh” electrolyte. It appears that possible decomposition of the electrolyte, such as the chemical reactivity of PF$_5$ and LiPF$_6$ with EC and DMC as reported by Kinoshita and coworkers$^{40}$, could produce oxidizing species, which could be a causative factor in the dissolution.

6.4 Conclusions

The dissolution of battery-grade copper foil in Li-ion battery electrolytes was quantitatively studied using flame AAS. The results showed that there was a small amount of dissolution (~ 50 ppm) in “fresh” electrolyte solution after storage (up to 20 weeks), which was suggested to result from oxidation by impurities in the electrolyte solution. Also, atmosphere impurities (O$_2$, moisture, etc.) had some influence on the stability of the copper. A short exposure to air (~ 30 min) caused a large amount of copper dissolution in “fresh” electrolyte solution. Copper foils in “aged” electrolyte solutions also showed large amounts of dissolution, which appeared to have a different mechanism from that in “fresh” electrolyte. It appeared that possible decomposition
products formed during electrolyte storage were detrimental to copper stability. The results in this work showed that the condition of electrolyte is critical to copper stability.
Chapter 7 - Quantitation of the Dissolution of Graphite-Coated Copper Foils in Lithium-Ion Battery Electrolytes by Flame Atomic Absorption Spectroscopy (AAS)

7.1 Introduction

Large Li-ion batteries are currently under extensive study for electric vehicles and aerospace applications, which requires outstanding characteristics of high energy density, high power density, long cycle life, etc., of the batteries.\textsuperscript{1-3} Projects currently in process include a NASA-DoD interagency program of the development of Li-ion batteries for projected missions, such as Mars Landers, Rovers, Penetrators, Orbiters, Low Earth Orbit (LEO) and Geosynchronous Equatorial Orbit (GEO) satellites.\textsuperscript{41} The Partnership for a New Generation of Vehicles (PNGV) is a program between the Federal Government and USCAR that includes Daimler-Chrysler, General Motors and Ford Motor Company in the investigation of high-power Li-ion batteries for the application of new generation of hybrid electric vehicles.\textsuperscript{42} The US Department of Energy (DOE) initiated the Advanced Technology Development (ATD) Program in 1998 in the development of Li-ion batteries for hybrid electric vehicles, which involves many national labs, such as Idaho National Engineering and Environmental Laboratory (INEEL), Argonne National Laboratory (ANL), Sandia National Laboratories (SNL), Lawrence Berkeley National Laboratory (LBNL), and Brookhaven National Laboratory (BNL).\textsuperscript{43}
In the large applications, long-term chemical stability of each component in the Li-ion batteries is required. One concern is the electrochemical stability of the anode current collector. The anode in a Li-ion cell is a copper foil coated with graphite and binder. The active material of the anode is the graphite. The copper foil is the current collector. Preliminary results showed that the anode was susceptible to copper dissolution if the cell was not activated (charged) after assembly, which could lead to degraded performance.\textsuperscript{18, 19} Aurbach and Cohen found by \textit{in situ} atomic force microscopy (AFM) that copper foil at open-circuit in LiAsF$_6$/propylene carbonate (PC) is not completely inert and suggested that contaminants may oxidize the copper foil.\textsuperscript{11} Previous open-circuit voltage (OCV) studies in Chapter 4 also showed that the copper foil substrate is not completely inert in the Li-ion battery electrolytes and that an impurity of HF in the electrolyte solution might oxidize the copper foil substrate.

In order to quantitatively evaluate the stability of the copper foil in Li-ion battery electrolyte at OCV, atomic absorption spectroscopy (AAS) was used to detect the copper dissolution of the battery-grade copper foils (without graphite coating) over time in the electrolyte solutions in Chapter 6. AAS was shown to be an effective technique for quantitative evaluation of the stability of copper foils in the Li-ion battery electrolytes under various conditions. In this chapter, AAS was used to directly quantify dissolution of graphite-coated copper (Cu-C) foil in “fresh” and “aged” Li-ion battery electrolyte solutions. The results are compared with those obtained from uncoated copper foils as reported in Chapter 6.
7.2 Experimental Section

7.2.1 Materials

The graphite-coated copper (Cu-C) foil was supplied by Saft. The copper foil (12 µm thick) grade LP1/LP3, was obtained from Fukuda Metal Foil and Powder Co. The electrodeposited foil (one matte side and one shiny side) had a purity of 99.9% with the major trace element being Cr at ≤ 130 ppm. The coating consisted of a blend of 50 wt.% mesocarbon micro beads (MCMB 10-28) and 50 wt.% Timcal SFG-44 graphites using polyvinylidene fluoride (PVDF) as a binder. The carbon loading per electrode face is ~ 13 mg/cm² or 26 mg/cm² (double side coated).

The electrolytes used were 1 M LiPF₆ in ternary mixtures of (I) propylene carbonate (PC)-ethylene carbonate (EC)-dimethyl carbonate (DMC) [1:1:3 vol.] and (II) EC-DMC-methyl ethyl carbonate (MEC) [1:1:1 vol.]. The electrolyte solutions were obtained from EM Industries/Merck K. G. a. A. and were prepared from 99.98% purity solvents (< 20 ppm H₂O, as determined by a Karl Fischer titration) and Stella LiPF₆. The electrolytes were guaranteed at < 80 ppm HF and were analyzed at Saft as < 50 ppm HF using an acid-base titration. Electrolyte was frozen before degassing for 30 min and then thawed. The procedure was repeated three times before electrolyte solutions were moved into a dry box.

7.2.2 Sample Preparation

Samples were prepared by placing 1×1 cm² Cu-C foils (30.5 ± 0.1 mg) in 5 mL electrolyte solution. The sample preparation procedure was similar to that used in the
study of uncoated copper foils in Chapter 6. The sample preparation was performed in a dry box (less than 1 ppm $\text{O}_2$ and $\text{H}_2\text{O}$). The sample container were the Corning® 15 mL clear polypropylene centrifuge tubes and caps. For the study of impurities, the original cap of the Corning tube was replaced with a rubber septum, through which the impurities were added using a GC syringe (Hamilton). The samples were prepared and the tubes were sealed with Parafilm in the dry box before being taken out for impurity addition.

7.2.3 Apparatus

A flame atomic absorption spectrometer (SP9 Series, Pye Unicam Ltd.) was used with a Jarrell-Ash hollow cathode lamp (type 45435) for Fe-Cu-Mn. Absorbance measurement was made at the Cu principle line at 324.8 nm. The experimental conditions and instrumental setting were used as recommended by the manufacturer, which was described in Chapter 6.

7.2.4 Calibration

The calibration curves used were the same as those described in the study of the uncoated copper foils in Chapter 6. The calibration standard was copper cyclohexanebutyrate (Acros Organics). The stock and the standard solutions were prepared in the electrolytes immediately before the calibration measurements and stored in polyethylene containers.
7.3 Results and Discussion

The measurement of copper dissolution in each electrolyte was made right after the calibration. The estimated standard deviation of the sample concentrations was calculated using a weighted regression method since the assumption that the error in the absorbance is constant in the unweighted calculation was not correct here.

Dissolution of the graphite-coated copper foils was first studied in “fresh” electrolyte I. The electrolyte was transferred to a dry box (less than 1 ppm O\textsubscript{2} and H\textsubscript{2}O) immediately after it was received at Ohio University from Saft. All of the foil samples were prepared the next day in the dry box, and then sealed and stored in the dry box until they were taken out for the AAS measurements, which were made over a fourteen week interval. The results (Table 7-1) of the dissolution of the graphite-coated copper foil showed that only trace amounts of copper (< 1 ppm) were found in all the samples. As compared with the AAS study of uncoated Cu foils in Chapter 6, the dissolution of the Cu-C foils was severely diminished. As reported in Chapter 6, the copper dissolution reached ~ 50 ppm after 13 weeks of storage, which was believed to result from oxidation by an impurity of HF. Combined with the previous OCV findings in Chapter 4, it appeared that specific adsorption of HF by the graphite coating provided some protection to the underlying copper and hence, the dissolution of the Cu-C foil was markedly small.

During the AAS measurements, each sample in Table 7-1 was exposed to the air for ~ 30 min then resealed and stored in a desiccator. Fourteen weeks after the sample preparation week, all these resealed samples were measured by AAS again to
Table 7-1. Concentrations of copper detected by AAS in fresh 1 M LiPF₆/PC:EC:DMC (1:1:3) when 1×1 cm² Cu-C foils were stored in the electrolyte for up to 14 weeks. Samples were named by the type of foil and the week when they were taken out for AAS measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Duration Since Prepared (week)</th>
<th>Concentration (ppm) of Cu (mean ± s_d) (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-C-2nd Week</td>
<td>2</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>Cu-C-3rd Week</td>
<td>3</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>Cu-C-5th Week</td>
<td>5</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>Cu-C-7th Week</td>
<td>7</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>Cu-C-9th Week</td>
<td>9</td>
<td>0.6 ± 0.4</td>
</tr>
<tr>
<td>Cu-C-11th Week</td>
<td>11</td>
<td>0.6 ± 0.5</td>
</tr>
<tr>
<td>Cu-C-14th Week</td>
<td>14</td>
<td>0.5 ± 0.3</td>
</tr>
</tbody>
</table>
study the effect of atmospheric impurities (O\textsubscript{2}, moisture, etc.). Large amounts of
dissolution were detected as shown in Table 7-2. The dissolution of the Cu-C foils
progressed rapidly and reached more than 800 ppm at 12 weeks after the first sample
had been exposed to the air and resealed. Such a short exposure to the air (~ 30 min)
markedly changed the stability of the Cu-C foils in the electrolyte solution.
Atmospheric impurities had a much larger influence on the stability of Cu-C foils than
that of uncoated Cu foils in the same electrolyte. The dissolution tendency of the Cu-C
foils was almost twice as large as that of the Cu foils.

Additionally, the solutions were colorless in all of the samples, which shows
that copper ion is colorless in the nonaqueous organic carbonate electrolyte solutions
as compared with the characteristic blue color in aqueous solution.

Next, the stability of Cu-C foils in “aged” electrolyte solutions was studied.
Electrolytes I and II were stored in a dry box for six months before being used for
sample preparation. Both electrolytes appeared light brown color after this period of
storage. In this study, solution impurity effects were also studied by doping impurities
of H\textsubscript{2}O and HF into the electrolyte solution. Three sets of samples were prepared in
each electrolyte solution: (1) Cu-C foils in dry electrolyte, (2) Cu-C foils in electrolyte
doped with 500 ppm H\textsubscript{2}O, and (3) Cu-C foils in electrolyte doped with 1000 ppm HF
(49 wt % aqueous solution, Fisher). The results of these dissolution studies for Cu-C
foil stored in the “aged” electrolyte for up to eight weeks are summarized in Tables 7-3
and 7-4. It can be seen that the dissolution of Cu-C foils showed similar results in
both electrolyte solutions. It appeared that the composite of the electrolyte had limited
Table 7-2. Concentrations of copper detected by AAS from Cu-C foil samples which were exposed to air for ~ 30 min for measurement (as in Table 7-1) and resealed. Measurement was performed in the 14th week since the sample preparation week.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time Duration Since Opened and Resealed (week)</th>
<th>Concentration (ppm) of Cu (mean ± s_d) (n = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-C-2nd Week</td>
<td>12</td>
<td>819.5 ± 9.0</td>
</tr>
<tr>
<td>Cu-C-3rd Week</td>
<td>11</td>
<td>*</td>
</tr>
<tr>
<td>Cu-C-5th Week</td>
<td>9</td>
<td>494.6 ± 5.2</td>
</tr>
<tr>
<td>Cu-C-7th Week</td>
<td>7</td>
<td>378.8 ± 13.8</td>
</tr>
<tr>
<td>Cu-C-9th Week</td>
<td>5</td>
<td>177.4 ± 1.7</td>
</tr>
<tr>
<td>Cu-C-11th Week</td>
<td>3</td>
<td>105.5 ± 1.0</td>
</tr>
<tr>
<td>Cu-C-14th Week</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Sample was not kept.
Table 7-3. Concentrations of copper detected by AAS in aged 1 M LiPF$_6$/PC:EC:DMC (1:1:3) when 1×1 cm$^2$ Cu-C foils were stored in the electrolyte for up to 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Time Duration (week)</th>
<th>Dry Electrolyte</th>
<th>Electrolyte Doped with 500 ppm H$_2$O</th>
<th>Electrolyte Doped with 1000 ppm HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6 ± 0.3</td>
<td>0.8 ± 0.3</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>2.8 ± 0.3</td>
<td>1.2 ± 0.4</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td>3</td>
<td>33.2 ± 1.0</td>
<td>122.5 ± 3.8</td>
<td>134.9 ± 3.4</td>
</tr>
<tr>
<td>4</td>
<td>119.1 ± 3.8</td>
<td>262.0 ± 9.9</td>
<td>264.1 ± 9.0</td>
</tr>
<tr>
<td>5</td>
<td>191.6 ± 5.8</td>
<td>328.8 ± 10.9</td>
<td>392.1 ± 10.7</td>
</tr>
<tr>
<td>6</td>
<td>280.0 ± 9.1</td>
<td>387.7 ± 11.2</td>
<td>422.4 ± 12.2</td>
</tr>
<tr>
<td>7</td>
<td>356.0 ± 11.1</td>
<td>533.9 ± 17.3$^a$</td>
<td>544.2 ± 15.4$^a$</td>
</tr>
<tr>
<td>8</td>
<td>391.6 ± 13.4</td>
<td>680.9 ± 30.7$^b$</td>
<td>662.5 ± 21.5$^b$</td>
</tr>
</tbody>
</table>

$^a$ Partial graphite exfoliation.

$^b$ Total graphite exfoliation.
Table 7-4. Concentrations of copper detected by AAS in aged 1 M LiPF$_6$/EC:DMC:MEC (1:1:1) when 1×1 cm$^2$ Cu-C foils were stored in the electrolyte for up to 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Time Duration (week)</th>
<th>Concentration (ppm) of Cu (mean ± s.d) (n = 5)</th>
<th>Dry Electrolyte</th>
<th>Electrolyte Doped with 500 ppm H$_2$O</th>
<th>Electrolyte Doped with 1000 ppm HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 ± 0.4</td>
<td>0.6 ± 0.4</td>
<td>0.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.7 ± 0.4</td>
<td>2.6 ± 0.6</td>
<td>5.1 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>39.6 ± 1.0</td>
<td>126.6 ± 6.1</td>
<td>91.2 ± 5.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>186.8 ± 8.6</td>
<td>359.0 ± 17.8</td>
<td>353.9 ± 19.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>287.3 ± 12.4</td>
<td>462.3 ± 24.9</td>
<td>419.7 ± 23.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>293.6 ± 13.9</td>
<td>485.7 ± 25.8</td>
<td>519.7 ± 24.3$^a$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>317.8 ± 13.9</td>
<td>712.0 ± 33.7$^b$</td>
<td>618.7 ± 30.5$^b$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>357.0 ± 17.6</td>
<td>790.5 ± 37.2$^b$</td>
<td>718.2 ± 33.4$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Partial graphite exfoliation.

$^b$ Total graphite exfoliation.
influence on dissolution. In both electrolyte solutions, the dissolution increased rapidly over time in the dry electrolyte solution and the solution doped with impurities. In the dry electrolyte, the copper concentration reached ~ 350 ppm and ~ 400 ppm in electrolyte I and II, respectively, in eight weeks. The effect of the solution impurity was similar in both electrolyte solutions. The effect of H$_2$O was similar to that of HF in each electrolyte as well. Small amounts of impurities (500 ppm H$_2$O and 1000 ppm HF) greatly increased the dissolution tendency in both electrolyte solutions. The dissolution in the electrolyte solutions doped with impurities was about twice as large as that in dry electrolyte solutions.

As compared with uncoated Cu foils in the same “aged” electrolyte solutions, the dissolution of Cu-C foils showed different behavior. In the dry aged electrolyte, as compared with uncoated Cu foils, the dissolution of Cu-C foils commenced at a lower potential and increased more rapidly over time and exceeded that of Cu foils after four weeks. For bare Cu foils, H$_2$O and HF impurities appeared to decrease the dissolution whereas they seemed to accelerate dissolution of the Cu-C foils.

Exfoliation of the graphite coating on Cu-C foils was observed in the electrolyte solutions doped with H$_2$O and HF whereas the coating remained intact in the dry electrolyte solutions. In electrolyte I, partial graphite exfoliation was observed of Cu-C foils stored for seven weeks in electrolyte doped with HF or H$_2$O; total exfoliation was observed for samples stored for eight weeks. In electrolyte II, partial exfoliation of the graphite coating was shown after a Cu-C foil had been stored in
electrolyte doped with HF for six weeks and total exfoliation was shown in samples that had been stored for seven and eight weeks in electrolyte doped with HF or H₂O.

The exfoliation of the graphite coating seemed to relate closely to the amount of copper dissolved in the electrolytes. However, in the resealed Cu-C foil samples (as shown in Table 7-2), which were prepared in the “fresh” electrolyte solution, the graphite coatings remained intact even though they had similar amounts of copper dissolution as compared to those in the “aged” electrolytes. This suggests that the integrity of the Cu-C foils relates closely to the condition of the electrolyte solution. In an effort to scrub off the graphite coating from a Cu-C foil using a blade from a resealed sample was unsuccessful because the coating and copper foil adhered inseparably to each other and the whole foil was more fragile as compared to Cu-C foils stored in the “aged” electrolytes.

The influence of the volume of electrolyte on dissolution of Cu-C foils was also studied as shown in Table 7-5. It can be seen that the calculated total amount of dissolution was nearly the same in each volume of electrolyte, which indicates that the dissolution was independent of the amount of the electrolyte.

From the above AAS results, it can be seen that the stability of Cu-C foils in “fresh” electrolyte is quite different from that in “aged” electrolyte. The dissolution of Cu-C foils exhibited only trace amounts (< 1 ppm) in “fresh” electrolyte as compared with large amounts (≤ 400 ppm) in “aged” electrolytes. Similar to the study of foils in the same “aged” electrolytes, the possible decomposition of electrolyte over time, such
Table 7-5. Concentrations of copper detected by AAS when 1×1 cm$^2$ Cu or Cu-C foils were stored in different volumes of aged electrolytes for 8 weeks. Electrolyte solution was stored in a dry box for 6 months before sample preparation.

<table>
<thead>
<tr>
<th>Electrolyte Volume (mL)</th>
<th>Concentration (ppm) of Cu (mean ± s$_d$) (n = 5)</th>
<th>Total amount of Cu (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples in 1 M LiPF$_6$/PC:EC:DMC (1:1:3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>949.1 ± 25.6</td>
<td>1898 ± 51</td>
</tr>
<tr>
<td>5</td>
<td>391.6 ± 13.4</td>
<td>1958 ± 67</td>
</tr>
<tr>
<td>10</td>
<td>199.2 ± 7.3</td>
<td>1991 ± 73</td>
</tr>
<tr>
<td>15</td>
<td>129.8 ± 3.2</td>
<td>1947 ± 48</td>
</tr>
<tr>
<td>Samples in 1 M LiPF$_6$/EC:DMC:MEC (1:1:1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>945.8 ± 43.3</td>
<td>1892 ± 87</td>
</tr>
<tr>
<td>5</td>
<td>357.0 ± 17.6</td>
<td>1785 ± 88</td>
</tr>
<tr>
<td>10</td>
<td>179.1 ± 8.8</td>
<td>1791 ± 88</td>
</tr>
<tr>
<td>15</td>
<td>131.6 ± 7.6</td>
<td>1974 ± 114</td>
</tr>
</tbody>
</table>
as the chemical reactivity of PF$_5$ and LiPF$_6$ with EC and DMC, as reported by Kinoshita and coworker$^{40}$, could produce oxidizing species, which could be the causative factor of copper dissolution. The results in this work show that the condition of electrolyte is critical to the stability and integrity of the Cu-C foils in the Li-ion battery electrolyte. Possible decomposition products formed during electrolyte storage are detrimental to copper stability and coating integrity in the electrolyte.

7.4 Conclusion

For Cu-C foil, which is the negative electrode in a Li-ion cell, only trace amounts of copper dissolution were found in “fresh” electrolyte. However, atmospheric impurities (H$_2$O, moisture, etc.) had a great impact on the stability of the copper substrate and caused large amounts of dissolution. In “aged” electrolytes, large amounts of dissolution were observed and the small amounts of H$_2$O and HF impurities greatly increased the extent of the dissolution. The dissolution of Cu-C foils in “aged” electrolytes appeared to have a different mechanism from that in “fresh” electrolyte.
Chapter 8 - Surface Analysis of Copper Foil and Graphite-Coated Copper Foil by FTIR Microscopy after Storage in Li-Ion Battery Electrolyte Solutions

8.1 Introduction

In Chapters 6 and 7, the dissolution of Cu foils and Cu-C foils in Li-ion electrolyte solutions was quantitatively evaluated by atomic absorption spectroscopy (AAS). It was found that large amounts of dissolution of both Cu and Cu-C foil occurred in “aged” electrolyte solutions. In order to further study the reaction mechanism of the copper dissolution, surface analysis was performed by FTIR microscopy on foils stored in “aged” electrolyte solutions for different periods of time. FTIR microscopy was used to identify the species formed on the surfaces of the foils during their storage in the electrolyte solutions. Visual microscopy was used to investigate the surface change of the foils during their storage in the electrolyte solutions.

8.2 Experimental Section

8.2.1 Sample Preparation

The samples were prepared by placing 1×1 cm$^2$ Cu foils (9.5 ± 0.1 mg) or 1×1 cm$^2$ Cu-C foils (30.5 ± 0.1 mg) in 5 mL Li-ion battery electrolytes weekly over an eight week period. Two electrolytes were studied: (I) 1 M LiPF$_6$/PC:EC:DMC (1:1:3) and (II) 1 M LiPF$_6$/EC:DMC:MEC (1:1:1); which had been stored in a dry box for six
months before being used in the sample preparation. The details of the sample preparation were described previously in Chapter 6. When the samples were opened for the AAS measurement in the eighth week, the foils were removed from solution and wiped with Kimberly-Clark® Delicate Task Wipers to absorb electrolyte. The foils were immediately vacuum dried overnight in a desiccator and the surface analysis was performed the next day.

8.2.2 Apparatus

The technique used to study the surface of the foils was reflectance FTIR microscopy. The experiments were performed on a Perkin Elmer Spectrum 2000 FTIR Spectrometer, which was interface with an IR microscope (Spectra Tech IR-Plan Infrared Microscope). The IR spectra were collected at room temperature under atmosphere condition, i.e., without gas purging. The spectrum was obtained by ratioing the reflectance of sample foils, which had been stored in the electrolyte solutions for different periods of time, to the reflectance of the corresponding pure foils. The spectra were collected by averaging 256 scans and the spectral resolution was 4 cm$^{-1}$. The visual microscope images were obtained with a digital camera (Nikon Coolpix 880, 3.3 Mega Pixels) from the spots where the IR spectra had been obtained.
8.3 Results and Discussion

8.3.1 FTIR

FTIR reflectance was used to study the composition of the surface film formed on the foils during their storage in the electrolyte solutions. The FTIR spectra of a Cu foil and a Cu-C foil, which were stored in electrolyte I for eight weeks, are shown in Figures 8-1 and 8-2, respectively. The identifications of the major peaks in these spectra are summarized in Tables 8-1 and 8-2, respectively. The comparison of the major peaks in the spectra of Cu foils and Cu-C foils showed that all of the major peaks in both spectra are nearly identical, which indicates that the composition of the species formed on the surfaces of the Cu foil and Cu-C foil in the same electrolyte is the same. Similar results can be drawn for the other electrolyte.

The spectra and the identifications of the major peaks of a Cu foil and a Cu-C foil in electrolyte II are contained in Figures 8-3 and 8-4, and summarized in Tables 8-3 and 8-4, respectively. The comparison of Figure 8-3 and 8-4 showed that the composition of the species formed on the surfaces of Cu and Cu-C foil in electrolyte II is identical.

Comparison of the spectra of the foils in different electrolytes showed that most of the peaks are nearly identical except for one major peak. The spectra of the foils in electrolyte I showed a peak at 1329 cm\(^{-1}\) that the spectra of the foils in electrolyte II did not have. There are also some small peaks below 750 cm\(^{-1}\) that are different between them.
Figure 8-1. FTIR spectrum (reflectance mode) of a Cu foil stored in 1 M LiPF$_6$/EC: DMC:MEC (1:1:1) for eight weeks.

R – Reflectance spectrum from sample.
R$_0$ – Reflectance spectrum from reference.
Table 8-1. Identification of the major IR bands shown in Figure 8-1.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700 ~ 3700</td>
<td>NA</td>
</tr>
<tr>
<td>1801</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>1769</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>1632</td>
<td>$\nu_a$ (ROCO$_2^-$)</td>
</tr>
<tr>
<td>1482</td>
<td>$\nu$ (ROCO$_2^-$)</td>
</tr>
<tr>
<td>1406</td>
<td>NA</td>
</tr>
<tr>
<td>1284</td>
<td>NA</td>
</tr>
<tr>
<td>1050 ~1200, 1143, 1082</td>
<td>NA</td>
</tr>
<tr>
<td>835</td>
<td>NA</td>
</tr>
<tr>
<td>720</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA – Not Assigned  
$\nu_a$ – antisymmetric stretch  
$\nu$ – symmetric stretch  
(1) Band at 2363 results from atmospheric CO$_2$. 
Figure 8-2. FTIR spectrum (reflectance mode) of a Cu-C foil stored in 1 M LiPF$_6$/EC: DMC:MEC (1:1:1) for eight weeks.

R – Reflectance spectrum from sample.
R$_0$ – Reflectance spectrum from reference.
Table 8-2. Identification of the major IR bands shown in Figure 8-2.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700 ~ 3700</td>
<td>NA</td>
</tr>
<tr>
<td>1807</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>1778</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>1635</td>
<td>$\nu_a$ (ROCO$_2^-$)</td>
</tr>
<tr>
<td>1483</td>
<td>$\nu$ (ROCO$_2^-$)</td>
</tr>
<tr>
<td>1403</td>
<td>NA</td>
</tr>
<tr>
<td>1290</td>
<td>NA</td>
</tr>
<tr>
<td>1050 ~ 1200, 1128, 1082</td>
<td>NA</td>
</tr>
<tr>
<td>889</td>
<td>NA</td>
</tr>
<tr>
<td>693</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA – Not Assigned  
$\nu_a$ – antisymmetric stretch  
$\nu$ – symmetric stretch  
(1) Band at 2363 results from atmospheric CO$_2$. 

Figure 8-3. FTIR spectrum (reflectance mode) of a Cu foil stored in 1 M LiPF$_6$/PC: EC:DMC (1:1:3) for eight weeks.

R – Reflectance spectrum from sample.
R$_0$ – Reflectance spectrum from reference.
<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700 ~ 3700</td>
<td>NA</td>
</tr>
<tr>
<td>1800</td>
<td>ν (C=O)</td>
</tr>
<tr>
<td>1771</td>
<td>ν (C=O)</td>
</tr>
<tr>
<td>1635</td>
<td>ν(_a) (ROCO(_2^−))</td>
</tr>
<tr>
<td>1482</td>
<td>ν (ROCO(_2^−))</td>
</tr>
<tr>
<td>1406</td>
<td>NA</td>
</tr>
<tr>
<td>1329</td>
<td>NA</td>
</tr>
<tr>
<td>1286</td>
<td>NA</td>
</tr>
<tr>
<td>1050 ~ 1200, 1147, 1081</td>
<td>NA</td>
</tr>
<tr>
<td>839</td>
<td>NA</td>
</tr>
<tr>
<td>707</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA – Not Assigned

ν\(_a\) – antisymmetric stretch
ν – symmetric stretch
Figure 8-4. FTIR spectrum (reflectance mode) of a Cu-C foil stored in 1 M LiPF₆/PC: EC:DMC (1:1:3) for eight weeks.

R – Reflectance spectrum from sample.
R₀ – Reflectance spectrum from reference
Table 8-4. Identification of the major IR bands shown in Figure 8-4.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700 ~ 3700</td>
<td>NA</td>
</tr>
<tr>
<td>1799</td>
<td>(\nu) (C=O)</td>
</tr>
<tr>
<td>1760</td>
<td>(\nu) (C=O)</td>
</tr>
<tr>
<td>1634</td>
<td>(\nu_a) (ROCO(_2^-))</td>
</tr>
<tr>
<td>1480</td>
<td>(\nu) (ROCO(_2^-))</td>
</tr>
<tr>
<td>1393</td>
<td>NA</td>
</tr>
<tr>
<td>1330</td>
<td>NA</td>
</tr>
<tr>
<td>1290</td>
<td>NA</td>
</tr>
<tr>
<td>1050 ~ 1200, 1171, 1071</td>
<td>NA</td>
</tr>
<tr>
<td>833</td>
<td>NA</td>
</tr>
<tr>
<td>703</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA – Not Assigned
\(\nu_a\) – antisymmetric stretch
\(\nu\) – symmetric stretch
(1) Band at 2363 results from atmospheric CO\(_2\).
The IR spectra of PC, EC, DMC, and DEC were obtained from The Aldrich Library of Infrared Spectra, Edition III as shown in Figures 8-5 to 8-8. The major absorption peaks were identified and summarized in Tables 8-5 to 8-8.

Comparison of the spectra of the foils and those of the solvents showed that the IR spectra were different between the foils and the pure solvents. The carbonyl stretching vibration \([\nu (C=O)]\) in the foil spectra shifted to \(~1800\ \text{cm}^{-1}\) as compared with \(1750\ \text{cm}^{-1}\) in the spectra of the solvents. The peaks at \(1632\ \text{cm}^{-1}\) and \(1482\ \text{cm}^{-1}\), which are shown in all the foil IR spectra, could be ascribed to the antisymmetric stretching vibration \([\nu_a(RO-CO_2^-)]\) and symmetric stretching vibration \([\nu (RO-CO_2^-)]\), respectively, of the \(RO-CO_2^-\) structure unit.\(^{44, 45}\) It indicates that a carboxylic salt exists in the composition of the surface species. The rest of the peaks in the sample spectra are complex and are not ascribed.

From the above FTIR spectra, it can be seen that the functional groups of the solvents appeared in the composition of the species of the surface film formed on the foil surfaces. Kinoshita and coworker reported that the chemical reactivity of PF\(_5\) and LiPF\(_6\) with EC and DMC could result in possible decomposition of the electrolyte.\(^{40}\) Such decomposition of the electrolyte in the “aged” electrolytes might produce oxidizing species, which had the partial fragments of the solvents, and could be the causative factor of the copper dissolution. Hence, the fragments of the solvents appeared in the composition of the surface film as the anion of the copper salt.
Figure 8-5. IR spectrum of propylene carbonate (PC). [from The Aldrich Library of Infrared Spectra, Edition III.]
Table 8-5. Assignments of the IR bands for propylene carbonate (PC) as shown in the IR spectrum of Figure 8-5.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Relative Intensity*</th>
<th>Main Assignments**</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>W</td>
<td>(\nu_a) (C-H)</td>
</tr>
<tr>
<td>2950</td>
<td>W, sh</td>
<td>(\nu_a') (C-H)</td>
</tr>
<tr>
<td>1760</td>
<td>VS</td>
<td>(\nu) (C=O)</td>
</tr>
<tr>
<td>1475</td>
<td>W</td>
<td>(\delta) (C-H)</td>
</tr>
<tr>
<td>1395</td>
<td>M</td>
<td>(\delta') (C-H)</td>
</tr>
<tr>
<td>1350</td>
<td>M</td>
<td>NA</td>
</tr>
<tr>
<td>1180</td>
<td>S</td>
<td>(\tau) (CH(_2))</td>
</tr>
<tr>
<td>1120</td>
<td>S</td>
<td>(\omega) (CH)</td>
</tr>
<tr>
<td>1050</td>
<td>S</td>
<td>(\omega) (CH(_2))</td>
</tr>
<tr>
<td>950</td>
<td>W</td>
<td>(\delta_a) (R)</td>
</tr>
<tr>
<td>860</td>
<td>W</td>
<td>(\delta_s) (R)</td>
</tr>
<tr>
<td>775</td>
<td>M</td>
<td>(\delta) (C=O)</td>
</tr>
<tr>
<td>710</td>
<td>M</td>
<td>(\rho) (CH(_2))</td>
</tr>
</tbody>
</table>

* Relative Intensity Symbols: W = weak, M = medium, S = strong, VS = very strong, sh= shoulder.

** Assignments were performed according to N. P. G. Roeges, in *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, John Wiley & Sons, New York, 1994.

\(\nu_a\) antisymmetric stretch
\(\nu\) symmetric stretch
\(\delta\) in-plane deformation
\(\rho\) rocking vibration
\(\omega\) wagging vibration
Figure 8-6. IR spectrum of ethylene carbonate (EC). [from The Aldrich Library of Infrared Spectra, Edition III.]
Table 8-6. Assignments of the IR bands for ethylene carbonate (EC) as shown in the IR spectrum of Figure 8-6.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Relative Intensity*</th>
<th>Main Assignments**</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>W</td>
<td>(\nu_a) (C-H)</td>
</tr>
<tr>
<td>2950</td>
<td>W</td>
<td>(\nu_a') (C-H)</td>
</tr>
<tr>
<td>1750</td>
<td>VS</td>
<td>(\nu) (C=O)</td>
</tr>
<tr>
<td>1475</td>
<td>M</td>
<td>(\delta) (C-H)</td>
</tr>
<tr>
<td>1395</td>
<td>M</td>
<td>(\delta') (C-H)</td>
</tr>
<tr>
<td>1140</td>
<td>S</td>
<td>(\tau) (CH(_2))</td>
</tr>
<tr>
<td>1060</td>
<td>S</td>
<td>(\omega) (CH(_2))</td>
</tr>
<tr>
<td>970</td>
<td>M</td>
<td>(\delta_a) (R)</td>
</tr>
<tr>
<td>895</td>
<td>W</td>
<td>(\delta_s) (R)</td>
</tr>
<tr>
<td>770</td>
<td>M</td>
<td>(\delta) (C=O)</td>
</tr>
<tr>
<td>715</td>
<td>M</td>
<td>(\rho) (CH(_2))</td>
</tr>
</tbody>
</table>

* Relative Intensity Symbols: W = weak, M = medium, S = strong, VS = very strong, sh= shoulder.

** Assignments were performed according to N. P. G. Roeges, in *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, John Wiley & Sons, New York, 1994.

\(\nu_a\) antisymmetric stretch  
\(\nu\) symmetric stretch  
\(\delta\) in-plane deformation  
\(\rho\) rocking vibration  
\(\omega\) wagging vibration
Figure 8-7. IR spectrum of dimethyl carbonate (DMC). [from The Aldrich Library of Infrared Spectra, Edition III.]
**Table 8-7.** Assignments of the IR bands for dimethyl carbonate (DMC) as shown in the IR spectrum of Figure 8-7.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Relative Intensity*</th>
<th>Main Assignments**</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>W</td>
<td>(\nu_a) (C-H)</td>
</tr>
<tr>
<td>2950</td>
<td>M</td>
<td>(\nu_a') (C-H)</td>
</tr>
<tr>
<td>1750</td>
<td>VS</td>
<td>(\nu) (C=O)</td>
</tr>
<tr>
<td>1450</td>
<td>S</td>
<td>(\delta_a) (C-H)</td>
</tr>
<tr>
<td>1430</td>
<td>M, sh</td>
<td>(\delta_a') (C-H)</td>
</tr>
<tr>
<td>1280</td>
<td>VS</td>
<td>(\nu) [(O=C)-O]</td>
</tr>
<tr>
<td>1200</td>
<td>W, sh</td>
<td>(\rho) (C-H)</td>
</tr>
<tr>
<td>970</td>
<td>S</td>
<td>(\nu) (O-CH(_3))</td>
</tr>
<tr>
<td>910</td>
<td>M</td>
<td>(\nu') (O-CH(_3))</td>
</tr>
<tr>
<td>790</td>
<td>M</td>
<td>(\delta) (C=O)</td>
</tr>
</tbody>
</table>

* Relative Intensity Symbols: W = weak, M = medium, S = strong, VS = very strong, sh= shoulder.

** Assignments were performed according to N. P. G. Roeges, in *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, John Wiley & Sons, New York, 1994.

\(\nu_a\) antisymmetric stretch  
\(\nu\) symmetric stretch  
\(\delta\) in-plane deformation  
\(\rho\) rocking vibration  
\(\omega\) wagging vibration
Figure 8-8. IR spectrum of diethyl carbonate (DEC). [from The Aldrich Library of Infrared Spectra, Edition III.]
Table 8-8. Assignments of the IR bands for diethyl carbonate (DEC) as shown in the IR spectrum of Figure 8-8.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Relative Intensity*</th>
<th>Main Assignments**</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>M</td>
<td>$\nu_a$ (C-H)</td>
</tr>
<tr>
<td>2950</td>
<td>W, sh</td>
<td>$\nu_a'$ (C-H)</td>
</tr>
<tr>
<td>1750</td>
<td>VS</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td>1450</td>
<td>W</td>
<td>$\delta$ (C-H)</td>
</tr>
<tr>
<td>1360</td>
<td>M</td>
<td>NA</td>
</tr>
<tr>
<td>1260</td>
<td>VS</td>
<td>$\nu$ [(O=C)-O]</td>
</tr>
<tr>
<td>1090</td>
<td>W</td>
<td>$\rho'$ (CH$_2$)</td>
</tr>
<tr>
<td>1020</td>
<td>S</td>
<td>$\omega$ (CH$_2$)</td>
</tr>
<tr>
<td>850</td>
<td>M</td>
<td>$\rho$ (CH$_2$)</td>
</tr>
<tr>
<td>790</td>
<td>M</td>
<td>$\delta$ (C=O)</td>
</tr>
</tbody>
</table>

* Relative Intensity Symbols: W = weak, M = medium, S = strong, VS = very strong, sh= shoulder.

** Assignments were performed according to N. P. G. Roeges, in *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, John Wiley & Sons, New York, 1994.

$\nu_a$ antisymmetric stretch
$\nu$ symmetric stretch
$\delta$ in-plane deformation
$\rho$ rocking vibration
$\omega$ wagging vibration
After the IR experiment, the sample foils were left in the air and changed to a characteristic green color of Cu$_2$(OH)$_2$CO$_3$·3H$_2$O from the original gray color in about three weeks. These results suggested that ROCO$_2$Cu formed during storage of the copper foils in the electrolytes.

8.3.2 Microscopy

The visual microscope images (Figure 8-9) of Cu-C foils stored in electrolyte I for up to 8 weeks were obtained with a digital camera attached to the IR microscope right after the IR spectra were measured. The surface of the Cu-C foils became progressively darker over the storage period. The “sparkly” appearance of the fresh graphite had disappeared after the Cu-C foil had been stored for eight weeks. Next, the eight-week sample was bent to ~ 100 degree and then flipped back to 180 degree. Two IR images along the bent line were taken. The sparkly appearance of the graphite could be seen again along the crack of the surface film even though no obvious change could be observed with the unaided eye. This experiment suggested that during storage of the Cu-C foils in electrolyte, a film grew on the surface of the graphite coating over time. Such a film can only deposit on the surface of the graphite even though the graphite coating is porous.

The visual microscope images (Figure 8-10) of Cu foils were also measured. The results showed that the characteristic copper color tarnished to a dark red over time, and dark spots on the foil surface were observed in some of the Cu foils.
Figure 8-9. Visual microscope images of Cu-C foils stored in “aged” 1 M LiPF$_6$/PC: EC:DMC (1:1:3). Picture dimensions are ~ 250 × 300 μm. Eight Weeks A and B are the images along the bent line of the same sample of the image of Eight Weeks.
Figure 8-10. Visual microscope images of Cu foils stored in “aged” 1 M LiPF$_6$/PC: EC:DMC (1:1:3). Picture dimensions are ~ 250 × 300 µm.
8.4 Conclusion

From the visual microscope images, it can be seen that the surfaces of both Cu and Cu-C foils changed during their storage in the electrolytes. It appears that surface films formed on the foils and that they grew thicker over time. The FTIR spectra of the surface films revealed that fragments from solvent decomposition appeared in the composition of the surface film, which consisted of a carboxylic copper salt (ROCO$_2$Cu) and other possible copper salts. Combined with previous findings, the surface film appears to result from a reaction between decomposition products of the electrolytes and the copper substrate.
Chapter 9 - Summary and Future Work

9.1 Summary and Conclusions

Studies of the fundamental electrochemical behavior and stability of the anode materials (battery-grade graphite-coated copper foil) of Lithium-ion batteries in Li-ion battery electrolytes (nonaqueous organic carbonates) were performed in this dissertation.

In Chapter 1, a brief review of the technical aspects of Li-ion cells was given followed by a statement of the motivation of this research.

In Chapters 2 and 3, the intrinsic stability and electrochemical behavior of copper foil electrodes and graphite coated copper foil electrodes were studied in different Li-ion battery electrolyte solutions using various electrochemical techniques in half-cell reactions. Cyclic voltammetry was used to study the oxidation-reduction behavior of copper foil electrodes and graphite-coated copper foil electrodes. The reduction of electrolyte and its effect on the oxidation of the electrodes was also studied. Then, chronocoulometry and controlled-potential electrolysis were used to quantitatively study the dissolution of copper in dry electrolytes and in electrolytes doped with impurities of H₂O or HF.

It was found that copper oxidation occurred at 3.4 V vs. Li, which suggested that copper dissolution would commence if the cell were over-discharged to < 0.5 V for most cathodes. It was also found that the stability of the anode related closely to the composition of the electrolytes and that small amounts of impurities greatly
enhanced the oxidation tendency of copper. As compared with uncoated Cu foils, the 
graphite coating of Cu-C foils greatly influenced the oxidation-reduction behavior of 
the copper substrate. The quantitative dissolution data of the Cu foils and Cu-C foils 
under different polarized potentials provided some guidance in the appropriate battery 
design. These results were published in the Journal of the Electrochemical Society.\textsuperscript{18, 19}

During these studies, the open-circuit voltage (OCV) of the cell was found to 
be a variable value over time. Therefore, detailed studies on the OCV of the cell over 
time were performed as discussed in Chapters 4 and 5. The influence of aging of the 
reference electrode, the surface condition and edge effect of the copper foil, and 
solution impurities on the stability of the OCV were studied. The comparison studies 
using inert materials, such as a glassy carbon electrode, aluminum foil and graphite-
coated aluminum foil, were also performed. Both copper foil and graphite-coated 
copper foil showed a two-step process, in which the OCV first rapidly decreased until 
reaching a minimum, and then gradually increased until reaching a steady state. 
However, the causative factors were different. For the Cu foils, in the first step, 
organic carbonates adsorbed on the surface of the copper foil, which caused a negative 
shift of OCV. Then, the copper was oxidized by impurities until a metal-stable oxide 
film formed on the surface in the second process, which resulted in a positive shift of 
OCV to a meta-steady state. For Cu-C foils, the first step was related to the adsorption 
of carbonates on the graphite coating and the second step was related to a specific 
adsorption of HF by the graphite coating on the surface.

Next, the intrinsic stability of Cu foils and Cu-C foils at open-circuit was
evaluated by atomic absorption spectrometry (AAS) in Chapters 6 and 7. The stability of uncoated Cu foils was different from Cu-C foil in “fresh” electrolyte. For the uncoated Cu foils, there was a small amount of dissolution (~ 50 ppm) in “fresh” electrolyte solution after storage up to 20 weeks, which was suggested to result from oxidation by the trace amounts of impurities in the electrolyte solution. For Cu-C foil, less than 1 ppm copper dissolution was found in the same “fresh” electrolyte, which resulted from the protection provided by the graphite coating. However, atmosphere impurities (O₂, moisture, etc.) influenced similarly both foils, causing a large amount of dissolution in “fresh” electrolyte solution. The stability of both Cu and Cu-C foils in “aged” electrolyte solutions showed similar behavior with large amounts of dissolution occurring. It appeared that possible decomposition products formed during electrolyte storage were detrimental to copper stability. The results in this work showed that the condition of electrolyte is critical to copper stability.

Surface studies of Cu foils and Cu-C foils after storage in electrolytes was performed in Chapter 8 to investigate the species formed on the surface in order to better understand the reaction mechanism. FTIR reflectance and microscopy were used to study the surface change of the foil electrodes. Results showed that a carboxylic copper salt (ROCO₂Cu) and other possible copper salts existed in the surface film.
9.2  Suggestion for Future Research

In order to further investigate the causative factors of the electrochemical instability of the anode materials in Li-ion batteries, detailed study of the interface of the Cu foil electrode and the electrolyte solutions is required to understand the reaction mechanism at the molecular level. Electrochemical impedance spectroscopy (EIS) is an effective way to investigate the interface of the electrode and the electrolyte solution. EIS can provide information to establish the reaction mechanism.\textsuperscript{46} EIS could be used to investigate the interface change of the electrode and the electrolyte over time. Impurity (H\textsubscript{2}O or HF) effects on the interface also can be investigated. EIS experiments can be performed at OCV or under polarized conditions. Through these studies, a deeper understanding of the reaction mechanism would be expected.
References


