Studies of Ionic Liquid Hybrids: Characteristics and Their Potential
Application to Li-ion Batteries and Li-ion Capacitors

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in Materials Science and Engineering.

By

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Ionic liquids (ILs) have attracted much attention in electrochemical energy storage systems for their advantageous properties over traditional lithium salt/carbonate solvent electrolyte in terms of higher electrochemical potential windows, comparable ionic conductivity, negative vapor pressure and non-flammability. Ionic liquids can be used as the solvent-free electrolyte in electrochemical double layer capacitors (EDLCs) or can act as the important additives to the carbonate electrolyte in lithium ion batteries (LIBs). Recently, lithium ion capacitors (LICs) have emerge as a novel energy storage system to satisfy the demands for higher energy density and higher power density in portable and transportation systems. This Master thesis research is focused on three types of imidazolium based ionic liquids and their hybrids for potential applications to EDLCs, LIBs or LICs. The electrochemical characteristics, including ionic conductivities and stability windows of the three pristine ILs and their hybrids with additions of organic solvent diethyl carbonate (DEC), or common lithium ion electrolyte (LiPF₆/EC/DEC) are systematically investigated. The influences of temperature and the volumetric percentage
of the IL additive on their electrochemical behaviors are discussed. Finally, these ionic liquid hybrids were examined in LIB and LIC devices to assess their impacts on energy storage performances.
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Chapter 1: Introduction and Background

‘Green’ energy storage systems can be exploited as effective substitutions of current fossil fuel combustion systems. Solar, wind, hydropower, and geothermal energy have been rapidly developed and utilized. Electrochemical energy storage systems including batteries and supercapacitors play important roles as power supplies for stationery systems and portable electronics. They are very promising as energy storage solution in transportation systems such as electric vehicle (EV) and hybrid electric vehicle (HEV). In HEVs, electrochemical energy storage systems can deliver energy for acceleration and be recharged during braking or driving downhill. Recently, lithium-ion battery (LIB), lithium-ion capacitor (LIC), and electrochemical double layer capacitor (EDLC) are being widely equipped in EVs such as Tesla S-model, Chevrolet Volt, Nissan Leaf, and Mazda i-ELOOP.

1.1 Operating Principles of EDLC, LIB and LIC Systems

Figure 1.1 schematically illustrates the basic components and the operating principles of the three electrochemical energy storages systems, i.e. LIB, LIC, and EDLC. Three parts include the anode, cathode, and electrolyte. When liquid electrolytes are used, separators are necessary for compact device packing. The properties of each material can strongly determine the performances of these systems. The general distinction of the three energy
storage systems is, whether the redox reactions occur on both electrodes under charging or discharging processes [1-5].

Figure 1.1 Sketch of electrochemical energy storages systems: a) In LIB, lithium ions intercalate/dis-intercalate between cathode and anode; b) In EDLC, both cations and anions accumulate at the surface of both anode and cathode after charging; c) In LIC system, lithium ions intercalate into the anode structure and the corresponding anions accumulate on the cathode surface forming a double layer structure upon charging [1-5].
In LIBs, the redox reaction occurs at both the cathode and anode. In the charging process, lithium ions move from cathode to anode passing through electrolyte under the exterior electrical field [6-8]. Meanwhile, electrons move from cathode to anode through the external circuit. The anode material will gain electrons together with lithium ions to form a certain type of lithium intercalating or alloying compound. Alternately, during the discharging process lithium ions and electrons are delivered from anode to cathode. It is noteworthy that anions in the electrolyte will not participate in either the oxidation/reduction reaction or contribute the energy storage during charging and discharging processes.

For the EDLC system, the cations and anions in the electrolyte that accumulate are adsorbed or desorbed on the surface of anode and cathode during charging and discharging, respectively [9-12]. The energy storage is basically the function of static electric accumulation, without reduction/oxidation occurrence. For instance, in the charging process, the cations move to the anode side, while anions moves to cathode side. A double layer (compact and diffusive layer) of charged species form at each electrode/electrolyte interface. During the discharging process, cations and anions desorb from the anode and cathode gradually and restored in the electrolyte.

LIC is a novel concept that has emerged in the past decade [13-17]. In the LIC system, lithium ion come from electrolyte instead of the cathode. Upon charging, lithium ions are forced to intercalate into the structure of anode, and the corresponding anions in electrolyte are forced to move towards the cathode and form a double layer on the surface of the cathode material. During the discharging process, lithium ions are de-intercalated from the
bulk of anode, and the anions are desorbed out of the cathode. In this case, lithium cations and the corresponding anions are restored in the electrolyte.

According to distinctions of the operating principles of the LIB, LIC, and EDLC systems, performances metrics of these systems, such as energy density, power density, and cycle life, vary widely. Of the three energy systems, LIB has the highest specific energy density but lowest power density. EDLC has lowest energy density but highest power density. The cycle life’s ranking of these three energy systems from high to low is EDLC, LIC, and LIB because physical absorption/desorption which leads to less degradation of the electrode materials in EDLC, compared to chemical redox reaction in LIC and LIB.

The novel LIC system is a hybrid of LIB and EDLC. Therefore, LIC’s performance metrics typically fall between those of LIB and EDLC. For instance, in LIC the energy density is significantly higher than EDLC and the power density is larger than LIB. In addition, cycle life of LIC is significant higher than that of LIB. LIC avoid the disadvantages of LIB and EDLC while maintain the benefit of both, and this makes LIC a promising energy storage system in this new green energy era.

1.2 Common Electrode Materials Used in the Three Energy Storage Systems

The electrode is one of the most essential components in LIB, LIC and EDLC systems. The choice and combination of cathode and anode materials can vary in each system.

1.2.1 Carbon based materials

In LIB, LIC or EDLC system, the most widely used electrode materials are carbonaceous material. The most basic carbon is graphite. Graphite has a stack structure of
each carbon monolayer linked by van-der-Waals force with the average distance between the monolayers of approximately 3.35 Å (figure 1.2a, d). The monolayer of carbon atoms are covalently bonded with each other through sp² hybridization forming a hexagonal structure, each layer is referred to as graphene (figure 1.2b). Chemical exfoliation of graphite can introduce various functional groups such as hydroxyl (-OH), carboxyl (-COO-), carbonyl (-CO-), epoxyl groups, which can be partially eliminate but cannot be complete removed. This type of carbon is called graphene oxide or reduced graphene oxide (RGO, figure 1.2c). Because of the oxidation process and the introduction of other functional groups between the monolayers, the average distance in multilayered RGO is typically close to 3.6 Å [18-19].

Carbon-based materials can be obtained through thermal pyrolysis of various carbon-containing compounds. During thermal treatment at different temperature range, carbons form into different structures resulting in soft carbons, hard carbons, and activated carbons etc. Both soft and hard carbons contain of many nano-scale graphite stacks (figure 1.2e, f). Soft carbon has the relatively distorted structure compare to that of pure graphite. Soft carbon can be completely graphitized under high temperature’s (above 2000°C) treatment [20]. In contrast, hard carbon has the most disordered stacked structure and it cannot be completely graphitized through thermal treatment.

Activated carbons (AC) can be obtained from various types of carbonaceous materials such as wood, coal, nutshells and corn grain [21-22]. For example, the precursor materials were treated with steam, carbon dioxide or air under high temperatures around 700 to 1200°C. Typically, the precursor was chemically activated with agents such as potassium hydroxide, phosphoric acid and zinc chloride. Based on the difference of AC’s synthesis,
Figure 1.2 Schematics of various structures of carbons: a) graphite; b) monolayer graphene; c) monolayer reduced graphene oxide; d) pure graphite; e) soft carbon; f) hard carbon; and g) single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [23-25].
the distribution of pore sizes can be micropores (less than 2 nm), mesopores (2 to 50 nm), and macropores (large than 50 nm).

Carbon nanotubes (CNTs), another form of carbons, have one-dimensional cylindrical structure. CNT consisting of one rolled up monolayer graphitic sheet is called single-walled CNT (SWCNT). CNT nanostructure can be rolled up by multiple coaxial rolls of the monolayer carbon, and this type of CNT is called multi-walled CNT (MWCNT).

Because the stacking structure in graphite is weakly bonded by Van der Waals force, lithium ions and other ions can be reversibly intercalated into and out of graphite. Lithium ions can be stored in graphite forming LiC₆ compound which gives a theoretical capacity of 372 mAh/g. Due to the reduced symmetry in soft carbon and hard carbons, the potential amount of lithium ions that can be stored between the layers are reduced. However, lithium ions can be stored in nanopores present in hard carbons leading to high lithium storage capacity.

Graphene is becoming widely used as electrode material because of its advanced 2-D monolayer structure, high carrier mobility, outstanding electrical conductivity, better mechanical properties, and the high specific surface area [26-29]. Cations and anions can be stored on both sides of the monolayer structure during charging. Therefore, the specific gravimetric energy storage capacity is increased significantly. Moreover, the speed of ions and electrons’ transportation is more rapid. Graphene can be mixed with other types of electrode materials to enhance their performances.

ACs have been utilized as electrode material in LIC and EDLC system [30-31] because of their extremely high surface areas (close to 3000 m²/g) and their unique porous structure. It was found that appropriate pore size distribution in AC is a key important
parameter for the effective utilization of the electrode materials. Because ions in electrolyte have different sizes, the wide range of pore sizes in ACs can adapt to the various size of the ions migrating into/from pores smoothly during charge and discharge. To ensure better pore size distribution and the uniform microstructure, polymers such as polyacrylonitrile (PAN), polyvinyl chloride and polypyrrole (PP) are usually used as precursor in AC synthesis.

The CNTs are widely studied as electrode materials because of their unique pore structure, improved electrical properties, as well as their extraordinary mechanical and thermal stability. For instance, CNT has been applied as the LIB anode, which result in a high capacity, up to 600 mAh/g. The CNTs can be coated with other metal or transition metal oxide to increase lithium storage capacities for LIB or LIC. Tsai et al coated MWCNT with tin dioxide (SnO₂) and Cu, which was implemented as anode of the LIC. The capacitance of the anode is more than 450 F/g under the current density 0.3 A/g, and the Coulombic efficiency was approximately 100% after 200 cycles [32]. Compared with the AC electrode material, the CNT’s surface area is relatively smaller, less than 500 m²/g. The lower surface area cause the lower energy density in EDLC, and LIC systems. The higher electrical conductivity and open porosity structure allow for fast ion transport, providing a relatively high power density in the EDLC and LIC systems utilizing CNTs.

1.2.2 Lithium transition metal oxides

Lithium metal oxide cathodes most commonly used in LIB system, include the layer-structured lithium cobalt oxide (LiCoO₂) in which Co can be partially or completely
replaced with Ni, Mn etc.; spinel structured lithium manganese oxide (LiMn$_2$O$_4$), and olivine structured lithium iron phosphate (LiFePO$_4$) [33-34].

![Crystal structure of LiCoO$_2$: the red, blue and white balls represent the oxygen, cobalt and lithium atoms, respectively.](image1.png)

**Figure 1.3 a)** Crystal structure of LiCoO$_2$: the red, blue and white balls represent the oxygen, cobalt and lithium atoms, respectively; **b)** Crystal structure of LiMn$_2$O$_4$: the red, green and pink balls represent the oxygen, manganese, and lithium atoms, respectively; **c)** Crystal structure of LiFePO$_4$: the red, pink, yellow and white balls represent the oxygen, sulfur, iron and lithium atoms, respectively [35-36].

LiCoO$_2$ was used as the cathode material in the first commercial lithium ion battery produced by Sony Company in 1990. Because of its high energy density, this material is still in use today. The crystal structure of LiCoO$_2$ is exhibited in **figure 1.3a**. Cobalt and oxygen atoms link together to form an octahedral structure where cobalt atom is in the center of the octahedron surrounded by oxygen atoms. Each octahedron joins with another by sharing the edge then arranged into a layered structure. Lithium ions are bonded between these layers. During discharge and charge processes, lithium ions can be intercalated or removed between the layers. However, the crystal lattice can be affected easily under high electrochemical potential window.

Because of some crucial drawbacks of LiCoO$_2$ such as toxicity, relatively high cost of synthesis, and instability of its crystal structure, LiMn$_2$O$_4$ has been introduced. LiMn$_2$O$_4$ has a spinel crystal structure (**figure 1.3b**) in which lithium and manganese ions occupy
the center of the tetrahedral and octahedral sites, and oxygen atoms maintain the frame of the tetrahedral and octahedral structures. The MnO$_6$ octahedrons connect each other by edge sharing, and connect with LiO$_4$ tetrahedral by sharing corners. LiMn$_2$O$_4$ has a lower overall capacity around 105 mAh/g. When the temperature increases the spinel structured cathode will be distort causing significant capacity loss.

The LiFePO$_4$ is the most favorite and promising cathode material in LIB system, since Fe is less expensive and less toxic alternative to elements such as Co, Ni, or Mn used in other lithium metal oxide compound. The crystal structure is shown in figure 1.3c, in which the oxygen atoms bond with the iron to form FeO$_6$ octahedron, and the oxygen atoms bond with the phosphorous to constitute a PO$_4$ tetrahedron [36]. Tetrahedral and octahedral structures link by sharing edges, and none of two PO$_4$ tetrahedral structure touch each other. Lithium ions can be stored between the wavelike pathways, and can be inserted or extracted reversibly. The atoms’ arrangement in this olivine structure can hardly be changed during lithium ions’ intercalation or dis-intercalation even under the higher potential (around 3.5V vs Li/Li$^+$). LiFePO$_4$ has a relatively higher specific capacity of 170 mAh/g. Because of the limited way in which the lithium ions can move through this cathode, the diffusion process of the lithium ions is somewhat restrained. The major drawback of this materials is its low electronic conductivity of LiFePO$_4$ which is contributed to the semiconductor’s properties of LiFePO$_4$ with a bandgap of 0.3eV.

1.2.3 Exemplary applications of the electrode materials

For the EDLC, carbon based materials including activated carbon, graphene, graphite or reduced graphene oxide nanosheets have been utilized as both anode and cathode
materials. In LIB system the carbon based materials are often used as anode materials, and the LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$ are utilized as cathode materials. LIC systems have both symmetric and asymmetric styles [37]. The LIC in which the cathode and anode are made by the same material is referred to as a symmetric LIC; while the LIC whose cathode and anode are made by different materials is called an asymmetric LIC. In the symmetric LIC systems, CNT, graphite and graphene are usually used as electrode material. In the asymmetric LIC system, the anode of the LIC could be Li$_4$Ti$_5$O$_{12}$, TiO$_2$ or CNT and the corresponding cathode would be AC or MnO$_2$ coated CNT. However, both of symmetric and asymmetric LIC system’s anode should be pre-lithiated. The pre-doped lithium ions in the structure of anode materials is necessary to maintain the potential difference between cathode and anode. On the other hand, large amounts of lithium ions would be consumed during the formation of solid electrolyte interphase (SEI) layer at the interface of electrolyte and anode, so the pre-lithiated processes provide sufficient lithium ions to the system.

Some examples of the electrode improvements for commercial electric vehicles are as follows. In the Tesla Model S, thousands of cylindrical 18650 lithium ion batteries are installed in the frame of the car [38-41]. The Tesla Company primarily uses the porous graphite based materials which are doped with silicon as the anode to improve the performance of the energy supplying system. Specially, because the SEI layer is thinner and more uniform, the silicon doped graphite anode effectively reduces the irreversible capacity of the batteries during the initial discharge process. The cathode material in the S-model’s battery contains 80% Nickel, 15% Cobalt and 5% Aluminum in its layered structure. Both ionic and covalent bonds warrant the higher stability of the cathode during charging and discharging processes. For Chevrolet Volt, lithium ion battery consists of a
carbon based anode and manganese based cathode [42-43]. The unique energy control system avoid the effect of overcharge and overdischarge. A protective polymer material covers the surface of the battery system which can cool the system and avoid the gas permeation effectively. Lithium ion battery in the Nissan Leaf is made up of lithium nickel oxide doped with manganese cathode and graphite based anode [44-46]. The electrode materials are packed in a laminate structure to protect the batteries from vibration and to save space in the vehicle. The Nissan Leaf can run up to 84 miles on a single charge. The Mazda Company employ an EDLC system to collect the electrical energy in their hybrid vehicle because the EDLC can be charged rapidly, and the lifetime of EDLC system is much longer than the LIB and LIC [47-48]. The primary function of EDLC system in Mazda vehicles is to supply the energy for climate control, audio systems and other electrical system components.

1.3 Electrolytes in LIB, LIC, EDLC systems

Most electrolytes used in LIB, LIC and EDLC are liquid based. The electrolyte can be solid such as a ceramic and polymer in LIB system. A few researchers have explored polymer electrolyte in LIC system.

1.3.1 Ceramic based electrolyte

Batteries made with ceramic electrolyte can be operated in high temperature environments without safety concerns as well as some rigid working environments where the vibration and impact are inevitable [49]. The ceramic electrolytes include lithium oxide such as $\text{Li}_6\text{La}_2\text{CaTa}_2\text{O}_{12}$, $\text{Li}_6\text{La}_2\text{ANb}_2\text{O}_{12}$ or $\text{Li}_6\text{La}_2\text{CaTa}_2\text{O}_{12}$, lithium sulfides such as
Li$_{4.2}$Ge$_{0.8}$Ga$_{0.2}$O$_4$, Li$_{2.2}$Zn$_{0.1}$Zr$_{1.9}$S$_3$ and Li$_2$S – P$_2$S$_5$, and lithium phosphates like Li$_6$Ti$_{0.5}$Zr$_{1.5}$(PO$_4$)$_3$, and Li$_6$Fe(PO$_4$)$_3$. Regardless of the type of ceramic electrolyte, lithium ion will conduct through the defects and the vacancies in the crystal lattice. The most obvious disadvantage of the ceramic electrolytes is their low ionic conductivities which are mostly 2-5 orders of magnitude lower than liquid electrolytes.

1.3.2 Polymer based electrolyte

Most polymer based electrolytes consist of lithium salt such as lithium tetrafluoroborate (LiBF$_4$), lithium hexafluorophosphate (LiPF$_6$) and lithium perchlorate (LiClO$_4$), and high molecular weight polymer host like poly(ethylene oxide) (PEO) [50-51]. A Polymer electrolyte is more flexible than ceramic, suitable for application in flexible and conformal LIB. The lithium salt dissolved in the polymer host acts a conduction component and the ion conduction mechanism is significantly different from the ceramic one. Above the glass transition temperature of the polymer, the movement of segments of the polymer chains cause the movement of lithium ions.

Considerable efforts for improving performances of polymer electrolytes have been done, from mixing two or more different types of polymers, adding plasticizers such as ethylene carbonate (EC), diethyl carbonate (DEC), or doping with ceramic nanoparticles. For example, adding nano lithium aluminate powder (LiAlO$_2$) into the poly vinylidene fluoride-co-hexafluoro propylene (PVDF-co-HFP) increased the conductivity up to 0.515 S/m, five times which of the average value of polymer based electrolyte at room temperature. Liao and coworkers replaced the traditional liquid electrolyte by the cross linked copolymer electrolyte, and the electrochemical potential increased to 5.3V [52].
battery cycle life is significantly enhanced with more than 90% of the initial capacity after 150 cycles at 55 °C comparing to the liquid electrolyte cell just has 25% retention.

1.3.3 Liquid electrolyte

Normally liquid electrolytes used for LIB and LIC are made up of lithium salt and aprotic solvents. Li salts vary from LiBF$_4$, LiPF$_6$, lithium bis(trifluoromethane)sulfonimide (LiTFSI), to lithium tris (pentafluoroethane) trifluorophosphate (LiFAP). The aprotic solvent can be a blend of EC, DEC and/or dimethyl carbonate (DMC) under different molar or volumetric ratios for the improvement of the dielectric constant and viscosity. The ionic conductivity of the liquid electrolyte could exceed 1 S/m at room temperatures. However, the positive vapor pressure, low thermal stability and low electrochemical window restrict the traditional liquid electrolytes from applications at high temperature and high voltages.

1.3.4 Ionic liquid:

Ionic liquid (IL) are a compounds composed of large organic cation and certain types of small anion. In general, room temperature ionic liquids (RTILs) refer to the organic salts whose melting points are below 100°C. Table 1.1 lists several RTILs commonly used in LIB, LIC and EDLC. Based on their different kinds of cation, the ionic liquid can be classified as ammonium, pyridinium, isoquinolinium, imidazolium and pyrrolidinium bases [53]. The most prevailing types of RTILs which have been used in the battery and capacitor are the pyrrolidinium and imidazolium based IL. RTILs are a promising and attractive electrolyte alternative for EDLC, LIC, and LIB because of their lower flammability, high electrochemical stability, relatively higher ionic conductivity.
Table 1.1 Cations and anions’ chemical structures in some ionic liquids commonly used in LIB, LIC, and EDLC. a) EMIM$^+$: 1-ethyl-3-methylimidazolium; b) BMIM$^+$: 1-butyl-3-methylimidazolium; c) C$_8$MIM$^+$: 1-methyl-3-octylimidazolium; d) P$_{13}^+$: N-methyl-N-propylpyrrolidinium; e) P$_{14}^+$: N-butyl-N-methylpyrrolidinium; f) C$_{10}$MIM$^+$: 1-decyl-3-methylimidazolium; g) BF$_4^-$: tetrafluoroborate; h) PF$_6^-$: hexafluorophosphate; i) TFSI$^-$: Bis(trifluoromethanesulfonyl) imide; j) OTF$^-$: trifluoromethanesulfonate; k) TA$^-$: trifluoroacetate; l) BETI$^-$: Bis(perfluoroethylsulfonyl)imide [55-59].

<table>
<thead>
<tr>
<th>a.</th>
<th>b.</th>
<th>c.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Chemical Structure" /></td>
<td><img src="image2.png" alt="Chemical Structure" /></td>
<td><img src="image3.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>d.</td>
<td>e.</td>
<td>f.</td>
</tr>
<tr>
<td><img src="image4.png" alt="Chemical Structure" /></td>
<td><img src="image5.png" alt="Chemical Structure" /></td>
<td><img src="image6.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>g.</td>
<td>h.</td>
<td>i.</td>
</tr>
<tr>
<td><img src="image7.png" alt="Chemical Structure" /></td>
<td><img src="image8.png" alt="Chemical Structure" /></td>
<td><img src="image9.png" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>j.</td>
<td>k.</td>
<td>l.</td>
</tr>
<tr>
<td><img src="image10.png" alt="Chemical Structure" /></td>
<td><img src="image11.png" alt="Chemical Structure" /></td>
<td><img src="image12.png" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
Crucial parameters for ionic liquids are density, melting temperature, glass transition temperature, thermal deposition temperature, and ionic conductivity. These factors usually are dependent on molar weight of anion, the length of alkyl chain on cation, the size of anion, or the symmetricity of anion. Brennecke et al illustrated that the density of ionic liquid decreases with increasing working temperature, increasing alkyl substituted chain length on the cation, and decreasing of molecular weight of anion [54].

1.3.4.1 Pyrrolidinium based cations

Pyrrolidinium is a cation formed by bonding substitutional groups onto the nitrogen ring of the pyrrolidien, whose chemical structure has a saturated heterocycle structure with the nitrogen bonded to one hydrogen and two adjacent carbon atoms (figure 1.4a) [60]. The hydrogen atom can be protonated and substituted by alkyl groups of different lengths at the same time (see figure 1.4b). Some pyrrolidinium based ionic liquids are exhibited in figure 1.4 (c and d).

1.3.4.2 Imidazolium based cations:

The imidazolium based cation originate from imidazole. In imidazole, two nitrogen atoms are presented in pentagonal structure with one forming double covalent bonds with the adjacent carbon, while the other bonding with one hydrogen atom and two adjacent carbon atoms (figure 1.5a) [61]. The hydrogen atom is substituted by alkyl group, and the other nitrogen is protonated or substituted by another alkyl group resulting in the imidazolium based cations (figure 1.5b). Some normal imidazolium based ionic liquid
which are usually utilized in LIB, LIC and EDLC systems are showed in figure 1.5c and d.

**Figure 1.4** Chemical structures of a) Pyrrolidine; b) Pyrrolidinium cation in which $R^1$ and $R^2$ represent functional groups; c) 1-Ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; d) 1-Ethyl-1-methyl pyrrolidinium bromide [60].

**Figure 1.5** Chemical structures of a) Imidazole; b) Imidazolium cations, and $R$ and $R'$ represent functional groups; c) 1-Ethyl-2, 3-dimethylimidazolium hexafluorophosphate; d) 1-Hexyl-3-methylimidazolium trifluoromethansulfonate [61].
1.4 Objective of this Research and the Thesis Overview:

Because of the development of hybrid electric vehicle (HEV) and electric vehicle (EV), the demand for high performance batteries or supercapacitors is increasing significantly. Generally, the performances of the power devices highly depend on the properties of electrode and electrolyte materials. RTILs are a promising and attractive electrolyte in EDLC, LIC, and LIB because of their low flammability, high electrochemical stability, and acceptable ionic conductivity. This research is focused on the characterizations of three imidazolium based ionic liquid (same cation but different anions) and their hybrids, as well as an assessment of their potential applications in LIBs and LICs.

In Chapter 2, the general definitions of the dynamic viscosity and ionic conductivity of ILs are briefly addressed. In addition, the characteristics of various ionic liquids based electrolytes reported by other researchers are reviewed and some results are presented.

In Chapter 3, results of characterizing the selected ILs conductivities as a function of temperature are discussed. Further, the ILs were blended with DEC as well as LiPF₆/EC/DEC electrolyte, and the solutions conductivities as a function of the volumetric percentage were studied at room temperature. Moreover, electrochemical stability potentials of the neat ILs and their hybrids are investigated.

Finally, the ionic liquid hybrids were assessed in the LIB and LIC devices. RGO, prepared by Hummer’s method, were used as the electrodes in the test half-cell. The impacts of the IL hybrids on lithium storage capacity, specific capacitance, and energy density as well as Coulombic efficiency are analyzed. These results are presented in Chapter 4.

Chapter 5 summarizes the results throughout this research.
Chapter 2: Review of ILs for Applications to Energy Storage

2.1 Viscosity

Viscosity, one of the most important property of liquids, quantifies the resistance to gradual deformation under tensile or shear stress [62]. Under Newton’s law, dynamic viscosity $\mu$ (sometimes denoted by $\eta$) can be determined by the shear force $F$, velocity $u$, geometrical spacing parameters such as area $A$ and distance $y$, in which $F/A$ is the shear stress and $du/dy$ is referred to as the rate of shear deformation or shear rate (equation 2-1) [62]. Sometimes, liquids exhibit non-Newton’s behaviors which can be categorized by Shear-thickening, Shear-thinning, Thixotropic, Rheopectic liquids (figure 2.1).

The factors which can directly alter the dynamic viscosity include temperature, pressure, and composition of the solution. The dynamic viscosity as a function of temperature is shown in equation 2-2 [62], in which the coefficients $A$ and $B$ are determined empirically and directly related to the liquid substances. It is clear that the logarithm dynamic viscosities have linear relations (see figure 2.2) with the reciprocal of the absolute temperatures. The $A$ and $B$ values of different types of organic liquid were calculated by Duhne as presented in table 2.1.

\[
\mu = \frac{Fy}{Au} = \frac{\text{shear stress}}{\text{shear rate}} \quad (2-1).
\]

\[
\eta = A \exp(B/T) \quad \text{or} \quad \log(\eta) = \log A + \frac{B}{T} \quad (2-2)
\]
Figure 2.1 Schematics showing the variation of shearing stress changes with the shearing strain, illustrating different behaviors of liquids like Newtonian, Shear-thickening, Shear-thinning and Bingham plastic etc. [62].

Figure 2.2 Plots of log $\eta$ as a function of 1/T of different liquids: (I) acetone, (II) n-octane, (III) toluene, (IV) acetic anhydride, (V) pyridine, (VI) carbon tetrachloride, (VII) bromobenzene, (VIII) dioxane, (IX) isopropyl alcohol, (X) nitrobenzene, (XI) n-valeric acid, (XII) m-toluidine, (XIII) quinoline, (XIV) o-toluidine, and (XV) amyl alcohol [63].
Table 2.1: The coefficients A and B are calculated by Duhne for different liquids, and the calculation was dependent on the experimental data of dynamic viscosity and testing temperature [63].

<table>
<thead>
<tr>
<th>Formula</th>
<th>Substance</th>
<th>A</th>
<th>B</th>
<th>Temperature Range, °C</th>
<th>η, cP (at, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{19}H\textsubscript{38}</td>
<td>1 - Nono decene</td>
<td>-5.044</td>
<td>1944.0</td>
<td>25 to 125</td>
<td>4.56 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{19}H\textsubscript{38}</td>
<td>n - Tri decyl cyclohexane</td>
<td>-5.904</td>
<td>2357.0</td>
<td>20 to 120</td>
<td>7.67 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{19}H\textsubscript{38}</td>
<td>Tetra decyl cyclohexane</td>
<td>-5.328</td>
<td>2129.0</td>
<td>10 to 120</td>
<td>6.29 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{19}H\textsubscript{40}</td>
<td>n - Nona decane</td>
<td>-4.643</td>
<td>1827.0</td>
<td>35 to 300</td>
<td>4.00 (35.0)</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{34}</td>
<td>Tetra decyl benzene</td>
<td>-5.345</td>
<td>2147.0</td>
<td>15 to 160</td>
<td>6.60 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{30}</td>
<td>1 - Eicosene</td>
<td>-5.033</td>
<td>1982.0</td>
<td>35 to 125</td>
<td>4.20 (35.0)</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{40}</td>
<td>Tetra decyl cyclohexane</td>
<td>-5.998</td>
<td>2428.0</td>
<td>25 to 120</td>
<td>9.00 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{40}</td>
<td>Penta decyl cyclohexane</td>
<td>-5.387</td>
<td>2189.0</td>
<td>20 to 120</td>
<td>7.30 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{32}</td>
<td>n - Eicosane</td>
<td>-4.651</td>
<td>1868.0</td>
<td>40 to 300</td>
<td>4.14 (40.0)</td>
</tr>
<tr>
<td>C\textsubscript{21}H\textsubscript{36}</td>
<td>n - Pentyl decylbenzene</td>
<td>-5.416</td>
<td>2206.0</td>
<td>20 to 160</td>
<td>7.72 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{21}H\textsubscript{32}</td>
<td>n - Pentyl decyl cyclohexane</td>
<td>-6.078</td>
<td>2493.0</td>
<td>30 to 120</td>
<td>8.91 (30.0)</td>
</tr>
<tr>
<td>C\textsubscript{21}H\textsubscript{32}</td>
<td>Hedecyl cyclohexane</td>
<td>-5.459</td>
<td>2251.0</td>
<td>25 to 120</td>
<td>8.44 (25.0)</td>
</tr>
<tr>
<td>C\textsubscript{22}H\textsubscript{38}</td>
<td>Hexadecyl benzene</td>
<td>-5.428</td>
<td>2245.0</td>
<td>30 to 160</td>
<td>7.74 (30.0)</td>
</tr>
<tr>
<td>C\textsubscript{22}H\textsubscript{44}</td>
<td>n-Hexadecyl cyclohexane</td>
<td>-6.169</td>
<td>2560.0</td>
<td>35 to 120</td>
<td>8.76 (35.0)</td>
</tr>
</tbody>
</table>

Eyring and the coworkers have developed equation 2.3 in consideration that the viscous flow is caused by the certain reaction with an activated action to cross over the potential barrier (ΔF\textsuperscript{*}) [63]. In the equation, N, h, V, R, and T represented the Avogadro’s number, Planck’s constant, molar volume of the liquid, universal gas constant and absolute temperature, respectively. Specially, the parameter ΔF\textsuperscript{*} denotes the molar free activation energy in this equation.

\[
\eta = \frac{Nh}{V} \exp\left(\frac{\Delta F^*}{RT}\right) \quad (2.3).
\]
In order to better fit with experimental results of various liquids, and to obtain more precise values of parameter, equation 2-4 [63] was introduced by Vogel, in which A, B, and C represents the different parameters. To assure the characteristics of these experimental parameters, Dutt and Prasad calculated the values of A, B, and C based on experimental data of different substances, and the conclusion is displayed in table 2.2.

The above linear relation between the reciprocal temperature and logarithmic dynamic viscosity was found to be applicable restricted within certain temperature ranges. At every low and high temperatures, such as close to freezing or boiling points, the linear relation is no longer appropriate. To overcome the temperature confinement, Goletz and Tassios introduced a correcting coefficient to the parameter C as $C = 239 - 0.19T_B$, where $T_B$ is the liquid’s boiling temperature in Kelvin, however the $t$ is the testing temperature in Celsius (equation 2-5) [63].

\[
\eta = A \exp\left(-\frac{B}{C-T}\right) \quad \text{or} \quad \log(\eta) = \log(A) + \frac{B}{T-C} \hspace{0.5cm} (2-4).
\]

\[
\log(\eta) = \log(A) + \frac{B}{239 - 0.19T_B + t} \hspace{0.5cm} (2-5).
\]

There are some other forms to express the relationship between viscosity and temperature introduced by Girifalco (equation 2-6) and Thorpe (equation 2-7). The respective values of the coefficients were calculated and showed in Table 2.3 and Table 2.4 based on experimental data [63].

\[
\log(\eta) = A + \left(\frac{B}{T}\right) + \left(\frac{C}{T^2}\right) \hspace{0.5cm} (2-6).
\]

\[
\log(\eta) = \frac{C}{1 + (\alpha T) + (\beta T^2)} \hspace{0.5cm} (2-7).
\]
Table 2.2 The A, B, and C coefficients of various kinds of liquid were calculate based on equation 2-4 and the experimental data of Dutt. and Prasad [63].

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Temp. Range, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamide</td>
<td>C₂H₃NO</td>
<td>-4.6341</td>
<td>-422.90</td>
<td>149.84</td>
<td>360 to 500</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>C₄H₆O₃</td>
<td>-4.5804</td>
<td>-374.60</td>
<td>49.411</td>
<td>270 to 410</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>-4.6125</td>
<td>-298.48</td>
<td>26.203</td>
<td>180 to 320</td>
</tr>
<tr>
<td>Aceto nitrile</td>
<td>C₂H₅N</td>
<td>-4.8242</td>
<td>-430.37</td>
<td>13.170</td>
<td>280 to 360</td>
</tr>
<tr>
<td>Aceto phenone</td>
<td>C₃H₅O</td>
<td>-4.6251</td>
<td>-468.30</td>
<td>45.007</td>
<td>370 to 480</td>
</tr>
<tr>
<td>Acetyl chloride</td>
<td>C₂H₅ClO</td>
<td>-4.7447</td>
<td>-407.10</td>
<td>12.418</td>
<td>290 to 330</td>
</tr>
<tr>
<td>Allyl ether</td>
<td>C₄H₈O</td>
<td>-5.5716</td>
<td>-938.43</td>
<td>-130.23</td>
<td>290 to 360</td>
</tr>
<tr>
<td>Allyl iodide</td>
<td>C₃H₅I</td>
<td>-4.5436</td>
<td>-410.42</td>
<td>2.0868</td>
<td>270 to 380</td>
</tr>
<tr>
<td>Aluminum bromide</td>
<td>AlBr₃</td>
<td>-4.2262</td>
<td>-493.82</td>
<td>64.743</td>
<td>370 to 530</td>
</tr>
</tbody>
</table>

Table 2.3 The A, B, and C coefficients of various kinds of liquid were calculate based on equation 2-6 and the experimental data of Girifalco [63].

<table>
<thead>
<tr>
<th>Liquid</th>
<th>A</th>
<th>B x 10⁻²</th>
<th>C x 10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>-3.521</td>
<td>15.965</td>
<td>-15.759</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.7008</td>
<td>-13.287</td>
<td>38.52</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>-1.323</td>
<td>2.205</td>
<td>6.589</td>
</tr>
<tr>
<td>n-Butyl alcohol</td>
<td>-2.878</td>
<td>9.615</td>
<td>0.5588</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>-1.059</td>
<td>0.09764</td>
<td>5.871</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>-2.459</td>
<td>7.807</td>
<td>-1.145</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>-0.4312</td>
<td>-5.860</td>
<td>32.036</td>
</tr>
<tr>
<td>Formic acid</td>
<td>-0.9759</td>
<td>-0.7629</td>
<td>12.819</td>
</tr>
<tr>
<td>Glycerine</td>
<td>10.873</td>
<td>-72.23</td>
<td>145.78</td>
</tr>
<tr>
<td>n-Propyl alcohol</td>
<td>9.259</td>
<td>3.353</td>
<td>-1.875</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>-1.567</td>
<td>2.750</td>
<td>3.428</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>-0.09771</td>
<td>-4.690</td>
<td>26.37</td>
</tr>
<tr>
<td>Water</td>
<td>-0.3908</td>
<td>-6.8992</td>
<td>23.611</td>
</tr>
</tbody>
</table>
Table 2.4 The C, α, and β coefficients of various kinds’ liquid calculate based on equation 2-7 and experimental data [63].

<table>
<thead>
<tr>
<th>Substance</th>
<th>α</th>
<th>β x 10^4</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>0.00963</td>
<td>0.2953</td>
<td>0.002671</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.01826</td>
<td>0.8537</td>
<td>0.016867</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>0.01735</td>
<td>0.6122</td>
<td>0.012416</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.01064</td>
<td>0.3115</td>
<td>0.003949</td>
</tr>
<tr>
<td>Allyl bromide</td>
<td>0.01177</td>
<td>0.2871</td>
<td>0.006190</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>0.01111</td>
<td>0.2629</td>
<td>0.004059</td>
</tr>
<tr>
<td>Allyl iodide</td>
<td>0.01316</td>
<td>0.3361</td>
<td>0.009296</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>0.01801</td>
<td>0.6181</td>
<td>0.009296</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>0.02109</td>
<td>1.1073</td>
<td>0.022747</td>
</tr>
<tr>
<td>iso- Butyric acid</td>
<td>0.01917</td>
<td>0.9215</td>
<td>0.018872</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.00820</td>
<td>0.1302</td>
<td>0.004294</td>
</tr>
<tr>
<td>Carbon teta chloride</td>
<td>0.01801</td>
<td>0.6747</td>
<td>0.013466</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.01149</td>
<td>0.2588</td>
<td>0.007006</td>
</tr>
</tbody>
</table>

2.2 Ionic Conductivity

Ionic conductivity of an electrolyte has direct relation to ions’ mobility $u_i$ (see equation 2-8), where $\sigma$, $n$, $q$, and $\mu$ denote the conductivity, number of conductive particles, the charge of the conductive ion and the mobility of conductive ions, respectively [64]. The mobility is related with the diffusion coefficient of ions based on the Stokes-Einstein equation $D/kT$ (see equation 2-9) [64], where $D$, $k$ and $T$ are the diffusion coefficient, Boltzmann constant, and the temperature in Kelvin respectively. The diffusion coefficient $D$ is a function of dynamic viscosity $\eta$ and diameter of moving particles $r$, as expressed in equation 2-10 [64].

$$\sigma = ne\mu \quad (2-8).$$

$$\mu \text{ (mobility)} = D/kT \quad (2-9).$$

$$D = kT/6\pi\eta r \quad (2-10).$$
Ionic conductivity is also a temperature dependent parameter. The conductivity as a function of temperature can be expressed by Arrhenius equation (see equation 2-11) or Vogel-Fulcher-Tammann (VFT) equation (see equation 2-12) [65]. In both equations, $A$ is a parameter which can be regarded as maximum conductivity under an infinitely high temperature. $E_k$, $R$ and $T$ represent the activation energy, gas constant and temperature in Kelvin. In the VTF function, the coefficient $C$ represents a physical parameter. And sometimes it denotes the glass transition temperature of an ionic liquid.

$$\sigma = A \exp \left[ - \frac{E_k}{RT} \right] \quad (2-11).$$

$$\sigma = A \exp \left[ - \frac{E_k}{R(T-C)} \right] \quad (2-12).$$

### 2.3 Walden’s Rule

In 1906, P. Walden introduced his empirical discovery showing the general relationship between ionic conductivity and dynamic viscosity of liquid (see equation 2-13) [66]. It states that the product of molar conductivity $\Lambda_m^0$ and dynamic viscosity $\eta$ is constant, in which $\Lambda_m^0$ (S·m$^2$/mol) can be calculated based on $\Lambda_m^0 = \sigma M / \rho$, where $\sigma$, $M$, and $\rho$ denote the conductivity (S/m), molar weight (g/mol) and the density (g/m$^3$) of the liquid.

$$\Lambda_m^0 \eta = C(\text{constant}) \quad \text{or} \quad \text{Log} \Lambda_m^0 = \text{Log} C \ (\text{constant}) + \text{Log} \eta^{-1} \quad (2-13).$$

Accordingly, when the values of logarithmic viscosity are plotted as a function of logarithmic molar conductivity, a linear relationship is found independent of liquids. Walden Rule has been successfully applied to the diluted or aqueous liquids.
Based on the experimental data, the Walden Rule is found to be applicable to the non-aqueous ionic liquids (see figure 2.3). However, there is significant difference between non-aqueous ionic liquid and aqueous solution. In the latter case, inorganic salt dissolved in water can be totally dissociated into cations and anions, resulting in high iconic conductivity. In contrast, ionic liquid’s cations and anions cannot be completely separated to contribute fully to the conductivity. Seen in figure 2.3, it is clearly that the Walden plots of potassium chloride (KCl)’s aqueous solution pass through the origin of the coordinate. But many different types of ionic liquids’ lines fall under the ideal KCl line. The perpendicular distances between the ideal KCl line and the sample liquid lines represent
the iconicity of the ionic liquid. It is seen that ionic liquid’s ionicity is a few orders of magnitudes lower than the diluted KCl solution.

2.4 Ionic Conductivities of ILs

The ionic conductivities of ionic liquids have been studied extensively because this is a crucial parameter to determine whether the ionic liquids can be suitable as the electrolyte in LIB, LIC and EDLC. Based on the theory of conductivity and viscosity aforementioned, in general, the higher the temperature or the lower the viscosity is, the higher conductivity of the electrolyte. To enhance the ionic conductivity, two basic methods can be applied. One way is to increase the working temperature of LIB, LIC and EDLC. The second way to increase ionic conductivity is the addition of organic solvents with linear structures into the electrolyte.

2.4.1 Conductivities of pure ILs

The structure of an ionic liquid, such as the type/size of the anion, size of cation, and extra branch group, is crucial to determine the viscosity and hence the ionic conductivity.

Milan Vranes reported the relationship between ionic liquids’ conductivity and the length of side alkyl chain as well as the side chain’s position in the structure [67]. Three ionic liquids were studied in the research, which are 1-ethyl–3 methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][NTF₂], 1-hexyl–3 methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][NTF₂] and 1-octyl–3 methylimidazolium bis(trifluoromethylsulfonyl)imide [omim][NTF₂]. The N1 position had different length of side alkyl chains. Additionally, the authors introduced different groups on the C2 position,
so the corresponding ionic liquids are 1-ethyl–2, 3 methylimidazolium bis(trifluoromethylsulfonylimide [emim][NTF₂], 1-propyl–2, 3 methylimidazolium bis(trifluoromethylsulfonylimide [pmmim][NTF₂] and 1-butyl–2, 3 methylimidazolium bis(trifluoromethylsulfonylimide [bmmim][NTF₂]. The hydrogen on C2 position was substituted by methyl and the side alkyl chain at N3 position were different with increasing as 2, 3 and 4 as following the order of aforementioned. The pure conductivities of the ionic liquids from 20°C to 50°C were replotted and shown in figure 2.4. It is clear that by increasing the length of the side alkyl chain, the conductivity of the ionic liquid decreases (see figure 2.4 a and b). The methylated C2 also have significant influence on the conductivity of ionic liquid. The substitution of hydrogen on C2 increases the viscosity of the ionic liquid significantly, the ionic conductivity decreases immediately (see figure 2.4 c).

Kanakubo et al [68], investigated the conductivities of imidazolium based ionic liquid, i.e. 1-methyl-3-octylimidazolium hexafluorophosphate ([C₈mim]PF₆) and 1-methyl-3-octylimidazolium tetrafluoroborate ([C₈mim]BF₄), at different temperatures. The data from this paper was replotted and presented in figure 2.5. The general tendency showed that the conductivity increases with the increasing temperature. It is also seen that the ionic conductivities of [C₈mim]BF₄ are higher than [C₈mim]PF₆. As the anion size of BF₄ is smaller than PF₆, so the mobility is relatively higher, hence the higher ionic conductivity. Based on the Arrhenius equation, the activation energies of BF₄ and PF₆ were calculated 36,095 J/mol and 41,487 J/mol, respectively.
Figure 2.4 Conductivities of ILs changing with temperature: a) Series of [Emim][NTF₂], [Hmim][NTF₂] and [Omm][NTF₂] showing conductivities are highest for the shortest alkyl chain; b) Series of [Emimm][NTF₂], [Pmmim][NTF₂] and [Bmmim][NTF₂] also showing conductivities are highest for the shortest alkyl chain; c) Methylation of C2 reduced conductivities comparing [Emim][NTF₂] with [Emimm][NTF₂] [67].
Figure 2.5 Conductivities of 1-methyl-3-octylimidazolium hexafluorophosphate \([\text{C}_8\text{mim}]\text{PF}_6\) and 1-methyl-3-octylimidazolium tetrafluoroborate \([\text{C}_8\text{mim}]\text{BF}_4\) as a function of temperature [69].

Figure 2.6 Viscosities of DMF-[\text{C}_4\text{mim}]\text{PF}_6\) mixing systems under different mass fraction of DMF and temperature [69].
2.4.2 Conductivities of ILs mixed with organic solvent

Peng and the coworkers mixed organic solvents with imidazolium based ionic liquids, and observed a significant increase in their ionic conductivities [69]. In their research, N, N-dimethylformamide (DMF) was chosen because of its large dielectric constant and good solubility. DMF was mixed with \([\text{C}_4\text{mim}]\text{PF}_6\) with varying mass fractions from 0% to 100%. Figure 2.6 replotted their results and showed the variation of electrolyte’s viscosity in different testing temperatures (from 20°C to 45°C) and as a function of DMF mass fraction. The ionic liquid’s viscosity was less temperature dependent but changed significantly with the variation of DMF solution. DMF reduced the viscosity of the solution by two orders of magnitude.

Zhuo et al studied the imidazolium gluconate (\([\text{C}_n\text{mim}][\text{C}_6\text{H}_{11}\text{O}_7]\), n = 2, 4, 6, 8, 10, 12, 14) based ionic liquids with various alkyl chain lengths as well as the influence of different solvents such as water, ethanol and propyl alcohol on the properties of ILs [70]. Seen in Figure 2.7, the conductivity is more sensitive to the solvent, from high to low in the sequence of methanol, water, and propyl alcohol. The values of viscosity were analyzed based on the equation 2-14 [70], from which parameters A, B, and D were calculated.

\[
\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc + Dc^2 \quad (2-14).
\]

According to Zhuo, ‘A’ reflects the interaction between ionic liquid molecules. As value of ‘A’ increases with the increasing of alkyl chain length in the presence of water or propyl alcohol. When increasing the alkyl chain of ionic liquids, the intrinsic size of the solute’s cations will block the movement of ions and decreased the mobility of ions. The abnormal trending of ‘A’ values observed in the methanol solvent was considered to be caused by the influence of the hydrogen bonds or impurities in the solvent.
Figure 2.7 Change of molar conductivity (at 25ºC) with the alkyl chain length of cation n in the [Cₙmim][C₆H₁₁O₇] system. The ‘triangle’, ‘rectangle’, and the ‘circle’ symbols represent the IL system mixed with propyl alcohol, water, and methanol solvent, respectively [70].

Figure 2.8 Change of coefficient B with the alkyl chain length of cation n in the [Cₙmim][C₆H₁₁O₇] system. The ‘triangle’, ‘rectangle’, and the ‘circle’ symbols represent the IL system mixed with propyl alcohol, water, and methanol solvent, respectively [70].
The trend of ‘B’ denoted the solvent-solvent interaction in different solvent system. Comparing the same IL with different solvents, the order of B’s values, from low to high, is methanol, water, and propyl alcohol (see figure 2.8). Since the molecular size of propyl alcohol is larger than methanol, the ion-solvent interaction is stronger than methanol. Although the molecular size of the water is less than methanol, the value of B in water is larger than in methanol. Zhuo attributed this peculiar phenomenon to the strong hydrogen bonds between water and IL than those between methanol and IL. The increase of the ‘B’ values with increasing the IL alkyl chain length was caused by the more collisions between ions-solvent molecules and ions-solvent molecules when the alkyl chain increases.

2.4.3 Conductivities of IL mixtures

Lin et al illustrated the performances of the binary ionic liquids, i.e. N-methyl-N-propylpiperidinium bis(fluorosulfonyl) imide (PP$_{13}$FSI) and N-butyl-N-methylpyrroloidinium bis(fluorosulfonyl) imide (PYR$_{14}$FSI) at the weight ratio of 1:1 [71]. Figure 2.9a shows the conductivities in the temperature range of -70°C to 100°C. The interesting phenomenon can be recognized that the binary electrolyte’s conductivity was $10^{-6}$ S/cm at -70°C. However the conductivity values of neat ionic liquid PP$_{13}$ FSI and PYR$_{14}$ FSI fell to $10^{-9}$ and $10^{-7}$ S/cm around 0°C and -25°C, respectively. The conductivities of the blended ionic liquids at 20°C and 100°C are 0.49 and 2.89 S/m respectively. Furtherly, authors applied the binary blended ionic liquid in their EDLC system. Figure 2.9b shows the cycle voltammetry (CV) tests of the system at the operating temperature of 100°C. The rectangular shape of the curves represents that the ability of
EDLC maintain its stable capacitive behavior under rough environment. The wide range of scan rates shows the voltage approximately 3V without any side reactions.

![Graphs](image)

(a) (b)

**Figure 2.9** a) The conductivities of PP13 FSI, PYR14 FSI, and their mixture from -70°C to 100°C; b) The CV profiles of full EDLC cells with MWCNT electrodes at different scan rates [71].

### 2.4.4 Conductivities of ILs with lithium salts

Susanne et al. reported the viscosity changes upon adding ionic liquids into traditional lithium salt electrolyte, i.e. 1M LiPF₆ in EC and DEC with 1:1 molar ratio [72]. Two types of ILs were 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimTFSI) and 1-Ethyl-3-methylimidazolium hexafluorophosphate (EmimPF₆). The compositions of each hybrid system are listed in Table 2.5.
Table 2.5 Different electrolytes’ compositions and the acronyms. IL1 and IL2 refer to EmimTFSI and EmimPF₆, respectively. The molar percent of each electrolyte was labeled in the subscript. The weight percentage, converted from the molar percentage of ionic liquid, is in parentheses behind the abbreviations of different electrolyte [72].

<table>
<thead>
<tr>
<th>Sample 1: Emim TFSI</th>
<th>Sample 2: Emim PF₆</th>
<th>IL (x, mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP6 (0)</td>
<td>LP6 (0)</td>
<td>0</td>
</tr>
<tr>
<td>IL1₀·₅ (2)</td>
<td>IL2₀·₅ (1)</td>
<td>0.5</td>
</tr>
<tr>
<td>IL1₂ (7)</td>
<td>IL2₂ (4.5)</td>
<td>2</td>
</tr>
<tr>
<td>IL1₄·₅ (15.5)</td>
<td>IL2₄·₅ (11)</td>
<td>4.5</td>
</tr>
<tr>
<td>IL₁₉ (27)</td>
<td>IL2₉ (19.5)</td>
<td>9</td>
</tr>
<tr>
<td>IL₁₁₆ (42.5)</td>
<td>IL2₁₁₆ (32.5)</td>
<td>16</td>
</tr>
<tr>
<td>IL₁₂₂·₅ (53)</td>
<td>IL2₂₂·₅ (42.5)</td>
<td>22.5</td>
</tr>
<tr>
<td>IL₁₂₈ (60)</td>
<td>IL2₂₈ (49.5)</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>IL₂₃₆ (59.5)</td>
<td>36.5</td>
</tr>
</tbody>
</table>

Figure 2.10a and b illustrate the viscosities of these IL hybrids as a function of temperature and the hybrid composition. Seen in figure 2.10a, both IL1 and IL2 series, either neat or the blended systems, have linear relationship between logarithmic viscosity and reciprocal temperature, obeying the Arrhenius relationship. Further, it can be seen that their viscosity values increase with the addition of ionic liquid. The viscosity variation Δ, Δ = (Ƞₓ − Ƞ₅₀)/Ƞ₅₀, exhibited some interesting phenomena in relation with IL weight percentage (see figure 2.10b ). Here Ƞ₅₀ indicates the viscosity value of electrolyte that the ionic liquid concentration is 50 wt%. It is seen that a sudden increase of viscosity appears at 27.5 wt% and 18 wt% in TFSI and PF₆ systems respectively. The viscosity’s rapid increase was caused by the insufficient organic solvent because the function of the organic solvent is to dissolve the solute. The viscosity’s negative affect with the increasing amount of ionic liquid in EMIM TFSI is larger than EMIM PF₆.
Figure 2.10 a) Changes of dynamic viscosity as a function of temperature in the neat Li-ion electrolyte and blended with (IL1: EmimTFSI) and (IL2: EmimPF$_6$) at different compositions; b) Relative variation of dynamic viscosity as a function of the weight percentage of ionic liquid in the mixing systems [72].
2.5 Electrochemical Redox Stability Windows of ILs

The redox potential of electrolyte determines the maximum operating voltage in any electrochemical energy storage systems. Hence, electrochemical window values of different ILs have been extensively studied in the efforts towards improving energy storage capabilities in LIB, LIC, and EDLC. For instance, Xie studied 1-ethyl-3-methylimidazolium chloride (EmimCl), tetra-n-butylammonium perchlorate (TBAP) and the organic solvent acetonitrile (CH₃CN) [73]. The cyclic voltammetry (CV) tests were conducted using three electrodes, i.e. platinum counter electrode, glassy carbon working electrode, and platinum foil reference electrode. The author estimated the electrochemical potential of EmimCl was approximately around 5V. Nanjundiah et al reported that the cathodic and anodic limits of [Emim][TFSI] were -2.2V and 2.1V, so the electrochemical potential of [Emim][TFSI] was approximately 4.3V [74]. The electrochemical potentials of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][OTF]) and 1-ethyl-3-methylimidazolium trifluoroacetate ([Emim][TA]) were studied in Bonhote’s paper [75].

The CV plots of 1-ethyl-3-methylimidazolium based ionic liquid were displayed in figure 2.11a, shows the [Emim][OTF], and [Emim][TA] electrochemical potentials at 4.1 and 3.4V respectively. MacFarlane et al investigated the novel pyrrolidinium based ionic liquid [76]. The electrochemical potential of N-butyl-N-methylpyrrolidinium Bis(trifluoromethanesulfonyl)imide (P₁₄ TFSI) was examined and the CV curve was displayed in figure 2.11b. It is clear that the potential of neat P₁₄ TFSI is close to 6V. Some tiny current peaks found in the charging and discharging lines may be related with the moisture existing in the tested ionic liquid.
Figure 2.11 Cyclic voltammetry tests of different types of ionic liquid: a) Emim-based ILs at the scan rate of 50 mV/s; b) P14 TFSI at the scan rate of 100 mV/s [76].
The reported maximum stability potential values of common RTILs, obtained from various literatures and textbook, are summarized in Table 2.6.

Table 2.6 Electrochemical stability windows of various ionic liquids reported in literatures [73-76].

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>Electrochemical windows (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emim</td>
<td>Cl</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>BF₄⁻</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>TFSI</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>BETI</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>MSI</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>OTF</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>TA</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>F(HF)₂₃</td>
<td>3.3</td>
</tr>
<tr>
<td>Bmim</td>
<td>BF₄⁻</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>TFSI</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td>PF₆⁻</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>TA</td>
<td>5.7</td>
</tr>
<tr>
<td>C₈mim</td>
<td>TFSI</td>
<td>4.93</td>
</tr>
<tr>
<td>C₁₀mim</td>
<td>TFSI</td>
<td>4.89</td>
</tr>
<tr>
<td>PP₁₃</td>
<td>MSI</td>
<td>4.25</td>
</tr>
<tr>
<td>PP₁₄</td>
<td>TFSI</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>MSI</td>
<td>4</td>
</tr>
</tbody>
</table>

2.6 Ionic Liquid’s Applications in LIB, LIC, and EDLC

In LIB and LIC systems, the electrolyte should have a sufficient electrochemical stability window, high ionic conductivity, and the ability to form a stable solid electrolyte interface (SEI) on the surface of electrode, etc. Currently, the most common electrolyte is the solution of inorganic salts dissolved in cyclic or linear structure organic carbonate solvents. Such traditional carbonate organic electrolytes have some limitations which hinder the advancement of electrochemical storage systems. For example, the LiPF₆ based electrolyte has relatively lower thermal stability with decomposition starting at 55°C, generating toxic substance. Furthermore, LiPF₆ can react with trace of moisture producing hydrofluoric acid (HF) which can directly destroy the SEI layer and electrode materials, as
well as causing stability fading and safety problems. Other lithium salts have been investigated, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium-cyclo-difluoromethane-1, 1-bis(sulfonyl)imide (LiDMSI), lithium-cyclo-hexafluoropropane-1, 1-bis(sulfonyl)imide (LiHPSI), lithium bis(oxalato)borate (LiBOB) and lithium difluoro(oxalato)borate (LiDFOB). Among those, LiTFSI is one of the most promising electrolytes in LIB. However, it is expensive and has the tendency to dissolve the aluminum current collector when the potential reaches 3.5V Vs. Li/Li⁺.

The organic carbonate solvents can be ethylene carbonate (EC) and propylene carbonate (PC), and/or a linear linkage such as diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC). EC is used for its high dielectric constant and increase of electrolyte’s electrochemical potential. However, EC has a very high viscosity and high melting point at 36°C. To mitigate these drawback of EC, linear structured organic solvent with lower viscosity need to be mixed into the electrolyte such as DEC or EMC. These linear organic solvents often exhibit a low flash points and low boiling points, hence the interested flammability of the electrolyte. Past efforts were to find an optimal ratio of linear and cyclic carbonate solvent to warrant the high electrochemical window, high ionic conductivity, and high thermal stability of the electrolyte at the same time.

An alternative approach is to use ionic liquid or to add IL into the existing electrolyte in LIB, LIC, and EDLC systems. Ionic liquids are the promising choice because of their negative vapor pressure, high thermal stability, high electrochemical stability, high conductivity at temperatures higher than 60°C, and outstanding faradic and electrical statistic behaviors.
2.6.1 Impacts of ionic liquid in the electrolyte in LIBs

Presently, researchers often blend ionic liquid with traditional lithium electrolyte in LIB systems to assess the performances such as electrochemical potential, cycling performance and thermal stability. Zhang et al introduced 1-ethyl-3-methylimidazolium triluoromethanesufonate ([Emim][TF]) into their gel polymer electrolyte (GPE) consisting of LiPF$_6$ in EC/PC (1:1) [77]. Their testing cells were assembled with graphite anode and LiMn$_2$O$_4$ cathode. Figure 2.12 exhibits the cycle performance of different cells tested at 4.5V and the constant current of 5 mA. The discharge capacities of the cell with no IL is relatively lower than those with ionic liquid blended samples. However, the higher percent ionic liquid samples such as 60%, 75% and 100% shows the faded capacity after 20 cycles because the undesired reactions which can cause direct damage of the internal material of the cells. In contrast, the 40% and 50% ionic liquid samples have the excellent performance with discharging capacity more than 95 mAh/g and columbic efficiency nearing 98%.

Figure 2.12 The cycle performance of graphite/LiMn$_2$O$_4$ cells, using an electrolyte containing different volume percentage of ionic liquid ([EMIM][TF]) [77].
2.6.2 Impacts of ionic liquid in LICs

Koo introduced ionic liquid mixed with lithium salt into the Poly (ethylene oxide) (PEO)/polysilsesquioxane (SQ) system [78]. The Si-O-Si backbone in the polymer matrix structure increased the removable space of ions and hence the mobility of the electrolyte significantly, in addition to the improving mechanical properties. The ionic liquid was N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMP][TFSI]) and the lithium salt was lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). Figure 2.13a shows their ionic conductive behavior. The ionic liquid electrolyte LiTFSI + [BMP][TFSI] showed the conductivity value of 0.096 S/m at 30°C. The PEO-HI5 (5 wt% PEO-SQ polymer blended with LiTFST and [BMP][TFSI]) has 0.062 S/m at 30°C. Increasing of the weight percent of the polymer host, the conductivity of electrolyte decreased because of more crosslinked branches and the matrix backbone blocking the movement of the ions. The conductivity of PEO-SQ electrolyte is much higher than TPTA15 (pure PEO polymer host) because the improvement of the matrix spaces due to the introduction of PSQ. Figure 2.13b exhibited the electrochemical potential of the PEO-HI5 based electrolyte as high as 7V under room temperature. At temperatures up to 80°C, the potential reduced to 5V finally, none extra current peak appeared during oxidation or reduction processes below 5V, confirming PEO-HI5 based electrolyte were appropriately used in high-voltage LIC system even under high temperature. Cycle test were completed in a LIC cell as seen in figure 2.13c. The discharge capacity kept at 0.281 mAh after 50 cycles at the 80°C, and the Coulombic efficiency was also as high as 97% after 100 cycles.
Figure 2.13 a) Conductivity of different electrolyte systems, i.e. 1M LiTFSI BMPTFSI, PEO-HI5: 5 wt% PEO-SQ polymer blended with LiTFST and BMPTFSI, PEO-HI10: 10wt% PEO-SQ polymer blended with LiTFST and BMPTFSI; TPTA15: 15wt% organic ionogels doping LiTFSI and BMPTFSI; b) Linear voltage sweeping plots of PEO-HI5 tested at 1mV/s scan rate and 20, 50 and 80°C; c) the charge/discharge cyclic performance and Coulombic efficiency of LIC made up of PEO-HI5 electrolyte and activated carbon-metallic lithium foil electrodes [78].
2.7 IL Applications in EDLC Systems

The electrolyte in EDLC can be aqueous solution such as potassium hydroxide (KOH) or sulfuric acid (H$_2$SO$_4$), or some organic salts dissolved in organic solvent such as ethyl carbonate (EC) and acetonitrile (ACN). One drawback of the aqueous and organic solutions are that the electrochemical stability is relatively low from 1 to 3V. The lower potential can directly reduce the EDLC’s energy and power density. In addition, organic solvents also have a positive vapor pressure and high flammability under high temperatures.

In Balducci’s works, the EDLC system using [PYR$_{14}$][TFSI] IL electrolyte with aluminum working electrode, activated carbon counter electrode and silver reference electrode has the electrochemical potential higher than 4.5V, a specific capacitance of 90 F/g at the scan rate of 5 mV/s (see figure 2.14a) [79]. Additionally, the symmetric EDLC system using activated carbon electrode demonstrated a good non-faradic behavior during charging and discharging, and the maximum energy density and power density of the EDLC system obtained as 31 Wh/kg and 8.6 kW/kg (see figure 2.14b), respectively. After 40000 cycles at 10 mA/cm$^2$ and charge cutoff voltage at 3.2V, the specific capacitance of the EDLC system stayed around 80 F/g constantly (see figure 2.14c), demonstrating an excellent cycle stability at high temperature with the assistance of the [PYR$_{14}$][TFSI].

Zhang and his group reported the performance enhancement at high temperatures for EDLC using IL electrolyte ([Emim][TFSI]) [80]. At 60°C, the capacitance of EDLC was initially at 121 F/g and 115 F/g after 10000 cycles (see figure 2.15), which was less than 5% capacitance loss. This result demonstrated excellent cycling performance of EDLC at high temperatures by using ionic liquid.
Figure 2.14 a) CV plot of an EDLC consisting of [PYR$_{14}$][TFSI] electrolyte at the scan rate of 20 mV/s; b) Voltage profiles at current density of 10 mA/cm$^2$ but different cutoff voltages, the symmetric EDLC cell used with activated carbon electrolyte and [PYR$_{14}$][TFSI] electrolyte; c) Cycle test of the symmetric EDLC system under different current density and cutoff potentials [79].
Figure 2.15 The charge-discharge profiles of the [Emim][TFSI] based EDLC system obtained at 60 °C with different operating current [80].

2.8. Summary

Ionic liquids are inflammable, electrochemical stable, and vapor pressure negative. Additionally, ionic liquid has favorable chemical and thermal stability. Furthermore, ionic liquid can blend with different types of organic solvents and lithium salts homogenously without undesired reactions. For these reasons, ionic liquid is one of the very promising electrolyte or additive for improving the performances of LIB, LIC and EDLC systems.

A most significant disadvantage of ILs is the high viscosity and hence low ionic conductivity at room temperature. Increasing operating temperature is an effective way to reduce the viscosity and hence to increase ionic conductivity of ionic liquids. Mixing with some organic solvents is another way to reduce the viscosity of ionic liquid and to meet the demands of sufficient conductivity at low temperatures.
Chapter 3: Electrochemical Characteristics of C₈mim-based ILs and Their Hybrids

3.1 Introduction

In this research, three kinds of 1-methyl-3-octylimidazolium based ionic liquids, C₈mimX (X=Cl, BF₄, and PF₆) are studied for potential applications in LIB, LIC, and/or EDLC systems. Additionally, the three neat ionic liquids are mixed with DEC at different volume percentages, aiming to find out the optimal ratio which maximizes the electrolytes’ conductivity. Furthermore, LiPF₆/EC/DEC electrolyte, which is commonly used in Li-ion batteries, is blended with the ILs at different volume percentage. The conductivities of the neat ionic liquids as well as their hybrids are measured in the temperature range, 25°C to 65°C. Their electrochemical potential stability windows are also examined using cyclic voltammetry (CV) at room temperature.

The structures of the C₈mim⁺ cation, BF₄⁻ and PF₆⁻ anions are illustrated in figure 3.1 and the basic properties of these three ILs are listed in table 3.1 [81-83]. The arrangement of atoms and the valence electrons of 1-methyl-3-octylimidazolium cation (C₈mim⁺) satisfies the Lewis rule where each non-hydrogen atom has eight electrons participating in covalent bonds. For the anions their chemical structure and electron arrangement is modeled by the valence shell electron – pair repulsion (VSEPR) model. Each boron atom is surrounded by four fluorine atoms by sp³ hybridization; and the BF₄⁻
ion has tetrahedral structure with bond angle 109.5°. For the PF$_6^-$ ion, one phosphorous atom is surrounded by six fluorine atoms by d$^2$sp$^3$ hybridization, these atoms form an octahedral structure with 90° bond angle.

![Molecular structures of C$_8$mim$^+$ cation, BF$_4^-$ anion, and PF$_6^-$ anion.](image)

**Figure 3.1** Molecular structures of C$_8$mim$^+$ cation, BF$_4^-$ anion, and PF$_6^-$ anion.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formulae</th>
<th>Molar weight (g/mol)</th>
<th>Density (g/ml) (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_8$mim BF$_4$</td>
<td>C$<em>{12}$H$</em>{23}$BF$_4$N$_2$</td>
<td>282.13</td>
<td>1.12</td>
</tr>
<tr>
<td>C$_8$mim PF$_6$</td>
<td>C$<em>{12}$H$</em>{23}$PF$_6$N$_2$</td>
<td>340.29</td>
<td>1.19</td>
</tr>
<tr>
<td>C$_8$mim Cl</td>
<td>C$<em>{12}$H$</em>{23}$ClN$_2$</td>
<td>230.78</td>
<td>1.01</td>
</tr>
</tbody>
</table>

**Table 3.1** Physical properties of the testing ionic liquids.

### 3.2 Experimental Aspects

#### 3.2.1 Conductivity measurements

The fundamental experimental setup of determining a liquid’s conductivity is displayed in **figure 3.2a**. A Swagelok cell (see **figure 3.2b**) is used to reduce the amount of liquid’s consumption. The conductivity of a liquid - $\sigma$ can be calculated based on the
Pouillet’s law (see **equation 3-1**), where ‘R’ is the resistance of the electrolyte, ‘L’ is the distance between the two parallel electrodes and ‘A’ is the geometrical surface area of the electrode in contact with the liquid.

\[
\sigma = \frac{L}{AR} \quad (3-1)
\]

A Swagelok cell has four parts, the closing cup, spacer, Teflon cylinder, and bottom container. For this type of configurational experiment, two pieces of porous polypropylene (PP) separators are used and the value of ‘L’ equals the sum of thickness of the two separators. The value of ‘A’ is equal to the surface area of the separator. The value of ‘R’ was determined by electrochemical impedance spectroscopy (EIS) with the assistance of a Gamry Instruments system (Reference600; Potentiostat/ Galvanostat/ ZRA).

**Figure 3.2 a)** The model of conductivity tests [83]; **b)** Configuration of Swagelok cell.

### 3.2.2 Sample preparation and testing cell assembling

The ionic liquids, DEC solvent and the traditional organic lithium electrolyte LiPF₆/EC/DEC were stored in a glove box which was controlled to maintain a moisture content less than 0.5 ppm. All plastic labwares necessary for preparing the mixtures and testing cells were dried in a furnace at temperatures around 60°C for 24 hours before use. All glasswares and all parts of Swagelok cells were dried in the furnace at 110°C for at
least 5 hours before being transferred to the glove box. For assembling the testing cells, double PP separators (total thickness of 40 µm) were used and laid between the spacer and bottom cup with sufficient bulk of tested liquid. The volume of per drop was approximate 25 µL.

3.2.3 Electrochemical impedance spectroscopy

![Nyquist plot](image)

**Figure 3.3** An example of a Nyquist plot showing an ionic liquid's real and imaginary impedance obtained at different frequencies [84].

An example Nyquist plot obtained from EIS measurement is shown in **figure 3.3**. It consists of two regions: the one at high frequencies is a semicircle shaped curve, and the low frequency region is a sloped line, approximately 45°. The diameter of the semicircle represents the intrinsic impedance from the tested liquid. The electrolyte impedance semicircle would disappear when the conductivity of the tested liquid electrolyte is
sufficiently high. The approximate 45° Warburg line appearing in this Nyquist plot corresponds to the diffusion impedance of ions.

In some cells when diffusion is not a dominant process in the electrode kinetics, the Warburg line will not appear. In an electrochemical cell system, the ions in the electrolyte migrate under the potential difference between cathode and anode, and the diffusion occurs at the interface of electrode and electrolyte. In these cases, another complete or incomplete semicircle may be present, corresponding to a charge transfer process at the electrode/electrolyte interface.

This study is focused on the ionic conductivities of ionic liquids, therefore any impedance corresponding to electrode kinetics are neglected. To make sure the conductivity values are accurate and repeatable, impedance measurements were repeated at least three times at each temperature and multiple testing results have been compared with each other.

In this research, a Gamry Instruments system was utilized for the electrochemical impedance spectroscopy tests. All samples were examined at frequencies from 1 Hz to 100 kHz with AC current amplitude of 0.1 mA.

3.2.4 Cyclic voltammetry

Cyclic voltammetry (CV) tests are essential for the researching of LIB, LIC and EDLC systems. Generally, the CV test can evaluate the electrochemical stability window of the electrolyte in a half-cell or a full-cell configuration. Moreover, the capacitance of EDLC or LIC systems can be determined under CV tests by the integration of the CV curve. A CV curve is plotted as current as a function of sweeping voltage. Upon voltage beginning
applied to the electrode/electrolyte the charge transfer reaction occurs and the current increases until the reaction is complete. CV plots reflect the oxidation and reduction status of cells, decomposition of the electrolyte, and sub-reactions. The shapes of the CV profile are highly depended on the scan rates and applied potentials.

In this study, the CV measurements were conducted using Gamry Instruments system. Two models of cells were selected for the CV tests. Cells in the first model consisted of two identical stainless steel electrodes with the tested electrolyte. In the first model CV tests, DEC was mixed with the C₈mim BF₄ and C₈mim PF₆ at 0%, 20%, 50%, and 70%’s volume percentages. The voltage was swept between -6V to 6V. Cells in the second model used lithium foil as the reference electrode while keeping the working electrode as stainless steel. The tested electrolytes were C₈mim BF₄ or C₈mim PF₆ mixed with LiPF6/EC/DEC electrolyte at volume percentages of 0%, 20%, 50%, 70%, and 100%. In this model, voltage range was set between 0 to 11V. In both models of the CV tests, the scan step was set to 10 mV and the scan rate was 100 mV/s. All the assembled cells were kept in the glove box more than 24 hours to guarantee the separators were fully wetted by the electrolyte. All cell behavior was recorded and analyzed by the Gamry analysis software.

3.3 Results and Discussion

3.3.1 Conductivities of neat ILs

Figure 3.4 displays the Nyquist plots of neat C₈mim BF₄, C₈mim PF₆, and C₈mim Cl in the high frequency regions obtained at the testing temperatures from 25°C to 65°C. The intercepts on the real x-axis represent the ionic liquid’s conductive impedance. Based on
the impedance values, the conductivities are calculated and plotted as a function of temperature for each different type of IL (see **Figure 3.5**).

**Figure 3.4** Nyquist plots of the three ionic liquids obtained at temperatures from 25°C to 65°C: 

a) C₈mim BF₄; b) C₈mim PF₆; c) C₈mim Cl.
Generally, conductivity of an ionic liquid increases with increasing temperatures. In an ionic liquid, cations and anions cannot be totally separated due to the strong interactions between them. This is different from inorganic salt aqueous solution such as potassium chloride dissolved in water. Increasing temperature will significantly promote the ionization of ionic liquids and weaken cation-anion interactions. Therefore, as the number of conductive cations and anions increase, it will lead to an increase in ionic conductivity.
From **figure 3.5b**, the activation energies of three neat ILs are calculated based on Arrhenius’ equation. The calculated activation energy of \( \text{C}_8\text{mim Cl} \), \( \text{C}_8\text{mim PF}_6 \), and \( \text{C}_8\text{mim BF}_4 \) are 37.3, 33.9 and 28.9 kJ/mol, respectively. Typically, the activation energy is the minimum energy to break the ionic bonds between cations and anions in the ionic liquid, therefore the higher the activation energy, the fewer free ions available to contribute to the conductivity. For this reason, the ionic conductivity of the ionic liquid has direct relation to the activation energy. The activation energy values suggest that ionicity of the ILs increase in the sequence of \( \text{C}_8\text{mim Cl} \), \( \text{C}_8\text{mim PF}_6 \), and \( \text{C}_8\text{mim BF}_4 \).

It can be seen in **figure 3.5a** that the three ILs’ conductivities at the same temperature follows the trend of \( \text{C}_8\text{mim Cl} < \text{C}_8\text{mim PF}_6 < \text{C}_8\text{mim BF}_4 \). The ionic conductivity and dynamic viscosity have the inverse relationship. As discussed in **chapter 2**, the size of the cation and anion have a direct influence on the viscosity of liquid. These ionic liquids have the same imidazolium based cation but different sizes of anions. The ions’ movement impeded by larger ions. When large ions are under movement, there is an increased chances to collide with each other and the collision will consume more energy, hence the mobility in solutions with large ions is low. Since the size of BF\(_4^-\) is smaller than PF\(_6^-\), the mobility and consequently the conductivity of \( \text{C}_8\text{mim BF}_4 \) will be greater than \( \text{C}_8\text{mim PF}_6 \).

The lowest conductivity value of \( \text{C}_8\text{mim Cl} \) can be explained by the influence of hydrogen bonds which are weaker than covalent and ionic bonds but much stronger than Van der Waals forces. It is reported that Cl\(^-\) anions can be surrounded by the \( \text{C}_8\text{mim Cl} \) dipoles with the interaction of hydrogen bonds. The size of solvated Cl\(^-\) will be much larger than the BF\(_4^-\) and PF\(_6^-\) anions. The larger conductive particles reduces the mobility of the ions. Furthermore, since the interaction between cations and anions are stronger in
C₈mim Cl than in C₈mim BF₄ and C₈mim PF₆, so too, the amount of conductive ions present in C₈mim Cl is less than that of C₈mim BF₄ and C₈mim PF₆ [85-86].

On the other hand, the Cl⁻ has the most asymmetric structure of the three anions. The BF₄⁻ structure is more stable than the PF₆⁻ structures because five d orbitals are not occupied completely. The order of rigidity of these anions is BF₄⁻ > PF₆⁻ > Cl⁻, and this arrangement relates to the conductivities observed.

Other researchers have observed similar results obtained in this study. Mitsuhiro et al measured the conductivities of C₁₀mim BF₄ and C₁₀mim PF₆ at room temperature and atmospheric pressure, showing that the BF₄⁻ based imidazolium ionic liquid’s conductivity is around 0.06 S/m while the PF₆⁻ conductivity is 0.025 S/m [87]. Shyh-Gang Su et al presented that C₄mim BF₄ and C₄mim PF₆ have conductivities of 0.232 S/m and 0.225 S/m, respectively [88]. Mao et al reported C₄mim Cl has a conductivity less than 0.1 S/m, which is lower than C₄mim BF₄ and C₄mim PF₆ [89].

It is noteworthy that conductivity is the one crucial property to evaluate the electrolytes’ performance but it is not the only one to determine the final choice of the electrolytes for practical application. Some other factors such as thermal and electrochemical stability are still significant factors, and all of these aspects need to be considered during the selection of ionic liquids.

### 3.3.2 Conductivities of IL+DEC hybrids

In equation 3-4, the relationship between the critical distance of cation-anion pair r and the dielectric constant is exhibited, where the parameters of Zᵢ, Zⱼ, e, ε₀, ε, Kₐ, and T represent the valence of ion i, the valence of ion j, unit charge, dielectric constant
in vacuum, dielectric constant in atmosphere, Boltzmann constant and the testing temperature respectively [90]. Decreasing the critical distance, i.e. promotion of ion’s separation, can be achieved by increasing the dielectric constant of the electrolyte directly.

\[ r' = \frac{Z_i Z_f e^2}{8\pi\varepsilon_0 \varepsilon K_B T} \]  

(3-4).

As mentioned in chapter 2, linear and cyclic structured carbonates are usually used in the traditional organic electrolytes. Because of the lower conductivity values of the neat ionic liquids C₈mimX, DEC was selected to add into ILs to promote the ion’s separation. In this section, the influence of DEC on ionic liquids’ conductivities will be discussed.

Experimentally, it was found that DEC has different solubility in the three ILs. In C₈mim BF₄, the DEC can be added from 0% to 85%. Up to 95 vol% DEC can be added into C₈mim PF₆. However, maximum 33% DEC can be mixed with C₈mimCl without phase separation.

Figure 3.6 presents the conductivities of C₈mim BF₄, C₈mim PF₆, and C₈mim Cl hybrids as a function of DEC volume percentage. Basically, the conductivity’s variation for C₈mim BF₄ and C₈mim PF₆ hybrids follow the same trend. The conductivity increases upon increasing of DEC but decreases after reaching a maximum value. The initial conductivity increases with the addition of DEC is the result of IL molecules dissociating into cations and anions through the interaction with DEC dipoles. When the amount of conductive ions from IL reaches the maximum, further addition of DEC will reduce the concentration and meanwhile DEC will also solvate with the anion resulting in the reduction of conductivity.
Figure 3.6 Conductivity as a function of DEC volume percentage in the ionic liquid-DEC hybrid system.

Seen in figure 3.6, the DEC percentage corresponding to the maximum conductivity for C₈mim BF₄ is in the vicinity of 50 vol%. In contrast, the C₈mim PF₆’s conductivity reaches its’ maximum value when the DEC volume percentage is close to 70%. It can also be observed that 1) when DEC’s volume percentage is less than 50%, C₈mim BF₄ groups have higher conductivity value than C₈mim PF₆; 2) after the DEC’s volume percentage passes the 50%, C₈mim PF₆ shows the better performance in conductivity than C₈mim BF₄ series. It can be concluded that C₈mim BF₄ is more sensitive to the influence of DEC’s addition than C₈mim PF₆. It would be assumed that the ionic bonds between C₈mim⁺ and BF₄⁻ are weaker than the interactions between C₈mim⁺ and PF₆⁻. Accordingly, DEC
solvent can readily dissociate anions and cations in C₈ mim BF₄ and hence, make more significant influence on its conductivities.

For the C₈ mim Cl, the conductivity has a unique variation under the changing of DEC’s volume percentage. The trend is similar to C₈ mim BF₄ and C₈ mim PF₆ but the slope of the conductivities’ variation line is relatively lower than the others. This phenomenon can be explained by DEC dipoles that make contact with Cl⁻ anions more tightly because the positive particles’ attraction of Cl⁻ is stronger. In C₈ mim Cl, the strong interaction between cation and anion results in the formation of a macromolecular cluster, which reduces impacts of DEC on ions’ movement as well as DEC solubility [91].

3.3.3 Conductivities of IL+ traditional lithium ion electrolyte

In order to investigate the impact of lithium electrolyte on conductivities of ionic liquids, or vice versa, for their potential applications in LIBs or LICs, two ionic liquids, C₈ mim BF₄ and C₈ mim PF₆, were blended with the traditional organic lithium electrolyte LiPF₆/ EC/ DEC. The conductivities were determined as a function of volume percentage in the temperature range of 25°C to 65°C.

Figure 3.7a and b present the conductivities of the two ILs’ hybrids as a function of volume percentage obtained at different temperatures. Different from neat ILs, the lithium electrolyte has a higher conductivity than IL due to the presence of lithium salt. The electrolyte’s conductivity decreases with the increasing of the ionic liquid’s volume percentage because extra ionic liquid increases the electrolyte’s viscosity and reduces lithium ion concentration.
Figure 3.7 a) Conductivities’ variation of LiPF$_6$/EC/DEC-$\text{C}_8\text{mim BF}_4$ system as a function of ionic liquid’s volume percentage. b) Conductivities’ variation of LiPF$_6$/EC/DEC-$\text{C}_8\text{mim PF}_6$ system as a function of ionic liquid’s volume percentage.
Besides the general tendency of conductivity versus composition and temperature, another phenomenon can be observed in **figure 3.7**. At the 50% volume percent, both C₈mim BF₄ and C₈mim PF₆ groups’ conductivity increases abnormally. This conductivity ‘peak’ is attributed to the combination effect of the IL addition. Firstly, IL reduced the viscosity. On the other hand, IL introduced more moving cations and anion. As discussed previously, DEC which existing in the lithium electrolyte can promote ion dissociation in IL and increase ionic conductivity of IL. The conductivity reaches at the maximum value when the DEC’s volume percent is close to 50% in C₈mim BF₄ systems and 70% for C₈mim PF₆.

In the C₈mim PF₆-lithium salt system, the general tendency of conductivity is similar to C₈mim BF₄, and the conductivity ‘peak’ still can be seen clearly in the diagram. However, the conductivity ‘peak’ in C₈mim PF₆ system is less obvious than C₈mim BF₄, likely due to stronger interaction between cations and anions and hence there is less impact by DEC. Upon increasing temperatures, DEC’s influence becomes more pronounced.

**Figure 3.8a** and c present the conductivities as a function of temperature of the two ILs’ hybrids with different compositions. The electrolytes’ conductivities increase with increasing temperature. From **figure 3.8 b** and d, it is apparent that the logarithms of conductivities have linear relationships with the reciprocal absolute temperature, demonstrating the Arrhenius’ behavior, from which the activation energies of each hybrid system can be calculated.
Figure 3.8 a) Conductivities’ variation of LiPF₆/EC/DEC-C₈mim BF₄ system as a function of temperature; b) Arrhenius’ plot (log $\sigma$ vs $1/T$) of LiPF₆/EC/DEC-C₈mim BF₄ system; c) Conductivity variation of LiPF₆/EC/DEC-C₈mim PF₆ system; d) Arrhenius’ plot (log $\sigma$ vs $1/T$) of LiPF₆/EC/DEC-C₈mim PF₆ system.
Figure 3.9 The comparisons of activation energies between LiPF$_6$/EC/DEC-$C_8$mim BF$_4$ and LiPF$_6$/EC/DEC-$C_8$mim PF$_6$ systems as a function of IL volume percentage.

Seen in figure 3.9, $C_8$mim PF$_6$ system has a near linear relationship between activation energy and the IL volume percentage. In contrast, the activation energy change is less linear/regular in the $C_8$mim BF$_4$. Comparing the $C_8$mim BF$_4$ with the $C_8$mim PF$_6$ systems, it can be detected that when the ionic liquid’s volume percent is less than 50%, $C_8$mim BF$_6$-lithium salt, the electrolyte systems have larger activation energy than $C_8$mim BF$_4$. At the volume percent of ionic liquid between 50% and 70%, the $C_8$mim PF$_6$ system has lower activation energy values than the other.

The irregular activation energy change in the $C_8$mim BF$_4$ is similar to the observations by others. Thomas et al investigated the influence of various ionic liquids including 1,2-dimethyl-3-n-propylimidazolium tetrafluoroborate (DMPI BF$_4$) in polymer gel electrolytes [92]. Although conductivity values continuously decrease with the decreasing of ionic
liquid, the activation energies do not. The inconformity between the activation energy and the conductivity was attributed to the greater fitting error by the authors. However, Kevin et al also investigated the conductivities and activation energies but in different IL/polymer electrolyte systems. Again, they noticed that the gradual decrease in conductivity values did not follow the linear increase in activation energy. The authors attributed this phenomenon to a higher amount of mobile charge [93].

3.3.4 Electrochemical stabilities of IL and their hybrids

The electrochemical stabilities of two ionic liquids C₈mim BF₄ and C₈mim PF₆ and their hybrid systems were investigated with the help of CV measurements. Figure 3.10 presents the CV plots of these two ILs and their hybrids with DEC obtained in the first testing model. It can be seen that both C₈mim BF₄ and C₈mim PF₆ systems show slight emergence of cathodic and anodic peaks approaching the charge and discharge limiting voltages. C₈mim PF₆ is much more stable than C₈mim BF₄. Since both current values corresponding to the reaction are very low, it results that both ILs are electrochemically stable within the testing voltage windows, i.e. -6V to 6V. With the addition of DEC, redox reaction currents increased and the corresponding voltage at the peak current decreased. This phenomenon illustrated the lower stability of the aprotic solvent DEC compared to that of ILs.

According to the CV results, it can be seen that both C₈mim BF₄ and C₈mim PF₆ can maintain their properties in the voltage range from -6V to 6V. With the addition of DEC, the electrochemical stability window slightly reduces but is still greater than 10V. The broad voltage window is a great benefit to the EDLC system.
Figure 3.10  a) CV plots of $C_{8}$mim BF$_4$-DEC system; b) CV plots of $C_{8}$mim PF$_6$-DEC system; and all samples’ scan voltage: -6 to 6V, Scan rate: 100mV/s, and Scan step: 10mV. For better visualization, the plots corresponding to DEC 20%, 50% and 70% solutions are shifted up at the interval of 0.001A.
For LIB and LIC systems, a common organic lithium electrolyte LiPF$_6$/EC/DEC was blended with the above two ILs. Because of the existence of lithium ions in the solutions, lithium foil was used as the counter and reference electrode in this series of studies. Figure 3.11a and b present the samples’ CV profiles obtained during the first charging and discharging cycle, and figure 3.12 a and b show the CV plots obtained at the second cycle.

Seen in figure 3.11, pure IL has no reduction reaction but shows an oxidation reaction starting at 4V. With increasing lithium salt content in the solution, reduction reactions occur starting around 1.5V with the maximum current in the vicinity of 0.2V. The reduction currents possibly originate from the reduction reaction of carbonate solvent corresponding to SEI formation at the high voltage region (0.2-1.5V) and lithium deposition at the low voltage region (< 0.2V). The oxidation also occurs around 4V but the current is much larger than neat IL, suggesting the organic solvents also start to decompose upon increasing current.

The SEI can form on both anode and cathode but as seen from current results the SEI predominantly forms on anode. The compositions of SEI is complex which includes lithium oxide, some organic compounds, and solid lithium organic salts. The SEI has a positive effect on the cells by protecting the electrode material from corrosion which occurs by the decomposition of the electrolyte under a certain voltage. An optimal SEI layer can also prevent the formation of lithium dendrites.
The first cycle CV plots of lithium salt-ionic liquid systems, scan voltage is between 0 to 11V vs Li/Li$^+$, scan rate and scan step were set under 100mV/s and 10mV; a) LiPF$_6$/EC/DEC- C$_8$mim BF$_4$ system; b) LiPF$_6$/EC/DEC- C$_8$mim PF$_6$ system.

Figure 3.11
Figure 3.12 The second cycle CV plots of lithium salt-ionic liquid systems, scan voltage is between 0 to 11 V vs Li/Li⁺, scan rate and scan step were set under 100mV/s and 10mV; a) LiPF₆/EC/DEC-C₈mim BF₄ system; b) LiPF₆/EC/DEC-C₈mim PF₆ system.
It is interesting to note the redox CV characteristics in the second cycle is dramatically different from the first cycle, especially in the anodic line. Seen in figure 3.12a and b, the reduction current peaks remain as in the first cycle, indicating the reversible lithium deposition process. With no lithium salt, i.e. in neat ionic liquid, no reduction peak is visible. On the other hand, the oxidation current maximized around 7V with the starting point at 4V. For hybrid systems this was only observed in the first cycle and disappeared in the following cycles. Accordingly, it is believed that this current peak is mainly caused by the decomposition of the trace moisture in the ILs and formation of a SEI on the cathode surface due to the decomposition of the electrolyte.

In the second cycle, neat IL’s oxidation current is significantly reduced and minor oxidation does not start until 9V, confirming superb electrochemical stability. With the addition of a lithium electrolyte, the oxidation current increases gradually. Different from other IL-electrolyte hybrids, pure lithium electrolyte and the one with 20% IL showed a broad oxidation peak at 4V emerging from 3V. This may be related to the decomposition of organic solvent in the electrolyte on the surface of stainless steel. These results suggest that pure lithium electrolyte and the one with 20% IL is much less stable. Moreover, it is seen in figure 3.12 the values of redox currents in C₈mim PF₆ systems are relatively smaller than in C₈mim BF₄, suggesting the C₈mim PF₆ has more stable electrochemical properties than C₈mim BF₄, tolerating the variation of working voltages.

3.4 Summary

Ionic liquid’s intrinsic properties such as ionic conductivity and electrochemical potential, varied significantly with the changing of external factors such as operating
temperature, types of additives, and concentration of additives, etc. In this study, the additives include organic solvent (DEC) and traditional lithium electrolyte (LiPF$_6$-EC-DEC).

Among the three neat ionic liquids, the conductivities of these ILs have the order of C$_8$mim BF$_4$ > C$_8$mim PF$_6$ > C$_8$mim Cl. This phenomenon is attributed to the chemical and ionic size differences of the three anions in these ILs, which influence the coordination and possible hydration. Increasing temperatures accelerate the dissociation between cation and anion of ionic liquid, increasing the concentration of mobile ions and their mobility, and subsequently increasing conductivities. The activation energies of neat C$_8$mim Cl, C$_8$mim PF$_6$, and C$_8$mim BF$_4$, calculated based on Arrhenius’ equation, are 37.3, 33.9 and 28.9 kJ/mol, respectively. The activation energy values suggest that ionicity of the ILs decrease in the sequence of C$_8$mim Cl, C$_8$mim PF$_6$, and C$_8$mim BF$_4$.

Since the conductivity values of the neat ionic liquids are insufficient for the practical applications to LIB, LIC and EDLC systems, an organic solvent with high dielectric constant, i.e. DEC, was added into the ionic liquid and the solvent-solvent interactions had been researched. In the hybrid of IL-DEC, the conductivity values of both BF$_4$ and PF$_6$ systems increase initially with the addition of DEC, and decrease with the further addition of DEC. Upon adding of DEC, the conductivity of the IL hybrid was increased by over an order of magnitude, reached 0.3 S/m at room temperature.

In the IL-LiPF$_6$/EC/DEC hybrid systems, it is interesting to observe a conductivity peak at 50 vol % hybrid. This is attributed to synergetic interaction between the lithium electrolyte and ionic liquid: 1) the addition of IL reduced net value for its low conductivity,
and 2) lithium salt and organic solvent like EC and DEC existing in the lithium electrolyte increase dissociation of cation-anion in ILs.

According to the CV results, redox current values are very low for both C₈mim BF₄ and C₈mim PF₆ indicating they can maintain their properties in the testing voltage range from -6V to 6V. C₈mim PF₆ has the higher stability than C₈mim BF₄. With addition of DEC, electrochemical stability window above 10V makes these types of systems advantageous for EDLC systems.

In the hybrid systems of ‘lithium salt electrolyte-ionic liquid’, obvious reduction and oxidation peaks can be found and CV behaviors are different between the first cycle and subsequent cycles. With the presence of a lithium electrolyte, SEI formation which relates to the oxidation of carbonate solvent or the irreversible reaction with lithium cannot be avoided on both cathode and anode. Traces of moisture can decompose in IL starting at 4V and reaching maximum around 7V during the first cycle. Afterwards, neat IL and electrolyte with high IL concentration can stable up to 9V vs Li anode.
Chapter 4: Impacts of ILs on the Performances of Graphene-based LIB and LIC.

4.1 Introduction

Previous studies of ILs and their hybrids on ionic conduction and electrochemical stability suggest that C₈mim PF₆ is the most promising candidate, among the three studied electrolyte systems, for LIBs and LICs. To assess such IL and its hybrid impacts on energy storage performances, half-cell LIB and full cell LIC were assembled. For this series of studies, reduced graphene oxide (RGO) was synthesized and its morphological and structural properties were determined. With the blending of C₈mim PF₆ into the common lithium electrolyte, i.e. LiPF₆/EC/DEC, lithium storage capacities in the RGO anode were assessed. Moreover, LIC’s specific capacitance, energy density, and cumbic efficiency were analyzed in the symmetric LIC setting.

4.2 Experimental Aspects

4.2.1 Synthesis of reduced graphene oxide (RGO)

The Hummer’s method was used for RGO synthesis. All reagents and the amount used in the experiment are summarized on table 4.1. Graphite powder HPM 850 has the surface area of 18.0 m²/g with typical size of 5μm and purity of 99.7%. The purity of the NaNO₃ and KMnO₄ used were 99% and 98%, respectively. Sulfuric acid with weight fraction
was 98%, and the purity of Hydrogen Peroxide was 30%. First of all, Graphite, NaNO₃, and H₂SO₄ were slowly added into a 1000ml Pyrex® beaker. Later, the beaker was placed on a hotplate at a temperature of 35°C and stirring speed of 400 RPM. About 10 minutes later, when the slurry became homogenous, KMnO₄ was slowly added and continuously stirred. During this process, distilled water was constantly added to maintain the liquid level. After a few days, temperature was increased to 150°C and the stirring rate was increased to 550 RPM. It was noticed the slurry color changed from black to purple, dark green, light pink, dark brown, and light brown, corresponding to the graphite oxidation, intercalation, and exfoliation evolution. To ease the process, 30% H₂O₂ was added into the beaker and the temperature was maintained to evaporate majority of the water.

Table 4.1 Information of reagents used for RGO synthesis

<table>
<thead>
<tr>
<th>Component</th>
<th>Using amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite HPM 850</td>
<td>2g</td>
</tr>
<tr>
<td>Sodium Nitrate (NaNO₃)</td>
<td>2g</td>
</tr>
<tr>
<td>Potassium Permanganate (KMnO₄)</td>
<td>12g</td>
</tr>
<tr>
<td>Sulfuric Acid (H₂SO₄)</td>
<td>100ml</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>10ml</td>
</tr>
</tbody>
</table>

The prepared carbon slurry was filtered and washed with the help of a medium porosity glass filter funnel and a peristaltic pump. This process needed to be repeated several times until the pH of the waste water reached 7. After that, 5% Hydrochloric acid (HCl) liquid was added to eliminate the residual manganese in the carbon powders. The oxidized graphene powder was dried and thermally reduced. In this study, the thermal treatment temperatures were varied from 200°C to 425°C with a 50°C interval. The obtained RGO was examined by X-ray Diffraction (XRD) and scanning electron microscopy (SEM).
4.2.2 Preparation of half-cells

The electrodes of the half-cell systems are made of lithium metal foil and RGO coated on copper foil. Firstly, RGO was mixed with the polyvinylidene fluoride (PVdF) binder with the mass ratio of 90:10 with N-methyl-2-pyrrolidone (NMP) as solvent. The RGO/PVdF/NMP slurry was doctor-bladed on the surface of the copper foil. After drying in the oven at 110°C for 24 hours, the coated membrane was pressed and cut into a 10mm diameter disk. The same method was used for the lithium foil. The examined electrolyte was LiPF₆/EC/DEC containing C₈mim PF₆ at different volume percentage, i.e. 0%, 16.67%, 25%, 33.3%, and 50% respectively.

Before transferring to the glove box for half-cell assembly, all parts of Swagelok cells were dried in 110°C for 6 hours. The sequence of assembling a testing half-cell is as follows: one disk of RGO electrode at the center of the bottom cap, two pieces of PP separators above the RGO electrode, a couple drops of electrolyte, a Teflon cylinder, and one piece of lithium foil disk on the top of the separators, a spacer, and the closing cap. After assembling, the cell was hand tightened.

4.2.3 Preparation of LIC full cells

For LIC studies, RGO was coated on aluminum and copper foils used as the cathode and anode, respectively. The electrolyte was an ionic liquid C₈mimPF₆ mixed with LiPF₆/EC/DEC at different volume percentage i.e. 0% (Neat LiPF₆/EC/DEC), 20%, 50%, 70%, and 100% (Neat C₈mim PF₆) respectively. The RGO on copper anodes was pre-lithiated by fully discharging the Li/RGO half-cells as described in the previous section. Afterwards, the half-cells were dissembled and the pre-lithiated RGO on copper was used
as the anode in LIC. The sequence of assembling a testing LIC full-cell is as follows: the pre-lithiated RGO, a separator, the desired electrolyte; and the RGO cathode coated aluminum. After assembling, the cell was hand tightened.

Land system (CT 2001A) was utilized to assess the discharge/charge characteristics of the LIC cells. In the pre-lithiation process, the discharge current was set at 0.1 mA. In the cycle tests of the LIC, the testing voltages were set at 3V and 4.5V respectively, and the working current was kept at 0.1 mA. Four complete charge/discharge cycles were set for every capacitor to assess the capacitance. The performance of each cell was recorded and analyzed.

4.3 Result and Discussion

4.3.1 Structural and morphological properties of RGO Powders

The Hummer method is the most popular way for synthesizing RGO due to its relatively low cost and easy processing. Because of the strong oxidant reagents, the functional groups such as hydroxyl (-OH), carboxyl (-COOH), and epoxyl will form on the surface of most graphite monolayers. Simultaneously the intercalation process will cause the distance of the closest monolayers to increase, and the Van der Waals forces between the stacked layers is weakened [94]. Heat treatment, at temperatures from 200°C to 425°C, leads to partial decomposition of those organic functional groups into carbon dioxide, carbon monoxide, water or other types of hydrocarbons.

The heat-treated samples were examined using XRD. Seen in figure 4.1, the strongest peak around the angle of 25° corresponds to the (002) plane. The distance of the adjacent
carbon monolayers \(d_{002}\) can be calculated based on Bragg's Law \(n\lambda = 2d\sin\theta\), where \(\lambda\) is wavelength of the X-ray source, the value of \(\lambda\) is equal to 1.542\(\text{Å}\) in our experiment; \(\theta\) is the diffraction angle, and \(d\) denotes the value of \(d_{002}\) in this experiment, \(n\) equals 1 in this experiment [95-96]. It is obvious that the diffraction angle of the strongest peak increased with the increasing of the treatment temperature suggesting increased crystallinity and increased restacking probability.

SEM images of these powders are displayed in figure 4.2. It can be seen that the morphology did not vary significantly. However, the samples with the treatment temperatures less than 350\(°\text{C}\) have thinner restacked structure when compare to the pristine graphite SEM image, which is corroborated by the XRD results.

**4.3.2 Influence of IL on lithium ions’ intercalation/dis-intercalation into RGOs**

Based on the above structural and morphological analysis, the RGO powders used in the following tests was thermally-treated at the temperature of 250 \(°\text{C}\). The reason for this choice is that residual functional groups are mostly eliminated at relatively high temperatures (above 250 \(°\text{C}\)) but the restacking is less significant at relatively low temperature (below 350 \(°\text{C}\)).
Figure 4.1 XRD diagrams of RGO powders thermally reduced at different temperatures and the initial graphite HPM 850 powder.
Figure 4.2 SEM images of RGO samples obtained at different reduction temperatures: a) 200°C; b) 250°C; c) 275°C; d) 300°C; e) 325°C; f) 350°C; g) 425°C; and h) pristine graphite.
Figure 4.3 shows the first five-cycle discharge/charge profiles of the Li/RGO half cells using different electrolytes. All the cells were discharged and charged from 0V to 3V at a constant current of 0.1 mA. Upon discharging, lithium ions can be absorbed on the surface and intercalated into the RGO structure to form the lithium-carbon compounds. At the same time, the ionic liquid C₈mim⁺ migrates towards the carbon electrode and the PF₆⁻ anions migrate and accumulate at the surface of lithium electrode. For the C₈mim⁺ cation, portions of the cations of the ionic liquid forms a double layer with the carbon electrode through electrostatic interaction while other cations of ionic liquid may decompose due to reduction and participating in the SEI’s formation. A few of the cations may combine with the RGO functional groups through some chemical reactions [97-98]. In Figure 4.3, two regions with different slopes can be seen in the voltage range of 1.25V - 3V and 0V - 1.25V in the first discharging profile, which reflects the processes of the formation of SEI and the intercalation of lithium ions. Upon charging, the cations and anions would be forced to move away from electrode.
Figure 4.3 Discharge/Charge profiles of Li/RGO (after 250 °C reduction process) half cells using different electrolytes: a) 0% C₈mimPF₆; b) 16.67% C₈mimPF₆; c) 25% C₈mimPF₆; d) 33.3% C₈mimPF₆; e) 50% C₈mimPF₆.

In figure 4.3a, it shows the first discharge capacity of 1000 mAh/g and the second discharge capacity of 600 mAh/g, which is much larger than the theoretical value of pristine graphite (372 mAh/g). This increased lithium storage capacity is a benefit of the RGO’s larger distance of adjacent carbon monolayers and some exfoliated graphene nanosheets. After the first discharging, the 1.25V sloping region disappeared suggesting this is an irreversible process which is reasonably attributed to the SEI’s formation and reaction saturation. In addition, the discharging sloping region below 1.25V shortened, indicating partially irreversible SEI formation and partial reversible lithium storage after the first cycle. Since there is no clear plateaus in graphite, but there is observed plateaus in the RGO discharging profiles, it suggests that all graphite was transformed into amorphous RGO and there is a relatively weak interaction between the lithium ions and the RGO anode materials.
SEI’s formation is the consequence of electrolyte decomposition and lithium reaction with the remaining function groups on RGO. The merit of the formation of the SEI is to protect the electrode material from the further corrosion. The SEI is a thin, ionic conducting and electronic insulating layer, which has good chemical and electrochemical stability. The drawback of the SEI formation is the irreversible consumption of lithium ions, causing the capacity loss in practical LIB and LIC systems [99-100].

With the addition of IL to the lithium electrolyte, the discharge and charge characteristics do not change except for the absolute discharge and charge capacity values (see figure 4.3b-e).

**Figure 4.4** summarizes the first complete cycle (0-3V) and partial cycles (1.25-3V, 0-1.25V) discharge capacities as a function of IL content. The partial cycle’s capacities above 1.25V in the first discharging profiles weakened with the increasing of ionic liquid. Hindrance of SEI formation can be seen clearly with the presence of ionic liquid. It is hypothesized that this phenomenon was caused by the factors of the large cation of ionic liquids absorbed on the surface of RGO’s nanostructure, blocking of organic solvent decomposition and lithium ions’ intercalation in this voltage range. Further reducing the voltage to 0V, there is slight capacity increase in the 16.67% sample but a rapid capacity fading with the further addition of IL. These results indicate that addition of amount of IL into electrolyte can significantly reduce lithium storage capacity attributing to the blocking of active site by IL cations, less than optimal SEI layer, and reduction of electrolyte conductivities etc.
Figure 4.4 The summarization of first cycle discharge capacitances (total between 0-3V, portion above 1.25V and portion below 1.25V) as a function of IL content in the electrolytes.

As discussed previously, too many IL cations adsorbed will not only block the organic solvent decomposition but also lithium adsorption which will reduce the effective lithium ions available for storage and hence the reversible capacity. This is seen in figure 4.4 showing the first total discharge capacity decreases with the addition of IL in the electrolyte. Figure 4.5 plots the discharge capacities obtained at the second and the fifth cycles. It follows the same trend, i.e. increasing IL content will reduce reversible lithium storage capacities in RGO.
Figure 4.5 The specific discharging capacities obtained at the 2\textsuperscript{nd} (blue line) and 5\textsuperscript{th} (orange line) cycles as a function of IL content in the electrolytes.

The charge over discharge Coulombic efficiencies of the first cycle and the fifth cycle as a function of the IL content in the electrolyte are summarized in figure 4.6. The first cycle’s Coulombic efficiency is relatively lower than the following cycles because of the consumption of the lithium ions for the formation of SEI. After the first cycle, the Coulombic efficiency of most samples are higher than 75%. With increasing IL content in the electrolyte, the first Coulombic efficiency gradually decreases suggesting most cations are participating in the irreversible SEI formation on the RGO electrode. This is not favorable for LIB application.
Figure 4.6 The summarization of Coulombic efficiencies during the 1st and 5th discharge/charge cycling changing with IL content in the electrolytes.

4.3.3 Influences of ILs on energy storage in RGO-based LIC full cell setting

As the previously aforementioned in the experimental section, the anode in the LIC needs to be pre-lithiated. All the anodes to be used in the five LIC testing cells were pre-lithiated RGOs with the first discharge capacities of 1.167 mAh, 1.202 mAh, 1.117 mAh, 1.226 mAh, and 1.071 mAh, respectively, conducted in the Li//LiPF₆/EC/DEC//RGO half cells. The specific capacities are all in the range of 700 mAh/g – 801.5 mAh/g. Considering the 56% Coulombic efficiency as discussed in the previous section, the net reversible lithium capacities are 392 mAh/g – 448.8 mAh/g, equivalent to lithium stored in the carbon
at the formula of Li$_x$C where $x = 0.18$ to 0.20. The Table 4.2 shows pre-lithiation lithium levels of the anode used in the five LIC cells.

Table 4.2 Five LIC testing cells: the three key components used in the different Swagelok cells.

<table>
<thead>
<tr>
<th>LIC</th>
<th>Cathode: RGO</th>
<th>Electrolyte</th>
<th>Anode: prelithiated RGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIC1</td>
<td>C</td>
<td>LiPF$_6$/EC/DEC</td>
<td>Li$_{0.19}$C</td>
</tr>
<tr>
<td>LIC2</td>
<td>C</td>
<td>20 vol% C$_8$mim PF$_6$</td>
<td>Li$_{0.20}$C</td>
</tr>
<tr>
<td>LIC3</td>
<td>C</td>
<td>50 vol% C$_8$mim PF$_6$</td>
<td>Li$_{0.18}$C</td>
</tr>
<tr>
<td>LIC4</td>
<td>C</td>
<td>70 vol% C$_8$mim PF$_6$</td>
<td>Li$_{0.20}$C</td>
</tr>
<tr>
<td>LIC5</td>
<td>C</td>
<td>100 vol% C$_8$mim PF$_6$</td>
<td>Li$_{0.18}$C</td>
</tr>
</tbody>
</table>

The galvanostatic tests were performed on the five LIC systems. The charge/discharge profiles obtained at the different charge voltages, 3.0V and 4.5V are presented in figure 4.7a and b. For better observation, all absolute value of working voltages in 20%, 50%, 70%, and 100% groups added at the interval of 3.0V or 4.5V, respectively. For the first four completed cycles performed on each sample, all exhibited the asymmetric triangle shaped discharge-charge plots denoting the combination of faradic and non-faradic reaction.

The specific capacitance, energy density, and power density were calculated using the equation 4-2 where the $\Delta t$, I, V, and M represent the discharging time (in seconds), working current (in amperes), working voltage (in volts), and total effective mass of anode and cathode (in grams); and $C_{SP}$, E and P represent the specific capacitance, energy density and power density respectively. [101-102].

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\[ C_{SP} = \frac{\Delta t I(A)}{V(v) M}; \quad E = \frac{\Delta t V(v) I(A)}{M}; \quad P = \frac{V(v) I(A)}{M} \quad (4-2) \]

Seen in figure 4.8, the Coulombic efficiencies for all five LIC systems are over 85% with most over 95% when the charging voltage is limited to 3.0V. The efficiency did not change significantly with the increasing of cyclic number. However, with the increasing of the working voltage, the first cycles’ Coulombic efficiency decreases dramatically. For instance, at 4.5V with 20 vol% IL or 50 vol% electrolytes, the first efficiencies decreased to 50-60%. Even with the increase in the following cycles, the net efficiency is still less than 85%. When pure lithium electrolyte was used, the Coulombic efficiency was reduced to 35% and remained less than 70% at the fourth charge/discharge cycle. In short, the LICs made of electrolyte with higher ratio of ionic liquid have higher Coulombic efficiency and lower efficiency variation between the first and following cycles at the voltage of 4.5V. The decreasing of the first cycle efficiency was mainly caused by the decomposition of electrolyte and formation of SEI. As discussed previously in electrochemical stability tests, organic solvents in lithium electrolyte can readily decompose at a voltage above 4.0V while IL can remain stable above 9V after the initial decomposition and SEI formation.
Figure 4.7 Galvanostatic charge/discharge behavior of five different LIC systems obtained at the constant discharging/charging current 0.1 mA but different charge voltage a) 0 to 3V; b) 0 to 4.5V.
In **figure 4.9**, the specific capacitance of different samples are exhibited. At 3V (**figure 4.9a**), it can be detected that the sample with a pure lithium electrolyte (with no IL) has the highest capacitance values. The reason was caused by the higher conductivity of the neat lithium electrolyte. It was proven that the capacity of RGO reach the maximum values without any combination of ionic liquid, and hence the capacitance in neat LiPF₆/EC/DEC sample showed the best performance.

In the capacitance plots obtained at 4.5V (**figure 4.9b**), it can be observed that the 20% sample has the highest capacitance because of the influence of the conductive parts were in the electrolyte, and the combination of faradic and non-faradic reactions on the anode side of the LIC system optimized the capacitance of the LIC. On the contrary, the 50% sample showed the worst capacitance. According to the conductivity tests, the cations and anions of the ionic liquid have a maximum number at the 50% sample, the non-faradic reactions dominated on the anode side of LIC; and based on the equation **4-2**, non-faradic reaction would shorten the discharging time; hence the capacitance was decreased.

In this study, the absolute capacitance values were relatively lower than those in published data. There are many factors possibly contributing to this. Likely primary reason is, the aggregation of the adjacent carbon layers of the graphene oxide after the reduction process existed; the residual functional groups after the reduction can influence the ions’ absorption/desorption during charging and discharging. Additionally, impurities in RGO’s synthesizing process was also a reason for the decrease in capacitance of LIC systems. Finally, the electrode material in this experiments was only based on RGO. Other researchers utilized several types of additives, such as manganese oxide, silicon oxide or carbon black, which was usually blended with carbon based materials for enhancement of
the ion’s mobility and conductivity. However, the lower capacitances of LIC systems did not affect the operation of different types’ electrolytes directly.

**Figure 4.8 a)** The Coulombic efficiency of different samples on the four complete cycles at 3V; **b)** The Coulombic efficiency of different samples on the four complete cycles at 4.5V.
Figure 4.9  a) Specific capacitance of different LiPF$_6$/EC/DEC-ionic liquid systems at 3V; b) Specific capacitance of different LiPF$_6$/EC/DEC-ionic liquid systems at 4.5V.
Figure 4.10 a) Energy density of different LiPF$_6$/EC/DEC-ionic liquid systems at 3V; b) Energy density of different LiPF$_6$/EC/DEC-ionic liquid systems at 4.5V.
In **Figure 4.10**, the energy densities of LIC using different IL hybrid electrolytes are summarized. The variations of energy density with IL content is similar to the changing of capacitance in each LIC system. The general relationship can be seen that the energy density increases with the increasing of working voltage. In **Figure 4.10a**, the energy density of neat traditional lithium salt system is still the highest than others because of the electrochemical reaction’s domination on the anode side; and during the absorption-desorption processes of ions, the diffusion time in faradic reaction is much larger than the non-faradic one. On the other hand, the higher conductivity’s influence in neat lithium salt group is still the reason which causes the larger values of energy density. In **Figure 4.10b**, the energy density in 20% sample has the highest value because of the optimized combination of faradic and non-faradic reactions.

It is demonstrated experimentally that the increasing in working voltage is an effective way to enhance the energy density from 43.24 Wh/Kg to 188 Wh/kg in the 20% sample; the power density also increased from 49 W/kg to 73.53 W/kg at 3V and 4.5V respectively.

### 4.4 Summary

In this study, RGO powders were synthesized using Hummer method and characterized as a function of the thermal reduction temperatures. RGO reduced at 250°C was found to the least amount of restacking and was selected as the anode in LIB and LIC systems.

The lithium storage capacity in the RGO was tested in half-cells with the addition of the ionic liquid C₈mim PF₆ to the traditional lithium ion conducting electrolyte. It is clear that the ionic liquid can hinder the SEI formation leading to reduced capacity loss above
1.25V but not significantly below 1.25V. Meanwhile, due to the adsorption of IL cations on RGO occupying the active sites, lithium storage capacity is reduced. Hence, the net irreversible discharging capacity, reversible capacity, and the first cycle’s Coulombic efficiency decrease with the increase of the ionic liquid.

Further, LICs made of different IL-lithium electrolyte hybrids are examined. At low voltage limits such as 3V, traditional electrolyte is the best choice for its high conductivity. Addition of IL will continuously reduce the specific capacitance and energy density. However, when increasing the voltage limit up to 4.5V for example, addition of IL will be beneficial because the traditional electrolyte starts to decompose around 4V. Slight addition of IL to the traditional electrolyte up to 20% can result in higher charge storage on the surface of RGO. Consequently, the specific capacitance and energy storage increases significantly. However, an excessive amount of ionic liquid blended in the electrolyte can weaken the capacitance and energy density of LIC systems. The optimized faradic and non-faradic reactions on the anode electrodes through tuning electrolyte with the help of ionic liquid in LIC can enhance the capacitance and energy density of LIC systems effectively.


Chapter 5: Summary of the Thesis Research

In this research, the neat ionic liquid, 1-methyl-3-octylimidazolium tetrafluoroborate ($\text{C}_8\text{mim BF}_4$), 1-methyl-3-octylimidazolium hexafluorophosphate ($\text{C}_8\text{mim PF}_6$) and 1-methyl-3-octylimidazolium chloride ($\text{C}_8\text{mim Cl}$), and their hybrids have been studied systematically with ionic conduction, electrochemical stability, and energy storage in reduced graphene oxides to assess their potential applications to lithium ion batteries and lithium ion capacitors.

Among the three neat ionic liquids, the increasing conductivities of these ILs have the order of $\text{C}_8\text{mim BF}_4 > \text{C}_8\text{mim PF}_6 > \text{C}_8\text{mim Cl}$. This phenomenon is attributed to the chemical and ionic sizes’ differences of the three anions in these ILs, which influence the coordination and possible hydration.

Since the conductivity values of the neat ionic liquids are insufficient for the practical applications to LIB, LIC and EDLC systems, an organic solvent with high dielectric constant, i.e. DEC, was added into the ionic liquid and the solvent-solvent interactions had been researched. Upon adding of DEC, the conductivity of the IL hybrid was increased by over an order of magnitude, reaching 0.3 S/m at room temperature.

Furthermore, the ionic conductivity of LiPF$_6$/EC/DEC-ionic liquid hybrid systems were examined. In general, the behaviors of hybrid systems were improved with increasing temperature and increasing of volume percent of the lithium salt. It is interesting to observe a conductivity peak at 50 vol % hybrid. This is attributed to a synergetic
interaction between the lithium electrolyte and the ionic liquid: 1) the addition of IL reduced the net value of its low conductivity, and 2) lithium salt and organic solvent like EC and DEC existing in the lithium electrolyte increased dissociation of cations and anions in ILs.

DEC did not significantly affect the electrochemical stability of the electrolyte. The electrochemical stability potentials of DEC-ionic liquid hybrid systems are around 10V. In the hybrid systems of lithium salt electrolyte-ionic liquids, obvious reduction and oxidation peaks can be observed and CV behaviors are different between the first cycle and subsequent cycles. Traces of moisture can decompose in IL starting at 4V and reaching a maximum around 7V during the first cycle. After the first cycle, neat IL and electrolyte with high IL concentration can be stable up to 9V vs Li anode. In contrast, lithium ion organic electrolytes will decompose on both cathode and anode corresponding to the SEI’s formation. The C₈mim PF₆ systems showed better electrochemical stability than the C₈mim BF₄.

Finally, it was found that the addition of the ionic liquid C₈mim PF₆ into traditional lithium electrolyte increased irreversible capacity loss and reduced the intercalation and dis-intercalation of lithium ions because of its relatively low conductivity and the influence of SEI formation at the interface of the electrolyte and electrodes. In the LIC, with both RGO as active anode and cathode, the capacitance of the neat lithium salt system showed the best performance under 3V. However, when the working voltage was increased to 4.5V, the electrolyte with 20 vol% IL exhibited its best performance because the optimization of both faradic and non-faradic reactions. It is hypothesized that IL may affect the formation of SEI, which is a drawback for LIB at low potential but a benefit for LIC because of high
electrochemical stability potential. Therefore, addition of the appropriate amount of ionic liquid can enhance the performance of the LIC or LIB systems.
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