

## ABSTRACT

Azeez, Fadhel Abbas, Transport Properties of Lithium bis(Oxalato)Borate-Based Electrolyte for Lithium-Ion Cells. ( Under the direction of Prof. Peter S. Fedkiw)

The need for compact, light weight rechargeable batteries offering high-energy densities has become necessary in the 21<sup>st</sup> century especially for portable electronics devices, hybrid electric vehicles, and load leveling in electric power generation/distribution. Among rechargeable batteries, lithium-based systems seem to be able to fulfill these needs.

The current state-of-art electrolyte of LiPF<sub>6</sub> dissolved in organic-carbonate solvents has disadvantages in low-temperature and high-temperature environments. At high temperature, the thermal instability of LiPF<sub>6</sub> is believed to be the main cause for the poor performance of lithium-ion batteries. At low temperature, the high viscosity of ethylene carbonate, which is a major component in the solvent mixture of state-of-art electrolyte, restricts the use of electrolyte to above -20 °C. These factors restrict the operation of lithium-ion batteries to be between -20 and 60 °C.

In an attempt to improve the performance of lithium-ion cells, we use a stable salt at high temperature, Lithium bis(oxalato)borate (LiBOB), and dissolve it in mixtures of  $\gamma$ -butyrolactone (GBL), ethyl acetate (EA), and ethylene carbonate(EC). The conductivity and

viscosity are measured for LiBOB in such mixtures as function of salt concentration, solvent composition, and temperature.

We find that LiBOB in a mixture of GBL + EA + EC yields a technologically acceptable conductivity, and it is an acceptable candidate for lithium-ion cells. For example, LiBOB based-electrolyte with a salt concentration of 0.7 M LiBOB in a GBL: EA: EC (wt ) composition of 1:1:0 has a conductivity  $\sim 6 \text{ mS cm}^{-1}$  at  $-3 \text{ }^\circ\text{C}$ , and at 1 M LiBOB in solvent composition of 1:1:0.1, the conductivity is  $\sim 22 \text{ mS cm}^{-1}$  at  $74 \text{ }^\circ\text{C}$ . The product of conductivity with viscosity was essentially independent of temperature but was dependent on solvent composition. Results from this study encourage us to examine in future studies the performance of full and half cells using LiBOB-based electrolyte to see if it can be used in lithium-ion cells.

**TRANSPORT PROPERTIES OF LITHIUM  
BIS(OXALATO)BORATE-BASED ELECTROLYTE  
FOR LITHIUM-ION CELLS**

By

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## **PERSONAL BIOGRAPHY**

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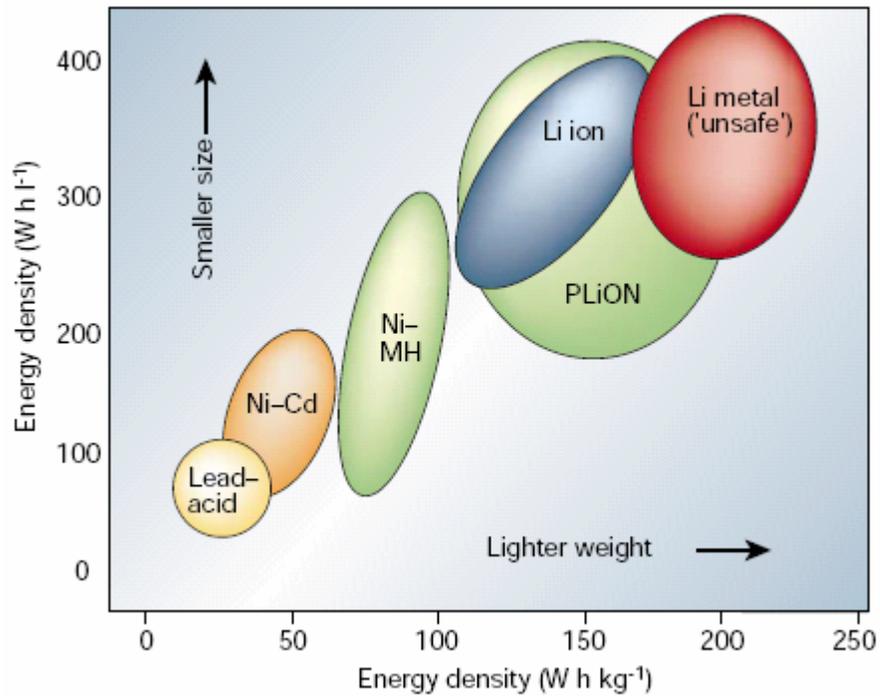
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# CHAPTER 1: AN OVERVIEW ON LITHIUM-ION BATTERIES

## 1.1. Introduction

The growth in portable electronics devices such as cellular phones and laptop computers during the past decade has created huge interest in compact, light weight batteries offering high energy densities that show good re-chargeability and reliability. In addition, strengthened environmental regulation and a more rational use of available energy resources prompt the development of advanced batteries for electric vehicles.

In portable devices, initially the rechargeable Ni-Cd battery took the biggest market share since its discovery in the last century. However, the environmental concerns of Cd and the low capacity of Ni-Cd cells have stimulated the development of Ni-MH batteries, which use hydrogen storage alloys as anodes. The Ni-MH battery started production first around 1990 and the demand for the Ni-MH battery keeps increasing. However, both the Ni-Cd and Ni-MH batteries have low cell voltages (~1.35 V). On the other hand, lithium batteries provide cell voltages as high as 4 V, and following the announcement of Sony Inc in 1990, rechargeable lithium batteries have captured the market share. The higher voltage of lithium cells lead to a higher volumetric and gravimetric energy density. The energy densities of the various secondary battery systems are compared in Figure 1.1 <sup>1</sup>, which clearly shows that the lithium batteries are smaller and lighter compared to other rechargeable system. In what follows, I First give some basic overview about batteries and then I focus on lithium and lithium-ion batteries.



**Figure 1.1. Comparison of the gravimetric and volumetric energy densities of rechargeable lithium batteries with those of other systems <sup>1</sup>**

## 1.2. What is a battery

A battery is an electrochemical device that converts chemical energy into electricity, by use of a galvanic cell. A galvanic cell is a fairly simple device consisting of two electrodes (an anode and a cathode) and an electrolyte solution. Batteries consist of one or more galvanic cells. Batteries can be classified to two types according to their ability of recharging:

1. Primary batteries
2. Secondary batteries

### **1.2.1. Primary battery**

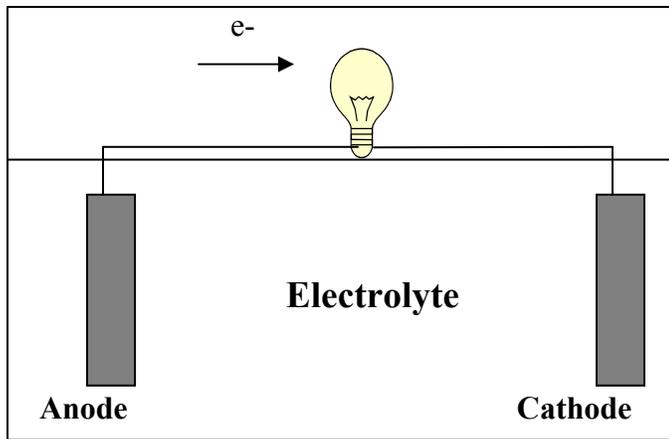
A primary battery is a battery that is designed to be used only once; it can not be recharged again. The amount of energy it can deliver is limited to that obtainable from the reactants that were placed in it at the time of manufacture.

### **1.2.2. Secondary battery**

A secondary battery (rechargeable battery) can be recharged and used again after being fully discharged. Its electrode reactions can proceed in either direction. During charging, electrical work is done on the cell to provide the free energy needed to force the reaction in the non-spontaneous direction. It is usually designed to have a lifetime of between 100 and 1000 recharge cycles, depending on the composite materials. Secondary batteries are, generally, more cost effective over time than primary batteries, since the battery can be recharged and reused.

### **1.2.3. How does a battery work?**

Figure 1.2 shows a simple galvanic cell. Two electrodes are placed in an electrolyte solution. External wires connect the electrodes to an electrical load. During the discharge, an anode, where the oxidation is occurring, release electrons. These electrons flow to the cathode where they get accepted by the reduction reaction. In the same time there is a flow of anions and cations to the anode and cathode, respectively. When the anode is fully oxidized or the cathode is fully reduced, the chemical reaction will stop and the battery is considered



**Figure 1.2. Galvanic cell during discharge process**

to be discharged. Recharging a battery is usually a matter of externally applying a voltage across the plates to reverse the chemical process.

The voltage and current that a galvanic cell produces are directly related to the types of materials used in the electrodes and electrolyte. The length of time the cell can produce that voltage and current is related to the amount of active material in the cell and the cell's design. Every metal or metal compound has an electromotive force, which is the property of the metal to gain or lose electrons in relation to another material. Compounds with a positive electromotive force will make good cathodes and those with a negative electromotive force will make good anodes. The larger the difference between the electromotive forces of the anode and cathode, the greater the amount of energy that can be produced by the cell. Table 1.1 shows the electromotive force of some common battery components. Over the years, battery scientists have experimented with many different combinations of material and have generally tried to balance the potential energy output of a battery with the cost of

manufacturing. Other factors, such as battery weight, shelf life, and environmental impact, also enter into a battery's design.

**Table 1.1. The electromotive series for some battery components**

<b>Anode Materials from worst (most positive) to best (most negative)</b>	<b>Cathode Materials from best (most positive) to worst (most negative)</b>
Gold	Ferrate
Platinum	Iron oxide
Mercury	Cuprous oxide
Palladium	Iodate
Silver	Cupric oxide
Copper	Mercuric oxide
Hydrogen	Cobaltic oxide
Lead	Manganese oxide
Tin	Lead oxide
Nickel	Silver oxide
Iron	Oxygen
Chromium	Nickel oxyhydroxide
Zinc	Nickel dioxide
Aluminum	Silver peroxide
Magnesium	Permanganate
Lithium	Bromate

#### **1.2.4. Galvanic cells vs. batteries**

A battery is one or more galvanic cells connected in series or in parallel. A battery composed of two 1.5 V galvanic cells connected in series, for example, will produce 3 V. A typical 9 V battery is simply six 1.5 V cells connected in series. Such a series battery, however, will produce a current that is the equivalent to just one of the galvanic cells. A battery composed of two 1.5 V galvanic cells connected in parallel, on the other hand, will still produce a voltage of 1.5 V, but the current provided can be double the current that just one cell would create. Such a battery can provide current twice as long as a single cell. Many galvanic cells can be thus connected to create a battery with almost any current at any voltage level.

#### **1.3. History of lithium batteries**

Lithium has the lightest weight, highest voltage, and greatest energy density of all metals. The theoretical specific capacity of lithium is 3860 mAh/g and the redox potential is -3.01 V versus standard hydrogen electrode. These features have attracted battery investigators. Research into lithium batteries started in 1950s when it was discovered that metallic lithium was stable in a number of nonaqueous electrolytes such as fused salts, liquid SO<sub>2</sub>, or organic electrolytes such as LiClO<sub>4</sub> in propylene carbonate. This stability was due to the formation of a passivation layer that prevents the direct chemical reaction between metallic lithium and the electrolyte but still allows for ionic transport. The first published interest in lithium batteries started with the work of Harris in 1958<sup>2</sup>. The work eventually led

to the development and commercialization of a variety of primary lithium cells during the 1970s.

The higher energy densities associated with lithium batteries motivated huge interest to develop lithium insertion compounds as cathodes for rechargeable lithium batteries. Studies of fast-ion conduction in solids showed that alkali metal ion could move quickly in an electronically conducting lattice containing transition metal atoms in a mixed-valence state. This led to the development of room temperature rechargeable lithium cells using lithium insertion compounds as positive electrode. In the mid 1970s, Exxon announced its intentions to commercialize the system Li/TiS<sub>2</sub><sup>3</sup>. Since then, large numbers of rechargeable systems with different cathode materials using either transition metal chalcogenides (TiS<sub>2</sub>, MoS<sub>2</sub>, NbSe<sub>3</sub>) or transition metal oxides (V<sub>2</sub>O<sub>5</sub>, V<sub>6</sub>O<sub>13</sub>, MnO<sub>2</sub>), different metallic lithium or lithium alloy based anodes and electrolytes have been investigated and developed, as illustrated in Table 1.2<sup>4</sup>. Of these, the rechargeable Li/MnO<sub>2</sub> “Molice” AA size cell manufactured by Moli Energ. Ltd. (British Columbia, Canada) in the late 80s was probably the most sophisticated. product Apart from a few small size secondary coin cell products, these chemistries have not generally survived into the 1990s. Cells with AA and larger size have proved difficult to make safe and there have been incidents of fires in equipment powered by secondary Li/MoS<sub>2</sub> cells which led to a product recall. A big achievement in the rechargeable lithium battery systems was in June 1990 when Sony Energytec Inc. commercialized a lithium-ion battery including a LiCoO<sub>2</sub> cathode and a non graphitic carbon anode. This battery was much safer than Li metal anode batteries.

**Table 1.2. Sequence development of components and systems for rechargeable lithium batteries <sup>4</sup>**

Overview of the sequence of development of components and systems for rechargeable lithium batteries (LE stands for liquid organic electrolyte, PE for polymer electrolytes).

Year	Development of components			Systems
	anode	cathode	electrolyte	
1970's	lithium metal (Li) lithium alloys	transition metal sulfides (TiS <sub>2</sub> , MoS <sub>2</sub> )	liquid organic electrolytes	Li/LE/TiS <sub>2</sub>
		transition metal oxides (V <sub>2</sub> O <sub>5</sub> , V <sub>6</sub> O <sub>13</sub> ) liquid cathodes (SO <sub>2</sub> )	solid inorganic electrolytes (Li <sub>3</sub> N)	Li/SO <sub>2</sub>
1980's	Li-intercalation (LiWO <sub>2</sub> )  Li-carbon (LiC <sub>12</sub> ) (coke)	selenides (NbSe <sub>3</sub> ) discharged cathodes (LiCoO <sub>2</sub> , LiNiO <sub>2</sub> )	polymer electrolytes	Li/LE/MoS <sub>2</sub> Li/LE/NbSe <sub>3</sub> Li/LE/LiCoO <sub>2</sub>
		manganese oxide (Li <sub>x</sub> MnO <sub>2</sub> )	plasticized polymer electrolytes	Li/PE/V <sub>2</sub> O <sub>5</sub> , V <sub>6</sub> O <sub>13</sub>
1990's	Li-carbon (LiC <sub>6</sub> ) (graphite)	manganese spinels (LiMn <sub>2</sub> O <sub>4</sub> )		Li/LE/MnO <sub>2</sub> C/LE/LiCoO <sub>2</sub>
				C/LE/LiMn <sub>2</sub> O <sub>4</sub>

### 1.3.1. Problems with metallic lithium anode

Although metallic lithium anodes offer a greater energy capacity (3860 mAg/h) than lithiated carbon (372 mAg/h), difficulties stem from using metallic lithium as anode inhibit its development. The problem of using metallic lithium is its reactivity with the electrolyte and changes to its surface morphology after repetitive charge/discharge cycling. For example, when lithium is electroplated during recharge onto a metallic lithium electrode, it forms a mossy, and in some cases dendritic, deposit with a larger surface area than the original metal. While the thermal stability of lithium metal foil in many organic electrolytes is good, with minimal exothermic reactions occurring up to temperature near the melting

point of lithium (181°C), the large surface area of dendrites increases lithium reactivity, thereby lowering the thermal stability of the system. This makes cells become increasingly sensitive to abuse as they are cycled. In addition, the fine metallic lithium can easily penetrate into the separator which can cause an internal short circuit, resulting in heat generation and ignition.

Another problem is the failure of attaining 100% lithium cycling efficiency. This occurs because lithium is not thermodynamically stable in the organic electrolytes and the surface of lithium is covered with a film of reaction products between the lithium and electrolyte. Every time the lithium is stripped and replaced during discharge and charge, a new lithium surface is exposed and then passivated with a new film, which mean more lithium is consumed. Because of the mossy deposit, some lithium becomes electrochemically unreactive on repeated cycling. In order to obtain a reasonable cycle life, a 3 to 5 fold excess of lithium is required. The failure to control the surface area of the lithium anode remains a problem, limiting the commercialization of lithium anode cells with liquid organic electrolytes.

The reactions of lithium electrode with electrolyte were studied extensively and this included a number of strategies to modify the reactivity of the lithium solution interface and thus improve its utility and safety. The best strategy was to eliminate metallic lithium anode and replace it with lithiated carbon. In early 1990 Sony Energy commercialized the first lithium-ion battery. The theoretical specific capacity of the lithiated graphite  $\text{LiC}_6$  is only 372 mAh/g, much lower than that of metallic lithium (3860 mAh/g). In spite of the lower energy density, the current rechargeable lithium battery (lithium-ion battery) technology uses a

lithiated carbonaceous anode <sup>5-7</sup> since it offers a significant advantage in terms of safety and cycle life.

### 1.4. Lithium-ion batteries

In early 1990, a breakthrough was announced by Sony Energy Tech.: an anode based on lithium intercalated carbon or graphite for rechargeable lithium battery. These cells, which contain lithium insertion compounds as both cathodes and anodes, are called lithium-ion cells or rocking chair cells since the lithium ion shuttles or rocks between the cathode and anode hosts during the charge/discharge process as illustrated in Figure 1.3. <sup>8</sup>

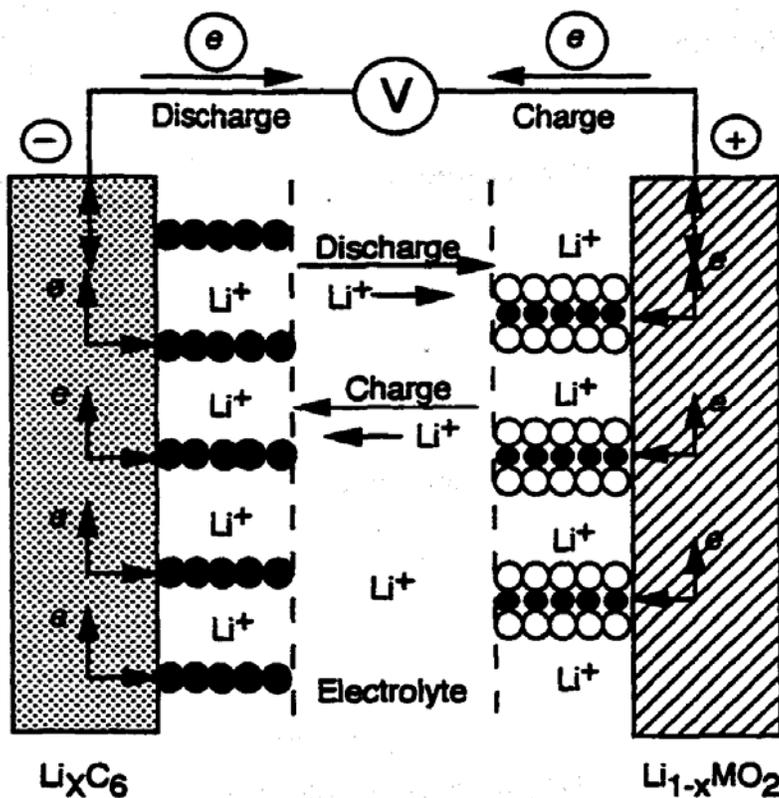


Figure 1.3. Lithium-ion battery operation <sup>8</sup>

During charge, the positive material (cathode) is oxidized and the negative material (anode) is reduced. In this process, lithium ions move from cathode to anode through the electrolyte and electrons flow through the external circuit from the cathode to the anode. The reverse reaction occurs during the discharge process.

Lithium-ion batteries typically consist of (i) a graphite negative electrode (anode) on a copper current collector, (ii) a lithium metal oxide positive electrode (cathode) typically a metal oxide with a layered structure, such as lithium cobalt oxide ( $\text{LiCoO}_2$ ), or a material with a tunneled structure, such as lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), on a current collector of aluminum foil, (iii) a microporous separator between the electrodes, and (iv) a liquid electrolyte that consists of a lithium salt dissolved in an organic solvent. Typical electrolytes are composed of  $\text{LiPF}_6$  salt dissolved in organic-carbonate solvent. The separator does not support ion conductivity itself, but instead allows lithium ions in the electrolyte to move between the electrodes and diffuse into the porous structure of the electrodes.

The lithium-ion battery is currently replacing all other battery types in the market, particularly in the field of electronics, computers, and communications. In recent years, the application of lithium-ion batteries for more power demanding applications such as power tools, stationary, and transportation has started.

In lithium-ion cells, the anode and cathode insertion hosts should have low and high voltages, respectively, versus metallic lithium in order to maximize the cell voltage while satisfying the other required criteria. Accordingly, among the various known lithium insertion compounds,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMnO}_4$  oxides having a high electrode potential of 4V versus metallic lithium have become attractive cathodes for lithium-ion cells. On the

other hand, graphite and coke having a lower electrode potential of <1V versus metallic lithium and being lightweight have become attractive anodes, as illustrated in Figure 1.4 <sup>8</sup>.

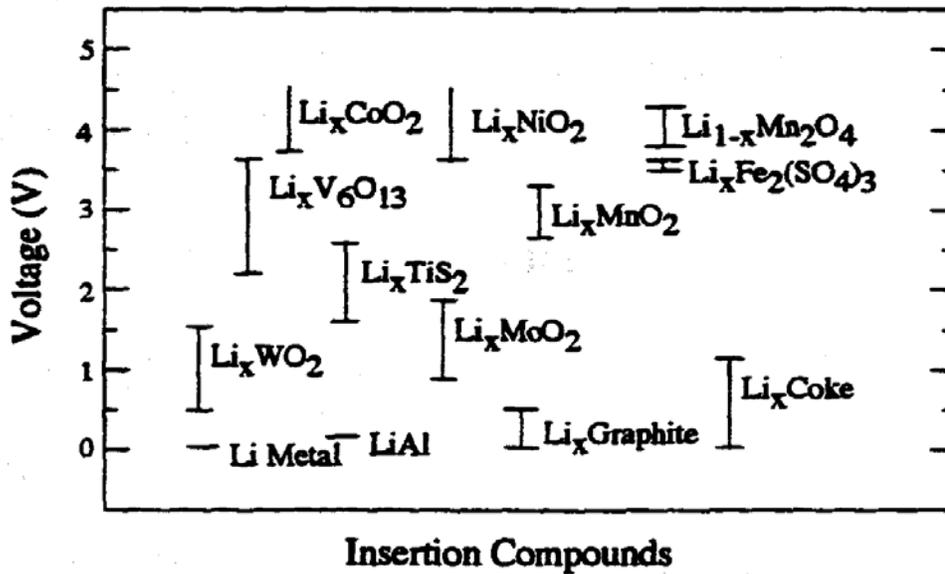


Figure 1.4. Electrochemical potential ranges of some lithium insertion compounds in reference to metallic lithium <sup>8</sup>

The first batteries to be marketed, and the majority of those currently available, use LiCoO<sub>2</sub> as the positive electrode material since LiCoO<sub>2</sub> offers good electrical performance, is easily prepared, has good safety properties, and is relatively insensitive to process variation and moisture. More recently lower cost or higher performance materials, such as LiMn<sub>2</sub>O<sub>4</sub> or lithium nickel cobalt oxide (LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub>), have been introduced, permitting development of cells and batteries with improved performance. The batteries that were first commercialized employed cells with coke negative electrode materials. As improved graphite became available, the industry shifted to graphitic carbons as negative electrode materials as they offer higher specific energy with improved cycle life and rate capability.

## **1.5. Features and benefits of lithium-ion cells**

Rechargeable lithium-ion batteries offer significant advantages compared to Ni-Cd and Ni-MH cells. Li-ion batteries are lighter, about half the weight of Ni-Cd batteries, 30-50% smaller in volume, yet have a life span and energy density nearly twice that of Ni-Cd batteries. Lithium-ion batteries also do not suffer from many of the problems of Ni-Cd batteries. For example, Ni-Cd batteries show a self-discharge (capacity loss during storage due to internal leakage between the positive and negative cell plates) of 20-30% over a month, compared to the 5% of a Li-ion battery. Lithium batteries recharge more quickly, with an 80% charge (1C, a discharge of 1C draws a current equal to the rated capacity) in an hour, and full charge within 2.5 hours. Lithium-ion cells also do not present environmental hazards (i.e., those with lithium manganese oxide cathodes), especially compared with Ni-Cd batteries, because they contain no lead, cadmium or mercury. Most importantly, Li ion batteries have no memory effect; memory effect refers to a change in crystalline formation from the desirable small size to a large size which leads to reversible capacity loss, which happens because of earlier incomplete charge/recharge cycles. For Ni-Cd batteries, memory effect is a serious issue. Lithium-ion batteries store three times the voltage of competing cells, so that a single 3.7V Li ion battery can replace three Ni-Cd or Ni-MH cells. By weight, Li-ion batteries provide roughly twice the energy density (~150 Wh/Kg) of Ni-Cd cells. Consequently, to provide the same output as a Ni-Cd or Ni-MH battery, a Li-ion battery will weigh about half as much, an important factor in portable equipment. By volume, Li-ion cells provide about 25% and 40% more energy (~400 Wh/L) than Ni-MH or Ni-Cd cells, respectively. The greater energy in a small volume is an important factor in some of the most

critical applications for batteries: laptop computers and cellular phones. In addition, Li-ion batteries have a wide temperature operating range. The lithium-ion cell can be charged between 0 and 45°C and discharged between -20 and 65°C. Also Li-ion cells can typically be discharged at rates up to 1.5C continuously. High capacity, higher drain multi-cell packs are achieved by connecting multiple cells in parallel – something which is not easily achieved when using Ni-Cd or Ni-MH cells. Finally, lithium-ion batteries offer long cycle life (greater than 1000 cycles). These features are summarized in Table 1.3<sup>9</sup>

**Table 1.3. General performance characteristics of lithium-ion batteries<sup>9</sup>**

Characteristic	Performance range
Operational cell voltage	4.2 to 2.5 V
Specific energy	100 to 158 Wh/kg
Energy density	245 to 430 Wh/L
Continuous rate capability	Typical: 1C High rate: 5C
Pulse rate capability	Up to 25C
Cycle life at 100% DOD	Typically 3000
Cycle life at 20 to 40% DOD	Over 20000
Calendar life	Over 5 years
Self discharge rate	2 to 10%/month
Operable temperature range	-40°C to 65°C
Memory effect	None
Power density	2000 to 3000 W/L
Specific power	700 to 1300 W/Kg

The most significant challenges to the broader application of lithium-ion technologies are related to stability at high temperature, safety, and low-temperature performance. While batteries may be exposed to temperature as high as 70 °C for short periods, the rate of degradation of current lithium-ion batteries is significant above 65 °C. At high temperatures lithium-ion batteries lose their capacity permanently.

## 1.6. Design principles

From a materials design point of view, the cathode and anode insertion compounds should satisfy several important criteria such as:

1. The cathode insertion compound should have a high Li chemical potential ( $\mu_{\text{Li}(c)}$ ) to maximize the cell voltage. This implies that the transition metal ion  $M^{n+}$  in  $\text{Li}_x\text{M}_y\text{X}_z$  should have a high oxidation state.
2. The anode insertion compound should have a low Li chemical potential ( $\mu_{\text{Li}(a)}$ ) to maximize the cell voltage. This implies that the transition metal ion  $M^{n+}$  in  $\text{Li}_x\text{M}_y\text{X}_z$  should have a low oxidation state.
3. The insertion compound  $\text{Li}_x\text{M}_y\text{X}_z$  should allow a large degree  $x$  of lithium insertion/extraction, to maximize the cell capacity. This depends on the number of available lithium sites and the accessibility of multiple valences for M in the insertion host. A combination of high capacity and cell voltage can maximize the energy density, which is given by product of the capacity and voltage.
4. The lithium insertion/extraction process should be reversible with no or minimal changes in the host structure over the entire range  $x$  of Li insertion/extraction in order to provide a good cycle life for the cell. This implies that the insertion compound  $\text{Li}_x\text{M}_y\text{X}_z$  should have good structural stability without breaking any M-X bonds.
5. The insertion compound should support mixed conditions. It should have good electronic conductivity  $\sigma_e$  and good lithium ion conductivity  $\sigma_{\text{Li}}$  to minimize polarization losses during the discharge/charge process and thereby to support a high current density and power density. Factors like crystal structure; geometry

and interconnection of the lithium sites; nature and electronic configuration of the  $M^{n+}$  ion; and the relative position of the  $M^{n+}$  and  $X^{n-}$  energies control if the insertion compound have good electronic and lithium ion conductivities.

6. The insertion compound should be chemically stable without undergoing any reaction with the electrolyte over the entire range,  $x$ , of lithium insertion/extraction.
7. The redox energy of the cathode and anode in the entire range,  $x$ , of lithium insertion/extraction should lie within the band gap of the electrolyte, as shown in Figure 1.5 <sup>8</sup>, to prevent unwanted oxidation or reduction of the electrolyte.
8. From a commercial point of view, the insertion compound should be inexpensive, environmentally benign, and lightweight. This implies that the  $M^{n+}$  ion should preferably be from the 3d transition series.

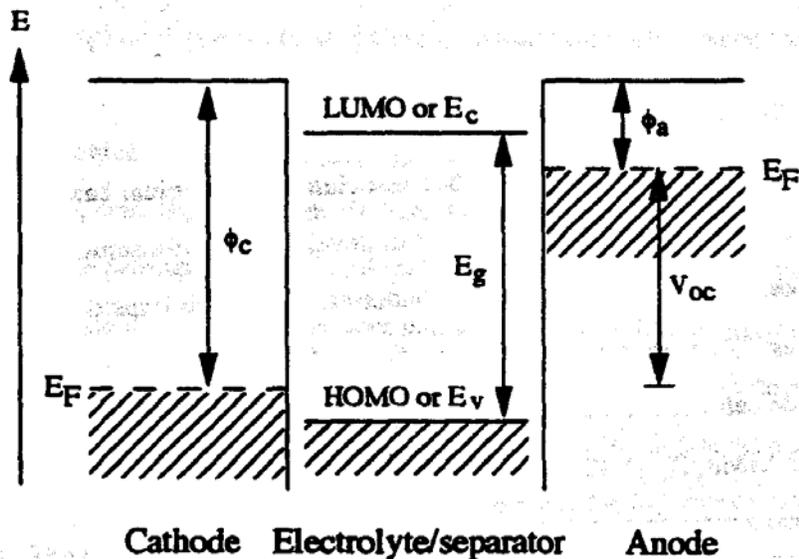


Figure 1.5. Schematic energy diagram of a cell at open circuit <sup>8</sup>

In addition to these requirements of insertion electrode materials, several other criteria are important in designing a good lithium-ion cell that can offer high performance with long cycle life. The electrolyte should have high lithium ion conductivity but should be an electronic insulator in order to avoid internal short circuiting. A high ionic conductivity in the electrolyte is essential to minimize IR drop or ohmic polarization and achieve good rate capability. With a given electrolyte, the IR drop due to electrolyte resistance can be reduced and the rate capability can be improved by having a higher electrode interfacial area and thin separators. The electrolyte should also have good chemical stability and should not undergo any chemical reaction with the electrodes. Additionally, the engineering involved in cell design and fabrication plays a critical role in the overall cell performance. For example, high electronic conductivity and lithium ion diffusion rate in the electrodes are essential to minimize cell polarization and the electronic conductivity of the electrodes can be improved by adding electronically conducting additives such as carbon. However, the amount of additive should be minimized to avoid any undue sacrifice in gravimetric or volumetric capacity. Finally, cell safety, environmental factors, and raw material fabrication costs are additional important considerations in both materials selection and cell design.

## **1.7. Lithium-ion battery components and their development**

A battery consists of a positive electrode (cathode), negative electrode (anode) and an electrolyte. In addition to these major active components, a separator between the cathode and anode compartments and current collectors attached to the electrodes are also involved. A brief discussion about these components and recent research to improve their performance is discussed in the following sections.

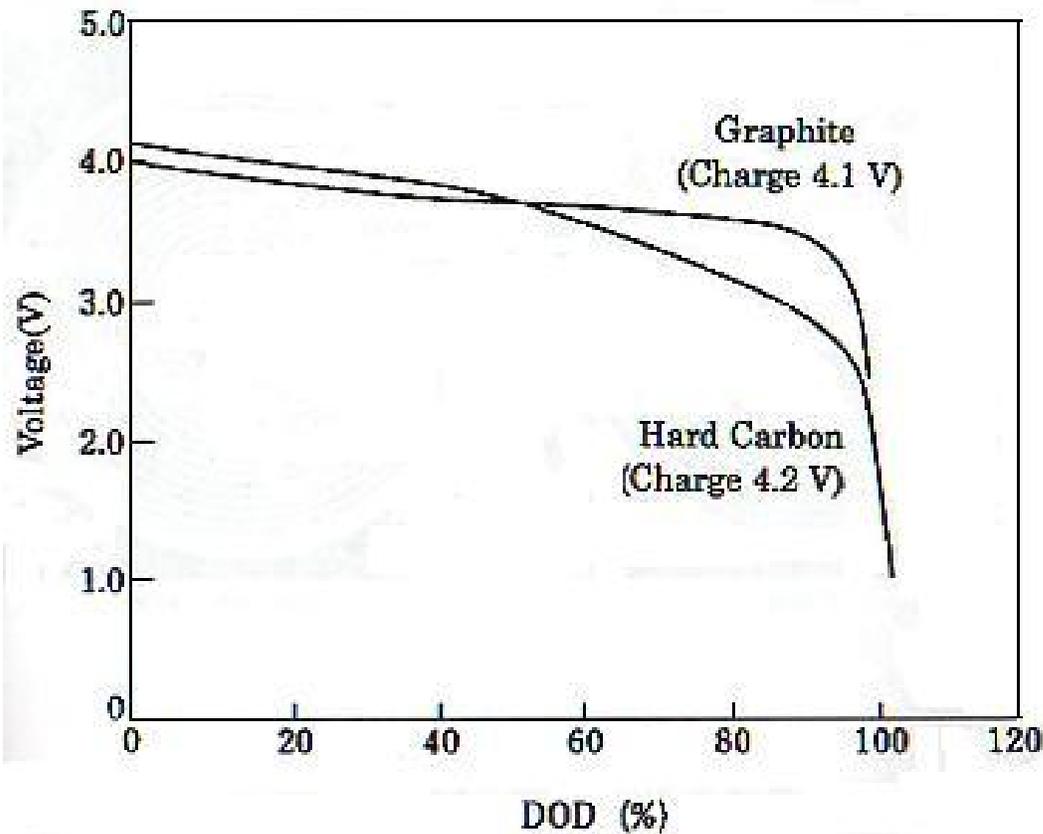
### 1.7.1. Anode hosts

Carbon is the material which is used for anode in the present generation of lithium-ion cells<sup>10, 11</sup>. The light weight and low electrochemical potential near that of metallic lithium (Figure 1.4) have made carbon an attractive anode. It has a theoretical capacity of 372 mAh/g, which corresponds to an insertion of one lithium per 6 carbon atom ( $x=1$  in  $\text{Li}_x\text{C}_6$ ).

One of the drawbacks with the carbon anodes is the occurrence of significant amount of irreversible capacity during the first charge-discharge cycle. During the first electrochemical intercalation of lithium into carbon, some lithium is irreversibly consumed forming a solid electrolyte interface (SEI) and cannot be recovered in the following discharge, resulting in loss of capacity. This SEI depends on the electrolyte solution and the type of carbon material. When the film is sufficiently thick to prevent electron tunneling, the electrolyte reduction is suppressed and the electrode can be cycled reversibly. The capacity on the second and subsequent cycles is about the same, and lithium intercalation during charge and discharge is nearly 100% reversible. In an electrolyte containing propylene carbonate (PC), natural graphite cannot be charged as it leads to gas evolution at around 1V. However, with electrolytes consisting of other solvents such as ethylene carbonate (EC) and diethyl carbonate (DEC) or electrolytes contain lithium bis(oxalato)borate LiBOB salt<sup>12</sup>, the side reactions are suppressed and it can be cycled without much difficulty.

Carbon materials can be classified into soft carbon (graphitic carbon) and hard carbon (glassy carbon). Soft carbon is relatively crystalline and shows preferred orientation like graphite. Hard carbon such as petroleum coke is relatively poorly crystalline. Hard carbon has the advantage of yielding higher capacity, which is thought to be due to the adsorption of

lithium on both sides of the single graphene sheets, accommodation of extra lithium into nanometer size cavities, and storage of additional lithium at the edges and surfaces. In addition, hard carbon can be used with PC-based electrolyte unlike graphite. However, hard carbons show a sloping discharge profile unlike graphite, which shows a nearly flat discharge profile as shown in Figure 1.6 <sup>13</sup>



**Figure 1.6. Discharge characteristics of lithium-ion with coke and graphite electrodes** <sup>13</sup>  
*Cathode:  $\text{LiCoO}_2$ , cell: 18650 type, charge: 1 A for 2.5 hours, discharge 0.2 C*  
*100% DOD corresponds to the capacity at 2.0 V*  
*DOD is depth of discharge*

With an aim to improve the performance of carbon anodes, structural modifications such as texture control, surface modifications by mild oxidation and coating, and incorporation of other elements such as B, O, S and P have been studied. A few oxides, nitrides, phosphides, and inter metallic compounds have also been investigated as anode hosts. Metal nitrides and phosphides offer lower voltages versus lithium due to the covalent character and stabilization of lower oxidation states. Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  offers 175 mAh/g at around 1.5 V<sup>14</sup>, but it is less attractive compared to carbon due to its lower capacity and higher voltage. Tin dioxide ( $\text{SnO}_2$ ) shows a reversible capacity of as high as 600 mAh/g at 0 to 2 V, but it exhibits a highly irreversible capacity loss during the first cycle<sup>15</sup>. Rutile type  $\text{MoO}_2$  and  $\text{WO}_2$ <sup>16, 17</sup>,  $\text{Fe}_2\text{O}_3$ <sup>18</sup>,  $\text{MnP}_4$ <sup>19</sup> and inter metallic compounds<sup>13</sup> such as  $\text{Cu}_6\text{Sn}_5$  having the NiAs-type structure have also been investigated. These anodes, including carbon, do not contain lithium and they can be coupled only with cathodes such as  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  that already contain lithium. With respect to finding anodes that could be coupled with cathodes free from lithium, some lithiated transition metal nitrides<sup>20</sup> and inter metallic compounds<sup>21</sup> have become appealing. For example,  $\text{Li}_{7-x}\text{MnN}_4$  and  $\text{Li}_{3-x}\text{FeN}_2$  exhibit capacities of around 200 mAh/g with a flat discharge voltage of around 1.2 V.  $\text{Li}_{2.6-x}\text{Co}_{0.4}\text{N}$ ,  $\text{Li}_{2.6-x}\text{Cu}_{0.4}\text{N}$ , and  $\text{Li}_{2.7-x}\text{Fe}_{0.3}\text{N}$  that have structures similar to that of  $\text{Li}_3\text{N}$  exhibits much higher capacities of around 500 mAh/g at 0.2 to 1.3 V due to formation of an amorphous phase during the initial stages. Two lithium per formula unit could be reversibly extracted from  $\text{Li}_2\text{CuSn}$ <sup>21</sup>. However, further work is necessary to assess the full potential of these anodes especially their fast capacity fading due to the large change in volume upon insertion/extraction. If successful, they have the possibility of being coupled with some of the lithium-free cathodes.

### 1.7.2. Cathode materials

In lithium-ion batteries, substances should be used as cathode materials which can intercalate/de-intercalate lithium ions at a highly positive potential (compared to the intercalation into the carbon anode) and with only low-kinetic hindrance, i.e., at low over voltage or nearly reversible. The first requirement is fulfilled especially by transition metal oxides and halides and also, to a lesser extent, by sulfides. The second requirement of low-kinetic hindrance for insertion and release of lithium ions is meant as a requirement of high mobility of lithium ions and electrons within the cathodic lattice and of unhindered mass transfer across phase boundaries as far as phase transitions happen in the host lattice during insertion and removal of lithium. As the transition metal halides are poorer electronic conductors than oxides, only the latter are used in practice. Candidate cathode materials include layered compounds such as  $\text{LiCoO}_2$ <sup>22-26</sup>,  $\text{LiNiO}_2$ <sup>27-30</sup>,  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  and three-dimensional  $\text{LiMn}_2\text{O}_4$  spinel phase. Although the 4 V cathodes are preferred for lithium-ion cells, cathodes with < 4 V are preferred for polymer lithium batteries, which use metallic lithium anode and solid polymer electrolytes. The instability of polymer electrolytes at higher voltages forces the use of cathodes having about 3V in polymer lithium batteries. As a result,  $\text{V}_6\text{O}_{13}$  has become an attractive cathode for polymer batteries. In addition to voltage, cell capacity is an important factor to achieve high energy density. The preference of high capacity over high voltage is beginning to dominate in the electronics industry. Although one Li per Co could be extracted in principle, the electrolyte instability limits the practical utility to 0.5 Li per Co in  $\text{Li}_{1-x}\text{CoO}_2$ . Similarly only about 0.4 Li per Mn could be reversibly extracted from  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ . Another 0.5 Li per Mn can be inserted into  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  in the 3V range, but the 3V region exhibits drastic capacity fading. The sudden voltage change from 4

to 3 V and the poor cycle ability in the 3V region limit the practical capacity of  $\text{LiMn}_2\text{O}_4$  to 0.4 Li per Mn. Thus  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  exhibit a practical capacity of about 140 and 120 mAh/g, respectively.  $\text{LiCoO}_2$  is currently in widespread use as a cathode material in lithium-ion batteries. Due to its high cost, however, other materials such as  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and a large number of doped or substituted materials are being extensively studied as lower cost substitutes with high electrochemical performance. Many studies were conducted to improve  $\text{LiCoO}_2$  performance. The electrochemical cycling of  $\text{LiCoO}_2$  at a high cutoff voltage results in a significant deterioration of the stability of the cathode. The capacity loss is related to nonuniform structural change<sup>22, 31,32</sup> and an increase in cobalt dissolution into the electrolyte<sup>33</sup>. To improve the electrochemical performance of  $\text{LiCoO}_2$  above 4.2 V, an innovative approach involved coating the particles with some metal oxides to avoid the unwanted surface reactions and protect the electrode from the bulk<sup>26, 34-38</sup>. This method changes the surface properties of the cobalt materials. Recent reports on surface modifications to cathode materials such  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  with  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{ZnO}_2$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{SnO}_2$  have shown that surface coating is an effective way to stabilize the structure of the materials and improve their electrochemical performance.

### 1.7.3. Electrolyte

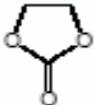
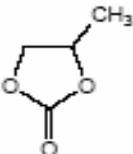
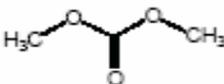
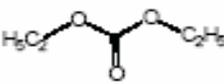
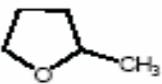
The electrolyte in lithium rechargeable batteries falls into one of the following categories: non aqueous liquid electrolyte, a polymer electrolyte, a solid fast ionic conductor, or a combination of one or more of the above. Due to the low conductivity of solid electrolytes, particularly dry polymers, liquid electrolytes dominate in most electrochemical systems.

The battery electrolyte should satisfy the following properties:

1. High ionic conductivity to minimize cell resistance and resistive heating of the device.
2. Good electrochemical stability to withstand the high voltage difference ( $>4V$ ).
3. High chemical stability to prevent decomposition of electrolyte.
4. Low reactivity toward the components of the battery such as the electrodes, current collectors, and separators
5. Non-toxicity to be accepted environmentally for ease of handling, mass production, and waste treatment.
6. Low melting point to provide good conductivity at low temperatures.
7. High boiling point to avoid explosions resulting from high pressure build-up in the cell.
8. Low cost to compete with existing power sources using aqueous electrolytes.

The solvents should be aprotic to be stable at negative potentials and should have high polarity to dissolve lithium salts and yield high ionic conductivity. The dielectric constant and viscosity of the solvents are the most important properties that determine the ionic conductance of the electrolyte solution<sup>39</sup>. Some of solvents and their properties are given in Table 1.4<sup>40, 41</sup>. Alkyl carbonates have widely been used as excellent solvents in lithium batteries. Cyclic esters like propylene carbonate (PC) and ethylene carbonate (EC) have high dielectric constant because of their high polarity, but their viscosity is high due to strong intermolecular forces. These solvents are mixed with low-viscosity solvents like dimethyl carbonate (DMC) or diethyl carbonate (DEC) to compensate for the viscosity.

**Table 1.4. Structure and properties of some solvents used for lithium battery electrolytes**<sup>40, 41</sup>

<i>Solvent name and abbrev.</i>	<i>Structural fomula</i>	<i>Melting point (°C)</i>	<i>Boiling point (°C)</i>	<i>Dielectric constant, <math>\epsilon</math></i>
Ethylene carbonate, <b>EC</b>		39-40	248	89.6 (40°C)
Propylene carbonate, <b>PC</b>		-49	240	64.4
Dimethyl carbonate, <b>DMC</b>		4.6	91	3.12
Diethyl carbonate, <b>DEC</b>		-43	126	2.82
2-Methyl-tetrahydrofuran, <b>2Me-THF</b>		-137	79	6.29
Dimethoxy ethane, <b>DME</b>		-58	85	7.20
$\gamma$ -Butyrolactone, <b><math>\gamma</math>-BL</b>		-43	204	39.1

Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is a common salt for application in rechargeable lithium-ion batteries. In spite of its high-ionic conductivity,  $\text{LiPF}_6$  electrolyte has distinctive disadvantages such as limited thermal stability and hydrolytic instability. Upon contact with water,  $\text{LiPF}_6$  decomposes to generate toxic gaseous products, most notably hydrofluoric ( $\text{HF}$ )<sup>42</sup>. Hydrofluoric reacts with the electrodes and increases the electrodes impedance.

To develop new electrolytes with better performance, researchers have focused on replacing alkyl carbonate with other solvents. Trans butylenes carbonate was found to be a suitable solvent in which graphite electrodes behave highly reversibly<sup>43</sup>. Chlorinated and fluorinated alkyl carbonate were also found to be very suitable<sup>44, 45</sup> for graphite anodes. The major importance of these solvents is their use as a replacement for EC, whose freezing point is too high. There are studies of pyrocarbonate (ROCO<sub>2</sub>CO<sub>2</sub>R) and bicarbonate (ROCO<sub>2</sub>ROCO<sub>2</sub>R) as co-solvents. Their major advantage relates to modification of surface chemistry of both anodes and cathodes and an improvement of the high-temperature performance.

In addition to changing the solvents, there were many attempts to introduce new families of salts. Merck developed the LiPF<sub>3</sub>(CF<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>(LiFAP) salt<sup>46</sup>. It was proven that this salt is much more stable than LiPF<sub>6</sub>. Its solution is less acidic and more thermally stable than LiPF<sub>6</sub> solutions. Recently, LiBOB was suggested as a stable and non acidic salt<sup>47</sup>. Both Li-C and Li<sub>x</sub>MO<sub>y</sub> cathodes seem to behave highly reversible in its solution. However, more work is needed to confirm that this salt is a viable alternative to LiPF<sub>6</sub>.

#### **1.7.4. Separator materials**

Lithium-ion cells use a microporous film, which has a thickness between 10 to 30 μm, to electrically isolate the positive and negative electrodes. All commercially available liquid electrolyte cells use microporous polyolefin materials as they provide excellent mechanical properties, chemical stability and acceptable cost. Some of separators used in different lithium batteries are given in Table 1.5. Requirements for lithium-ion separators include:

1. High machine direction strength to permit automated winding.
2. Does not yield or shrink in width.
3. Resistant to puncture by electrode materials.
4. Effective pore size less than  $1\mu\text{m}$
5. Easily wetted by electrolyte.
6. Compatible and stable in contact with electrolyte and electrode materials.

Microporous polyolefin materials in current use are made of polyethylene, polypropylene or laminates of polyethylene and polypropylene. The low melting point of polyethylene (PE) materials enables their use as a thermal fuse. As the temperature approaches the melting point of polymer,  $\sim 135\text{ }^{\circ}\text{C}$  for polyethylene and  $\sim 165\text{ }^{\circ}\text{C}$  for polypropylene (PP) porosity is lost. The following tables <sup>48</sup> summarize the major manufacturers of lithium-ion separators along with their major products (Table 1.6), manufacturing process of typical microporous films (Table 1.7), typical properties of some commercial microporous membranes (Table 1.8), thermal mechanical analysis (TMA) data for typical Celgard separators (Table 1.9), and safety and performance tests for lithium-ion batteries and the corresponding important separator and its effect on the cell performance and/or safety (Table 1.10).

**Table 1.5. Separators used in secondary lithium batteries <sup>48</sup>**

Battery system	Type of separator	Composition
Lithium-ion (liquid electrolyte)	microporous	polyolefins (PE, PP, PP/PE/PP)
Lithium-ion gel polymer	microporous	PVdF (polyvinylidene fluoride)
	microporous	polyolefins (PE, PP, PP/PE/PP) coated with PVdF or other gelling agents
Lithium-polymer (e.g. Li-V <sub>6</sub> O <sub>13</sub> )	polymer electrolyte	poly(ethylene oxide) with lithium salt

PE= Poly ethylene

PP= Poly propylene

**Table 1.6. Major manufacturers of lithium-ion battery separators along with their typical products <sup>48</sup>**

Manufacturer	Structure	Composition	Process	Trade name
Asahi Kasai	single layer	PE	wet	HiPore
Celgard LLC	single layer	PP, PE	dry	Celgard
	multilayer	PP/PE/PP	dry	Celgard
	PVdF coated	PVdF, PP, PE, PP/PE/PP	dry	Celgard
Entek Membranes	single layer	PE	wet	Teklon
Mitsui Chemical	single layer	PE	wet	-----
Nitto Denko	single layer	PE	wet	-----
DSM	single layer	PE	wet	Solupur
Tonen	single layer	PE	wet	Setela
Ube Industries	multi layer	PP/PE/PP	dry	U-Pore

**Table 1.7. Manufacturing process of typical microporous film** <sup>48</sup>

Process	Mechanism	Raw material	Properties	Typical membranes	Manufacturers
Dry process	drawing	polymer	simple process anisotropic film	PP, PE, PP/PE/PP	Celgard, Ube
Wet process	phase separation	polymer + solvent	isotropic film	PE	Asahi, Tonen
		polymer + solvent + filler	large pore size high porosity	PE	Asahi

**Table 1.8. Typical properties of some commercial microporous membranes** <sup>48</sup>

Separator/ properties	Celgard 2730	Celgard 2400	Celgard 2320	Celgard 2325	Asahi Hipore	Tonen Setela
Structure	single layer	single layer	trilayer	trilayer	single layer	single layer
Composition	PE	PP	PP/PE/PP	PP/PE/PP	PE	PE
Thickness (um)	20	25	20	25	25	25
Gurley (s) <sup>a</sup>	22	24	20	23	21	26
Ionic resistivity <sup>b</sup> ( $\Omega$ cm <sup>2</sup> )	2.23	2.55	1.36	1.85	2.66	2.56
Porosity (%)	43	40	42	42	40	41
Melt temp. (°C)	135	165	135/165	135/165	138	137

<sup>a</sup> Gurley is the time in seconds required to pass 10 cc of air through one square inch of product under a pressure of 12.2 inches of water

<sup>b</sup> In 1 M LiPF<sub>6</sub> EC:EMC (30:70 by volume)

**Table 1.9. TMA data for typical Celgard separators** <sup>48</sup>

Test	Celgard 2400	Celgard 2325
shrinkage onset temp. (°C)	121	106
deformation temp. (°C)	156	135, 154
rupture temp. (°C)	183	192

**Table 1.10. Safety and performance tests for lithium-ion batteries and the corresponding important separator property and its effect on cell performance and/or safety**<sup>48</sup>

<b>Cell property</b>	<b>Separator property</b>	<b>Comments</b>
cell capacity	thickness	cell capacity can be increased by making the separator thinner
cell internal resistance	resistance	separator resistance is a function of thickness, pore size, porosity, and tortuosity
high rate performance	resistance	separator resistance is a function of thickness, pore size, porosity, and tortuosity
fast charging	resistance	low separator resistance will aid in overall faster charging by allowing higher and/or longer constant current charging
high-temp. storage	oxidation resistance	oxidation of separators can lead to poor storage performance and reduce performance life
high-temp. cycling	oxidation resistance	oxidation of separators can lead to poor cycling performance
self-discharge	weak areas, pinholes	soft shorts during cell formation and testing can lead to internal current leakage
long-term cycling	resistance, shrinkage, pore size	high resistance, high shrinkage and very small pore size can lead to poor cycling performance
overcharge	shutdown behavior; high-temp. melt integrity	separator should completely shutdown and then maintain its melt integrity at high temp
external short circuit	shutdown behavior	separator shutdown stops the cells from overheating
hotbox	high-temp. melt integrity	separator should be able to keep the two electrodes apart at high temp
nail crush	shutdown (to stop delayed failure)	in the case of internal shorts, the separator may be the only safety device to stop the cell from overheating
bar crush	shutdown (to stop delayed failure)	in the case of internal shorts, the separator may be the only safety device to stop the cell from overheating

## **1.8. Overcharge/ over discharge**

A strict charging regime is necessary to properly and safely charge lithium-ion batteries. Most batteries contain a protective circuit to prevent overcharge and over discharge. This circuit limits the charge voltage to a maximum 4.3 V, and also contains a thermal sensor, which disconnects the cell if the temperature reaches 90 °C. If a cell is inadvertently overcharged, the cell may heat up and vent with a flame. Lithium-ion batteries permanently lose capacity when exposed to elevated temperature greater than 65 °C. The protective circuit also limits the discharge voltage to between 2.7 and 3.0 V per battery. In spite of these preventative measures, over discharge may still occur. If a lithium battery has dwindled to a voltage of less than 1.5 V per battery, recharge should be avoided since copper shunts may form inside the battery, causing a partial or total short circuit. In this case, the battery becomes unstable, charging the battery would cause excessive heat, and safety cannot be assured.

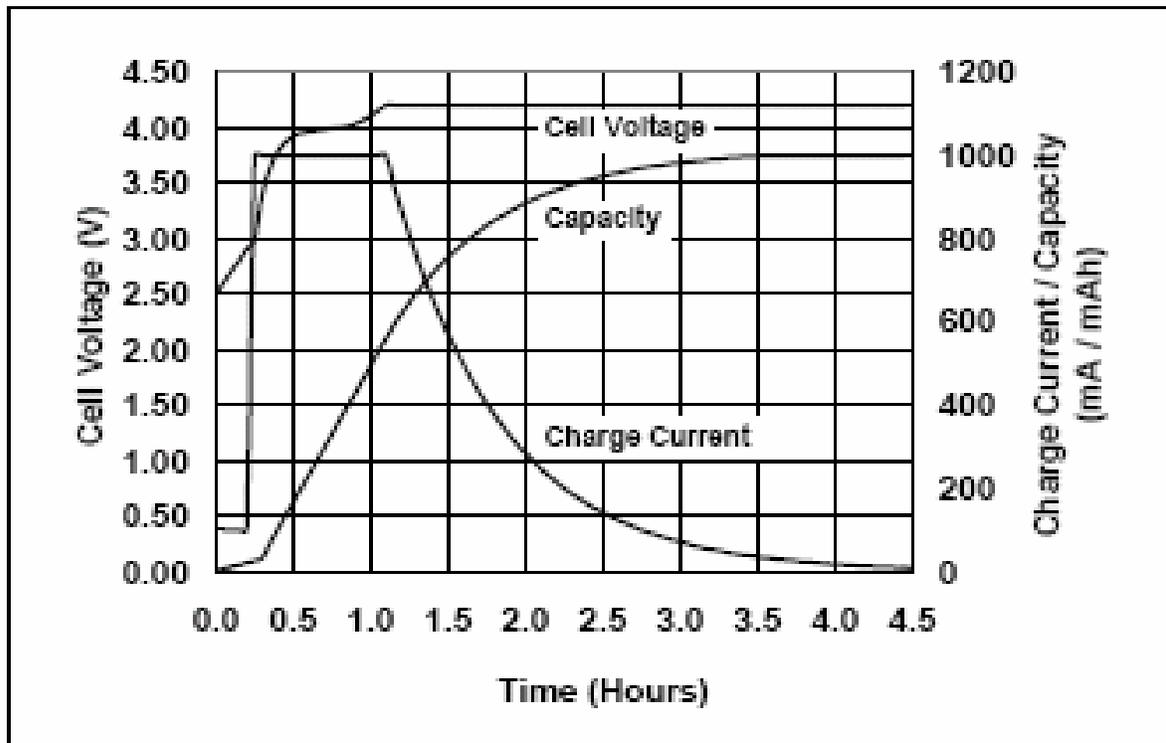
### **1.8.1. Discharge characteristics**

At a constant current discharge rate, the lithium-ion battery maintains a relatively flat voltage discharge profile with a steep decrease in the profile near the end of discharge. The battery should not be discharge to less than 3.0 V per battery.

### **1.8.2. Charging characteristics**

Operating temperatures for charging are 0 to 45°C. Lithium-ion batteries require a controlled charge regime to properly charge and prevent overcharge. A two-stage charge

cycle must be performed to fully charge the battery as illustrated in Figure 1.7<sup>49</sup>. This is called a CC/CV charge cycle. The first stage of the charge cycle is a constant current charge until the battery voltage reaches 4.1 to 4.2 V. Upon reaching this peak voltage, a constant voltage charge is initiated until the charge current reduces to 3% of the rated current. Upon



**Figure 1.7. Lithium-ion battery charge**<sup>49</sup>

completing charge, a top off charge may be used to counteract the self-discharge of the battery and protective circuit. This top off charge may be initiated when the open circuit voltage of the battery reaches less than 4.05 V and terminate upon reaching the full charge voltage of 4.1 to 4.2 V. Depending on the battery, this top off charge may be repeated once every 20 days.

### **1.8.3. Protection circuit**

Lithium-ion batteries require a protection circuit that limits each cell's peak voltage during charge and prevents its voltage from dropping too low on discharge. The protection circuit not only limits the maximum charge and discharge current but also monitors the cell temperature. Commercial lithium-ion battery packs contain redundant protection devices to ensure safety under all circumstances. Typically, a field effect transistor opens if the charge voltage of any cell reaches 4.30V, and a fuse activates if the cell temperature approaches 90 °C. In addition, a pressure switch in each cell permanently interrupts the charge current if a safe pressure threshold is exceeded, and internal voltage control circuits cut off the battery at low and high voltage points. Exceptions are made to spinel packs, which use a lithium manganese oxide as a cathode, containing one or two cells. The lithium-ion battery is typically discharged to 3V per cell. The lowest "low-voltage" power cut-off is 2.5V per cell. During prolonged storage, however, a discharge below this voltage level is possible. Manufacturers recommend a "trickle" charge to gradually raise such a battery back into the "acceptable" voltage window. Not all chargers are designed to apply a charge once a lithium-ion battery has dipped below 2.5V per cell. Some batteries feature an ultra-low voltage cut-off that permanently disconnects the pack if a cell dips below 1.5V. This precaution is done to prohibit recharge if a battery has dwelled to 1.5V. A deep discharge causes copper plating, which can lead to a short circuit in the cell. Most manufacturers do not sell lithium-ion cells by themselves, but make them available in a battery pack, complete with a protection circuit. This precaution is understandable when considering the danger of explosion and fire if the battery is charged and discharged beyond its safe limits. A major concern arises if static

electricity or a faulty charger has managed to destroy the battery's protection circuit. Such damage often causes the solid-state switches to fuse to a permanent "on" position without the user's knowledge. A battery with a faulty protection circuit may function normally, but does not provide the required safety. If charged beyond the safe voltage limits with a poorly designed accessory charger, the battery may heat up, then bulge and, in some cases, vent with flame. Shorting such a battery can also be hazardous.

## **1.9. Summary**

Lithium-ion batteries receive good grades in performance and reliability. From the above discussion, however, we see that there is room for improvement. The Lithium-ion battery has found a strong market position with portable devices demanding small form factors. The future challenge will be to develop a simple oxide cathode without other elements (such as P in  $\text{LiFePO}_4$  which reduce the energy density of the battery) in which at least one lithium ion per transition metal ion could be reversibly extracted/inserted to give close to 300 mAh/g (for example,  $\text{LiCoO}_2$  takes 0.5 Li per Co and it gives 140 mAh/g so if it can take 1 Li per Co it will give 280 mAh/g) while keeping the material cost and toxicity low. Such cathodes can double the energy density compared to the present level. There are also possibilities to increase the capacity of anodes perhaps by focusing on amorphous materials and metal nitrides.

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# CHAPTER 2: ELECTROLYTES FOR LITHIUM-ION BATTERIES

## 2.1. Introduction

Electrolytes are essential in any electrochemical device. The function of electrolyte is to serve as a medium for the transfer of ions between electrodes. There are many types of electrolytes but the most used electrolyte in present lithium-ion batteries is a liquid consisting of a lithium salt dissolved in nonaqueous solvents. Also of importance in an electrolyte is the interaction between the electrolyte and electrodes in the battery. The interface between the electrodes and electrolyte usually affects battery performance significantly.

Li-ion batteries typically operate at a high voltage ( $\sim 4.2$  V), which requires organic solvents stable to oxidation. A battery electrolyte in general needs to meet requirements such as:

1. High-ionic conductance and electronic insulator to minimize cell resistance and achieve good rate capability and keep self-discharge at minimum.
2. High-thermal and chemical stability
3. Wide potential window, which is defined as the range in voltage between the oxidative and reductive decomposition limits of the electrolyte
4. Low reactivity toward other components in the battery
5. Non-toxic and safe
6. Low melting point to help provide conductivity at low temperatures.

7. High boiling point to prevent pressure build-up in the cell, which may lead to an explosion.
8. Low cost

The next two sections provide a brief discussion about solvents and salts that are used in lithium-ion battery research.

### **2.1.1. Solvents**

An ideal electrolyte solvent should have the following properties:

1. High-dielectric constant ( $\epsilon$ ) to dissolve salts well
2. Low viscosity ( $\eta$ )
3. Solvent should remain inert to all cell components
4. Low melting point ( $T_m$ )
5. High boiling point ( $T_b$ )
6. It should also be safe, nontoxic, and economical
7. The solvents should be aprotic and stable at negative potentials

The most important properties of the solvent for ionic conductance are the viscosity and dielectric constant. Many organic solvents have been investigated, and the majority of them may be classified as alkyl carbonates, esters and ethers. Tables 2.1 and 2.2 list various solvents used in lithium batteries <sup>1</sup>, along with their physical properties. As we see from these tables, no single solvent meets all requirements. For example, while all ethers and acyclic esters have low viscosities ( $\eta \sim 0.3-0.7$  cP), they also have low-dielectric constants ( $\epsilon \sim 2-7$ ) which make them poor media for salt dissociation. On the other hand, solvents with

high polarity ( $\epsilon \sim 40-90$ ) have high viscosity ( $\eta = 1.7-2.0$  cP) which limits ion mobility. To overcome this problem mixed solvents are used. For example two solvents may be used, one with a high-dielectric constant and the second with low viscosity. The reason why cyclic esters have a high-dielectric constant is their cyclic structure which helps to maintain a more ordered alignment of the molecule dipoles in contrast to open structure of the linear carbonates, which helps to cancel these dipoles.

**Table 2.1. Organic carbonates and esters as electrolyte solvents**<sup>1</sup>

Solvent	Structure	M. Wt	T <sub>m</sub> / °C	T <sub>b</sub> / °C	$\eta$ /cP 25 °C	$\epsilon$ 25 °C	Dipole Moment/debye	T <sub>f</sub> / °C	d/gcm <sup>-3</sup> , 25 °C
EC		88	36.4	248	1.90, (40 °C)	89.78	4.61	160	1.321
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
BC		116	-53	240	3.2	53			
$\gamma$ BL		86	-43.5	204	1.73	39	4.23	97	1.199
$\gamma$ VL		100	-31	208	2.0	34	4.29	81	1.057
NMO		101	15	270	2.5	78	4.52	110	1.17
DMC		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
DEC		118	-74.3 <sup>a</sup>	126	0.75	2.805	0.96	31	0.969
EMC		104	-53	110	0.65	2.958	0.89		1.006
EA		88	-84	77	0.45	6.02		-3	0.902
MB		102	-84	102	0.6			11	0.898
EB		116	-93	120	0.71			19	0.878

*a M. S. Ding, K. Xu, S. Zhang, T. R. Jow, J. Electrochem. Soc. 148, (2001), A299.*

**Table 2.2. Organic ethers as electrolyte solvents <sup>1</sup>**

Solvent	Structure	M. Wt	T <sub>m</sub> / °C	T <sub>b</sub> / °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T <sub>ρ</sub> / °C	d/gcm <sup>-3</sup> , 25 °C
DMM		76	-105	41	0.33	2.7	2.41	-17	0.86
DME		90	-58	84	0.46	7.2	1.15	0	0.86
DEE		118	-74	121				20	0.84
THF		72	-109	66	0.46	7.4	1.7	-17	0.88
2-Me-THF		86	-137	80	0.47	6.2	1.6	-11	0.85
1,3-DL		74	-95	78	0.59	7.1	1.25	1	1.06
4-Me-1,3-DL		88	-125	85	0.60	6.8	1.43	-2	0.983
2-Me-1,3-DL		88			0.54	4.39			

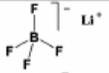
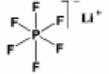
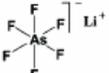
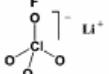
### 2.1.2. Salts

Lithium salts are used in lithium-ion batteries as a charge carrier for the current passed in the cell during the electrochemical process. A salt for a lithium-ion battery should meet requirements such as:

1. Good thermal stability
2. High oxidation and low reduction potentials
3. Good solubility and dissociation of the salt in appropriate solvents
4. Chemical stability with the solvents
5. High conductivity in solution
6. Low molecular weight
7. Low cost
8. Ability to passivate the aluminum current collector in lithium-ion batteries
9. Non-toxic

To have a high conductivity, the lithium salt must have good solubility and dissociate in the solvent. The requirement of good solubility eliminates using most simple lithium salts such as LiX (where X for example is Cl<sup>-</sup> and F<sup>-</sup>), since they do not dissociate well in low-dielectric solvents. Choosing bulky anions with low-negative charge density <sup>2</sup> usually improves its solubility and dissociation, which is why most lithium salts are based on complex anions. The most studied salts include LiClO<sub>4</sub><sup>3-6</sup>, LiAsF<sub>6</sub><sup>7-11</sup>, LiPF<sub>6</sub><sup>12-13</sup>, LiBF<sub>4</sub><sup>14</sup>, LiCF<sub>3</sub>SO<sub>3</sub><sup>15</sup> and LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>16</sup>. Some salts used in research and lithium-ion industry are shown in Table 2.3 along with some physical properties <sup>1</sup>. Each salt has advantages and

**Table 2.3. Typical salts used in research and industry for lithium-ion cells<sup>1</sup>**

Salt	Structure	M. Wt	T <sub>m</sub> /°C	T <sub>decomp.</sub> / °C in solution	Al-corrosion	σ /mScm <sup>-1</sup> (1.0 M, 25 ° C)	
						in PC	in EC/DMC
LiBF <sub>4</sub>		93.9	293 (d)	> 100	N	3.4 <sup>a</sup>	4.9 <sup>c</sup>
LiPF <sub>6</sub>		151.9	200 (d)	~ 80 (EC/DMC)	N	5.8 <sup>a</sup>	10.7 <sup>d</sup>
LiAsF <sub>6</sub>		195.9	340	> 100	N	5.7 <sup>a</sup>	11.1 <sup>e</sup>
LiClO <sub>4</sub>		106.4	236	>100	N	5.6 <sup>a</sup>	8.4 <sup>d</sup>
Li Triflate	Li <sup>+</sup> CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	155.9	>300	>100	Y	1.7 <sup>a</sup>	
Li Imide	Li <sup>+</sup> [N(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	286.9	234 <sup>b</sup>	>100	Y	5.1 <sup>a</sup>	9.0 <sup>e</sup>
Li Beti	Li <sup>+</sup> [N(SO <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>				N		

a. *Ue, M. J. Electrochem. Soc. 1995, 142, 2577.*

b. *Dominey, L. A.; Koch, V. R.; Blakley, T. Electrochim. Acta 1992, 37, 1551.*

c. *Hossain, S. Handbook of Batteries, 2nd ed.; Linden, D., Ed.; McGraw-Hill: New York, 1995; Chapter 36.*

d. *Schmidt, M.; Heider, U.; Kuehner, A.; Oesten, R.; Jungnitz, M.; Ignat'ev, N.; Sartori, P. J. Power Sources 2001, 97/98, 557.*

e. *Walker, C. W.; Cox, J. D.; Salomon, M. J. Electrochem. Soc. 1996, 143, L80.*

disadvantages, with the later described in the next paragraph.

Lithium perchlorate ( $\text{LiClO}_4$ ) and  $\text{LiAsF}_6$  cannot be used commercially because of the explosion risks of  $\text{ClO}_4^-$ <sup>17</sup> and the high toxicity of  $\text{AsF}_6^-$ <sup>9, 18-20</sup> and its degradation products, respectively. The main problem of  $\text{LiBF}_4$  is its low conductivity. For that reason there is not much interest in using it, although it was observed recently that electrolytes with it have good performance at low temperature<sup>21-24</sup>. The lithium triflate salt ( $\text{LiCF}_3\text{SO}_3$ ) has two shortcomings. First, it has poor ion conductivity in nonaqueous solvents. The poor ion conductivity is mainly due to two reasons:

1. The low-dissociation constant of  $\text{LiCF}_3\text{SO}_3$  in solvents with a low-dielectric constant<sup>20,25</sup>
2. The moderate ion mobility for  $\text{CF}_3\text{SO}_3^-$  as related to other salts<sup>26</sup>.

The second problem with using  $\text{LiCF}_3\text{SO}_3$  is the severe aluminum corrosion that occurs with it<sup>27</sup>, which is also a problem with  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ <sup>27</sup>. Among all salts mentioned,  $\text{LiPF}_6$  is the one used in commercial Li-ion batteries. Discussion about  $\text{LiPF}_6$  disadvantages in more detail is given in section 2.2.1.

## 2.2. State-of-art electrolyte

Although that there are many solvents and salts tested in the laboratory<sup>28-30</sup>, most commercial lithium-ion battery electrolytes consist of  $\text{LiPF}_6$  dissolved in alkyl carbonate solvents<sup>31</sup> consisting of EC as one component<sup>32</sup> and a co-solvent mixture that are acyclic alkyl carbonates such as DEC<sup>33</sup>, DMC<sup>34</sup>, EMC<sup>35</sup>, and PMC<sup>36</sup>. Ethylene carbonate is used because its high-dielectric constant leads to improved dissociation of the salt. However, the viscosity of ethylene carbonate is high, so co-solvents with low viscosity are added. Alkyl

carbonate solvents are used because they have a higher anodic stability and higher polarity than ethers and esters. In addition, they have the ability to form a solid electrolyte interface (SEI) on the anode, thereby protecting the electrolyte from further decomposition. The ability to form a good SEI is not available in ethers or esters<sup>28-30, 37-40</sup>. For example, the ethers can co-intercalate into graphite, which causes exfoliation of the graphite<sup>38</sup>, and the esters do not form an adhesive passive film. Since the major salt used salt in commercial lithium-ion batteries is  $\text{LiPF}_6$ , more detailed discussion about it is provided below.

### 2.2.1. $\text{LiPF}_6$

Lithium hexafluorophosphate has a combination of well-balanced properties such as high-ionic conductivity, good dissociation, and good ion mobility. However, a major disadvantage is the sensitivity of  $\text{LiPF}_6$  to residual water in the electrolyte. The  $\text{LiPF}_6$  reacts with water and forms HF, which has a detrimental effect on cell performance because HF reacts with the graphite anode and forms a surface film consisting of LiF<sup>41</sup>. The LiF film increases the impedance of the electrolyte/electrode interface due to its poor ionic conductivity. Another disadvantage of the  $\text{LiPF}_6$  is its thermal instability<sup>27, 42-44</sup> which is believed to be the main cause for the poor performance of lithium-ion batteries at elevated temperature<sup>41, 45-48</sup>. Another disadvantage is that  $\text{LiPF}_6$  cannot be used in gel electrolytes based on fumed silica (FS) because  $\text{LiPF}_6$  reacts with Si-OH to form HF which will react with silicon to form  $\text{SiF}_4$ . Because of these disadvantages, many researchers have focused on finding a new salt to replace  $\text{LiPF}_6$ <sup>49-58</sup>. Some of these novel salts are summarized in Table 2.4. One new salt that has attained a lot of interest is lithium bis(oxalato)borate ( $\text{LiBOB}$ )<sup>58-67</sup>. A brief discussion about  $\text{LiBOB}$  is given in next section.

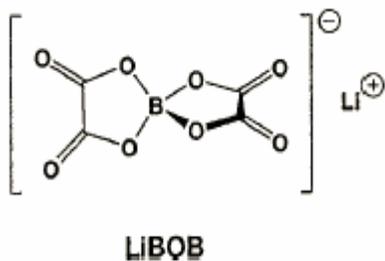
Table 2.4. Novel lithium salts and their major properties <sup>1</sup>

Salt	Structure	M. Wt	T <sub>d</sub> / °C <sup>a</sup>	E <sub>a</sub> / V <sup>b</sup> (solvent -electrode)	σ / mScm <sup>-1</sup> (0.7–1.0 M, 25 ° C / solvent)
LiMe		417.9	340	4.4 (THF-GC) 4.0 (EC/DMC-GC)	7.1 (EC/DMC) 12 (EC/MF/DMC)
aromatic Li borates		233.4~ 305.4	250 (n=0)	3.6 (PC-SS <sup>c</sup> , n=0 <sup>d</sup> ) 3.7 (PC-Au, n=1) 4.1 (PC-Au, n=4)	0.6 (PC, n=0) 5.6 (EC/DME, n=0) 0.77 (PC, n=1) 11.07 (DME, n=4) 1.22 (PC)
		334.1	320	3.75 (PC-Pt)	3.84 (PC/DME) 1.39 (PC/EC)
		290.0~ 427.7	260 (R <sup>1-3</sup> =Cl) 290 (R <sup>1-3</sup> =H) 310 (R <sup>1-2</sup> =Cl) 320 (R <sup>1</sup> =CH <sub>3</sub> )	4.0 (PC-SS, R <sup>1-3</sup> =H) 4.4 (PC-Pt, R <sup>1-3</sup> =Cl) 4.4 (PC-Pt, R <sup>1-3</sup> =H) 4.3 (PC-Pt, R <sup>1-2</sup> =Cl) 4.1 (PC-Pt, R <sup>1</sup> =CH <sub>3</sub> )	
		386.1			
		293.9		4.6 (EC/DMC-Pt)	
		219.9		3.95 (PC/DMC-Pt)	
non-aromatic Li borates		681.9	280	5.4 (DME-Pt) 5.0 (PC-Pt)	11.1 (DME)
		221.9	245		5.6 (DMSO)
		193.9	~300 (d)	4.5 (PC-Pt)	3.1 (PC) 9.0 (DME) 7.5 (EC/DMC)
		469.9~667.9	100	4.5 (PC-Pt)	8.0 (PC/DMC)
chelated Li phosphates		361.9 (n=0) 577.9 (n=4)	150 (n=0)	3.7 (PC-Ni, n=0) 3.95 (EC/DMC-Pt, n=1) 4.3 (EC/DEC-Pt, n=4)	3.89 (EC/THF, n=0) 2.09 (EC/DEC, n=4)
	Li FAP		451.9~433.9	5.0 (DME-Pt) 5.0 (EC/DMC-Pt)	8.17 (PC/EC/DMC, R <sup>1-2</sup> = <i>i</i> -C <sub>3</sub> F <sub>7</sub> , R <sup>3-6</sup> =F) 8.2 (EC/DMC, R <sup>1-3</sup> = C <sub>2</sub> F <sub>5</sub> , R <sup>4-6</sup> =F)
Li azolate		124.9			
Li imidazolid		209.9		4.85 (DMC-Pt)	5.06 (EC/EMC)

- a Thermal decomposition temperature determined by TGA.*
- b Anodic stability limit determined by cyclic voltammetry.*
- c Stainless steel working electrode.*
- d Number of fluorine substituents on the aromatic ring*

### 2.3. LiBOB

LiBOB (shown below) is a new salt that was independently discovered by Lischka et al. <sup>58</sup> in Germany and Angell et al. <sup>59</sup> in the USA. LiBOB (M.w =194 g/mol) contains



**Scheme 2.1: LiBOB structure**

Four carbonyl oxygen and four ether oxygen. There is only a single negative charge distributed among these atoms which make them very weakly coordinating. Consequently, LiBOB dissociation is high and expected to give a good ionic conductivity. In addition, the electrochemical stability of LiBOB is high (~4.5 V vs. Li<sup>+</sup>/Li) <sup>68</sup> and the decomposition temperature for LiBOB is 302 °C. LiBOB salt meets the requirements discussed in section 2.1.2 and in addition, it is found that LiBOB has the ability to stabilize the graphite anode for lithium-ion batteries in the presence of PC-rich solvent <sup>61-62</sup> without using EC or any additives, which was not achievable in the past for any lithium salt. The problem of using PC arises from its tendency to severely exfoliate graphitic structure, which results in cell destruction <sup>29, 69-72</sup>. With LiBOB there is no need to worry about exfoliation which leads to

more flexibility in solvent selection. Lithium bis(oxalato)borate has the ability to passivate the Al foil cathode current collector<sup>60-61</sup>. In addition, LiBOB salt has better thermal stability and better performance at elevated temperature than LiPF<sub>6</sub><sup>60</sup>. For example, it was shown that Li-ion cells which use graphite as an anode, lithium nickel based mixed oxide cathode, and LiBOB/EC:EMC (1: 1) (wt) electrolyte can be cycled at 60 and 70 °C without significant capacity fading<sup>60-61</sup>. In addition, Jow and coworkers proposed that an electrolyte with wide temperature range is attainable by using LiBOB salt<sup>73</sup>. For these reasons, LiBOB has attracted the attention of recent research<sup>62,-63, 68, 74-79</sup>

## **2.4. Limitation of the state-of-art electrolyte at low temperature**

As mentioned in Chapter 1, the normal operation range for most commercial lithium-ion batteries is -20 to 65 °C. The poor performance of state-of-art lithium-ion cells at temperatures below -20 °C restricts applications for lithium-ion batteries. The limited range of operation of lithium-ion batteries is attributed to many factors as will be shown in next paragraph.

The poor performance of state-of-art lithium-ion cells at low temperature (-20 to -50 °C) arises from the decrease of solution conductivity and Li salt solubility<sup>80-82</sup>. A survey conducted for major manufacturers in 2001 showed that the power rate and energy density of lithium-ion cells at -40 °C are only 1.25% and 5%, respectively, of those obtained at room temperature<sup>83</sup>. Another survey conducted in 2003 showed that 30% of room temperature capacity is achievable at -40 °C<sup>84</sup>. In addition to electrolyte effect, the poor low-temperature performance is also attributed to factors such as: increase of the surface film resistance between the electrode and electrolyte<sup>83-87</sup>, increase of the charge-transfer resistance at the

electrode/electrolyte interface<sup>23, 24, 88</sup>, and increase of the diffusion impedance of the lithium ion into graphite anodes<sup>89,90</sup>.

To overcome these limitations, researchers are trying to develop mixed-solvent electrolyte systems with improved performance at low temperature. The focus is on replacing the EC component, or at least reducing its concentration in the electrolyte, which will improve the low-temperature performance. However, reduction products of EC are known to be responsible for forming an effective solid electrolyte interface (SEI), and complete elimination of EC will affect negatively the performance of lithium-ion batteries. Many researchers have focused on reducing the EC content because EC is blamed for poor performance of the state-of-art lithium-ion cells at low temperature. The high melting point of EC (~36°C) also has a detrimental effect on low-temperature performance since the EC component will precipitate at low temperature<sup>91-93</sup>.

An attempt was made by Ein-Eli et al.<sup>92</sup> to make an electrolyte for low-temperature applications. They used methyl formate, which has a low melting point ~-99 °C, with EC at a volume ratio of 1:3. The reported conductivity for that electrolyte using LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> [lithium tris(trifluoromethanesulfonyl)methide], (LiMe) salt, at -40 °C was excellent (5.4 mS cm<sup>-1</sup>)<sup>92</sup>. Although it has a high ionic conductivity, the performance of the anode half cell was poor since only 50% of the room-temperature capacity is obtained at -2 °C. Other attempts to improve the low-temperature performance by using EC with alkyl carbonates that have a low melting point (e.g., EMC, DEC and DMC) were reported by many researchers<sup>82, 86, 87, 94-97</sup>. However, these electrolytes have failed to give a satisfactory performance below -30 °C<sup>97</sup>. Because of limited improvements using alkyl carbonate, linear alkyl esters have been examined by Smart et al.<sup>82, 95</sup>. Since MF has a negative effect on battery performance, they

chose to use other alkyl esters such as methyl acetate (MA) and ethyl acetate (EA)<sup>82, 95</sup>. The addition of MA or EA improved the low-temperature performance; however, both components have a detrimental effect on anode and cathode stability.<sup>82</sup> However, the work of Herreyre et al.<sup>98</sup> showed that EA and MA can be used as co-solvents for low-temperature electrolytes. They reported excellent results using EA or MA. For example, by using EC/DMC/EA with 1M LiPF<sub>6</sub> with vinylene carbonate as an additive in LiCoO<sub>2</sub>/graphite cells, the charge capacity at -30 °C was between 88-95% of that at room temperature. In addition, it was shown that capacity fading at high-temperature storage is comparable with cells using state-of-art electrolytes (0.05 % per cycle).

## **2.5. Objective of this study**

Our objective is to measure and assess the conductivity and viscosity in a wide temperature range of a candidate electrolyte for lithium-ion batteries. If the electrolyte shows promising results, other studies such as electrochemical cycleability and thermal stability of a half and complete cell using this electrolyte with different cathodes (lithium cobalt oxide, lithium manganese oxide, and lithium iron phosphate) will be done in future efforts that are beyond the scope of this MS thesis. The long term objective of this line of inquiry is to test the ability of the candidate electrolyte to form a gel using nanoparticulate fumed silica as a filler, which will prevent electrolyte leakage and enhance the safety of lithium-ion batteries.

To enable an electrolyte capable of working in a wide temperature range, our strategy is to choose a salt (other than LiPF<sub>6</sub>) that satisfies the requirements given in section 2.1.2 and gives a better high-temperature performance than the currently used LiPF<sub>6</sub>. Suitable solvents must be used with the chosen salt to improve low-temperature performance. We have chosen

LiBOB as the salt for this study, and mixtures of  $\gamma$ -butyrolactone (GBL), ethyl acetate (EA) and ethylene carbonate (EC) as the solvents.

The solvent  $\gamma$ -butyrolactone (GBL) is chosen because it has a reasonably high-dielectric constant ( $\sim 39$ ), relatively moderate viscosity ( $\sim 1.73$  cP), a similar structure to EC, and it has a good solubility for LiBOB<sup>99-101</sup>. In addition, it was reported that GBL can improve the low-temperature performance of a LiBOB based electrolyte system<sup>22,102-103</sup>. The solvent EA is chosen because it has a low-melting point ( $\sim 84$  °C), which will increase the liquid range of the electrolyte. In addition, the low viscosity ( $\sim 0.45$  cP) of EA will improve the conductivity of the electrolyte. Also, it has been reported that EA improved the low-temperature performance for lithium-ion cells.<sup>82, 95, 98, 104</sup> The solubility of LiBOB in GBL, EA, and EC is 1.55, 0.98, and 1.03 mol/kg, respectively<sup>105</sup>.

To achieve the above objective, electrochemical impedance spectroscopy is used to measure the conductivity of the LiBOB-based electrolyte as functions of salt concentration, solvent composition and temperature. A rheometer using the Coquette (concentric cylinder) sample geometry is used to likewise measure the viscosity of the electrolyte as functions of salt concentration, solvent composition and temperature.

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# CHAPTER 3: EXPERIMENTAL MATERIALS AND METHODS

This section summarizes methods for material preparations and characterizations of LiBOB-based electrolytes.

## 3.1. Liquid electrolyte preparation

Many samples were investigated in order to obtain a liquid electrolyte that possesses a technologically acceptable conductivity over a wide range of temperatures. To achieve this goal, the salt concentration and solvent composition were varied. The solvents used in this study are ethylene carbonate (EC), ethyl acetate (EA), and  $\gamma$ -butyrolactone (GBL) at the following weight compositions (GBL: EA: EC): 1:1:1, 1:1:0.5, 1:1:0.1, and 1:1:0. For each of these solvent compositions, the following LiBOB concentrations (mol/L) were prepared: 0.2, 0.5, 0.7, 1.0, and 1.2 M. Table 3.1 lists the various electrolytes investigated in this study.

**Table 3.1. Electrolyte compositions studied in this work**

		LiBOB Concentration (mol L <sup>-1</sup> )				
		0.2	0.5	0.7	1	1.2
Solvent Composition GBL:EA:EC	1:1:0	1:1:0	1:1:0	1:1:0	1:1:0	1:1:0
	1:1:0.1	1:1:0.1	1:1:0.1	1:1:0.1	1:1:0.1	1:1:0.1
	1:1:0.5	1:1:0.5	1:1:0.5	1:1:0.5	1:1:0.5	1:1:0.5
	1:1:1	1:1:1	1:1:1	1:1:1	1:1:1	1:1:1

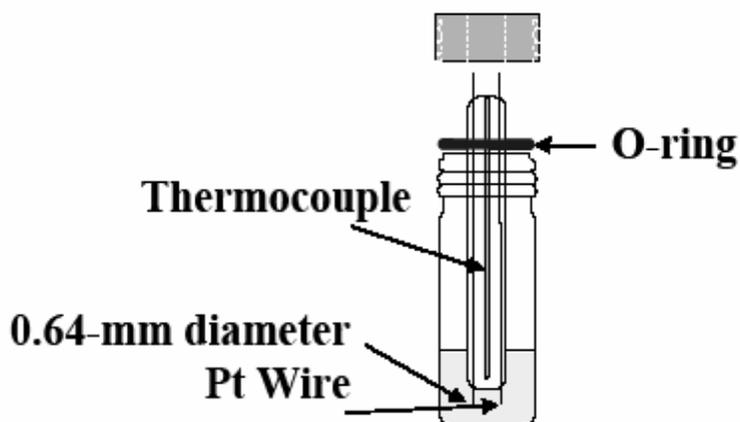
Ethylene carbonate, ethyl acetate, and  $\gamma$ -butyrolactone were obtained from Aldrich and dried over 4 Å molecular sieves (Fisher Scientific) for at least one week. Lithium bis(oxalato)borate was obtained from Chemtall as a gift and dried in a vacuum oven at 150 °C for at least 48 hours before it was added to the solvents.

The water content of solvents was measured to be below 20 ppm using a Mitsubishi CA-06/VA-06 Karl-Fisher titrator. To check the water content of the salt, a known amount of LiBOB (~ 0.1g) is placed in the oven boat of the Karl fisher titrator, as opposed to direct injection into the K-F reagent since it is known that LiBOB reacts with methanol in the K-F reagent to give water<sup>1</sup>. The amount of water in the LiBOB was around 350 ppm. The water content of the electrolyte solution is calculated as approximately 70 ppm from the measured water content in the salt and solvents.

Electrolyte formulation was performed under an argon atmosphere in a LABCONCO 50800 glove box. Liquid electrolytes were prepared by weighing an amount of LiBOB in a volumetric flask and adding an appropriate amount of solvent. Mixing of the liquid electrolytes was performed by sealing the flask and gently shaking by hand until the salt dissolved. The electrolyte is purified before use by filtration through a syringe filter (0.1 µm pore size) as recommended by LiBOB manufacturer (Chemtall).

### **3.2. Electrochemical measurements**

Electrochemical measurements were performed using a PAR 273 potentiostat and 5210 lock-in amplifier (Princeton Applied Research, Oak Ridge, TN). Samples were added to the conductivity cells ( Figure 3.1<sup>2</sup>) within the glove box to ensure low-moisture content.



**Figure 3.1. Schematic illustration of two-electrode cell for conductivity measurement.<sup>2</sup>**

Electrochemical impedance spectroscopy (EIS) is used to evaluate the electrochemical characteristics of an electrochemical system by applying an alternating potential (AC signal) at varying frequencies and measuring the current response. The AC impedance measurements were made using Power Sine software. AC data obtained from the measurements reflects ion migration and ionic polarization that occurs within the cell. Electrical information of the cell is derived using a circuit model.

### **3.2.1. Electrolyte resistance**

The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and cell geometry. In a rectangular bounded area with area  $A$  and length  $l$  carrying a uniform current the resistance is defined as:

$$R = \rho \frac{l}{A} \quad (3.1)$$

where  $\rho$  is the solution resistivity. The conductivity of the solution,  $\sigma$  (S cm<sup>-1</sup>), is more commonly used in solution resistance calculations. Its relationship with solution resistance is:

$$R = \frac{l}{A\sigma} \Rightarrow \sigma = \frac{l}{RA} \quad (3.2)$$

If we take the ratio of conductivity for two solutions we have the following:

$$\frac{\sigma_1}{\sigma_2} = \frac{l_1 R_2 A_2}{R_1 A_1 l_2} \quad (3.3)$$

If the geometry is fixed, then

$$\frac{\sigma_1}{\sigma_2} = \frac{R_2}{R_1} \quad (3.4)$$

We can calculate the conductivity for any sample by using a standard solution with a known conductivity and measure the resistance for the standard sample. Upon measurement of the resistance for the unknown sample, the conductivity of the unknown sample can be calculated using Equation 3.4

### 3.2.2. Electrolyte conductivity

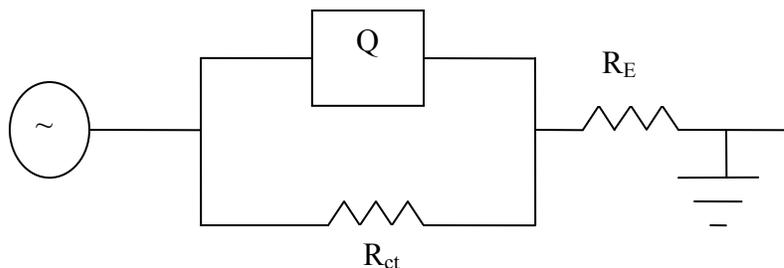
Ionic conductivity is a measure of total charge species in the electrolyte. High-conductivity electrolytes are favorable because they have lower ohmic potential losses. Conductivity is measured using EG&G Princeton Applied Research PowerSine software to control an EG&G Model 273 potentiostat and EG&G Model 5210 lock-in amplifier in the frequency range 100 kHz to 100 mHz. The cell constants were found using a KCl standard solution (1409  $\mu\text{S cm}^{-1}$  at 25°C) (Fisher Scientific) prior to and after each measurement.

The conductivity cell consists of a glass cell containing two blocking platinum wire electrodes (0.64-mm diameter, Fisher Scientific)<sup>3</sup>, a thermocouple opening, an o-ring seal, and glass vial. The conductivity cell has a diameter of ~1.5 cm and height of 5 cm. The design of the cell was described by Riley<sup>3</sup>, and a schematic of the conductivity cell is shown in Figure 3.1. The empty conductivity cells are placed in the oven at 80 °C for 1 day to remove moisture and then moved to the glove box where the electrolyte sample is inserted.

Temperature is controlled by putting conductivity cells inside wells in an insulated aluminum block with an internal-coolant circuit connected to a temperature-controlled circulating water bath (Isotope 1016P Fisher Scientific). Conductivities were measured over the temperature range of -3 to 74°C and the temperature of each sample is measured using a T-type thermocouple (Omega) placed in a sealed glass compartment fully submerged in the sample. The data acquisition system consists of a National Instruments Field point Module (FP 1000) connected to two National Instruments 8-channel thermocouple modules (FP-TC-120).

Two methods were used to calculate the resistance of the electrolyte  $Z_{RE}$  from the EIS data:

1. Take the intercept on a Nyquist plot of  $Z$  with the real impedance axis at high frequency
2. Use a program (ZSimpWin version two from EG&G Princeton Applied Research) to calculate equivalent circuit parameters. The used equivalent circuit for calculation is shown in Figure 3.2.



**Figure 3.2. Equivalent circuit which was used for electrolyte resistance calculation where  $R_E$  is bulk electrolyte resistance,  $R_{ct}$  is charge transfer resistance, and Q is constant phase element**

The first method was used in this study with the second method periodically used to verify the results. There was small difference in the resistance between two methods (<2%).

For each sample, the conductivity in five separate cells is measured with the reported value representing the average. The electrolyte conductivity is obtained from the cell constant and measured resistance using equation 3.5

$$\sigma_i = \frac{\sigma_{KCl} \times Z_{RE,KCl}}{Z_{RE,i}} \quad (3.5)$$

where  $\sigma_{KCl}$  is the conductivity of KCl standard [1409  $\mu\text{S cm}^{-1}$  at 25°C],  $Z_{RE,KCl}$  is the measured intercept of real impedance axis for the KCl standard [ohm], and  $Z_{RE,i}$  is the measured intercept of real impedance axis for sample i [ohm].

### 3.3. Viscosity measurement

Rheological measurements were conducted using a TA AR2000 stress rheometer. The liquid viscosities were determined using conical concentric cylinders. The inner radius

of the outer stator cylinder is 15 mm; the outer radius of the inner rotor is 14 mm; and the cylinder immersed height is 42 mm. Typically, the liquid sample volume is 19.6 ml.

Liquid viscosities were measured by a steady-state flow mode. Typical Newtonian behavior was observed for the liquid sample: viscosity does not vary with shear stress or shear rate; viscosity is constant with time of shearing; and stress in fluid immediately falls to zero when shear is stopped.

To check the effect of EC content and salt concentration on viscosity, the viscosity was measured at 4 temperatures (5, 10, 15, and 25 °C) for the following salt concentration and solvent compositions (GBL:EA:EC): 0.7 M LiBOB for 1:1:0, 1:1:0.1, 1:1:0.5, and 1:1:1.

To check the salt concentration effect on the viscosity, viscosity was measured at two temperatures (5 and 25°C) for 1:1:0.1 (GBL: EA: EC) with following LiBOB concentration: 0.2, 0.5, 0.7, 1, and 1.2 M.

### 3.4. References

1. H. G. Schweiger, M. Multerer, U. Wietelmann, J. C. Panitz, T. Burgemeister, and H. J. Gores, *J. Electrochem. Soc.*, (2005), 152, A622.
2. J. Zhou, PhD” Fumed Oxide-Based Nanocomposite Polymer  
Eelectrolyte For Rechargeable Lithium Batteries“ North Carolina State University, (2002).
3. M. Riley, P. S. Fedkiw, and S. A. Khan, *J. Electrochem. Soc.* 149, (2002), A667.

## CHAPTER 4: RESULTS AND DISCUSSION

The conductivity and viscosity results for LiBOB salt in GBL+EA+EC are first presented in Section 4.1, which is followed by a discussion of these results in Section 4.2. In order to focus the presentation and subsequent discussion on the effect of one variable at a time on the conductivity or viscosity, some data are presented in Section 4.1 more than once.

### 4.1. Results

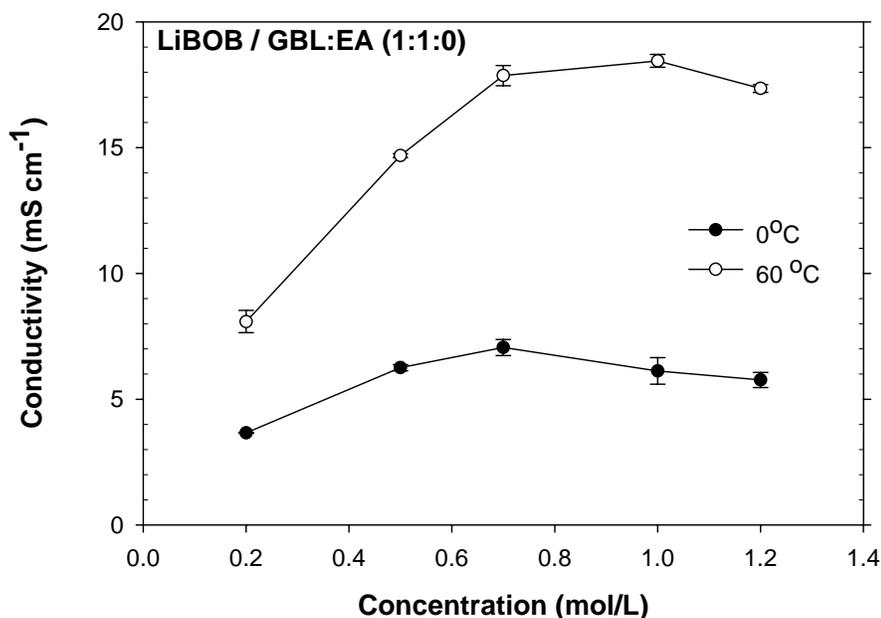
#### 4.1.1. Salt effect on conductivity and viscosity

Figures 4.1-4.4 show conductivity as a function of LiBOB concentration in GBL + EA + EC mixtures at 0 and 60 °C. Each figure is for a different composition of GBL+EA+EC of 1:1:0, 1:1:0.1, 1:1:0.5, and 1:1:1 (by wt), respectively. Conductivity has a maximum in salt concentration for all solvent compositions at 0 °C; however, at 60 °C for the GBL+EA+EC composition of 1:1:1, the conductivity monotonically increases with salt concentration up to 1.2 M. The salt concentration of maximum conductivity varies with temperature. For example, at 0 °C it is around 0.7 M and at 60 °C it is around 0.7-1.2 M, depending on the solvent composition. To enable a more direct comparison of these results, conductivities for all compositions at 0 and 60 °C are plotted in Figures 4.5 and 4.6, respectively.

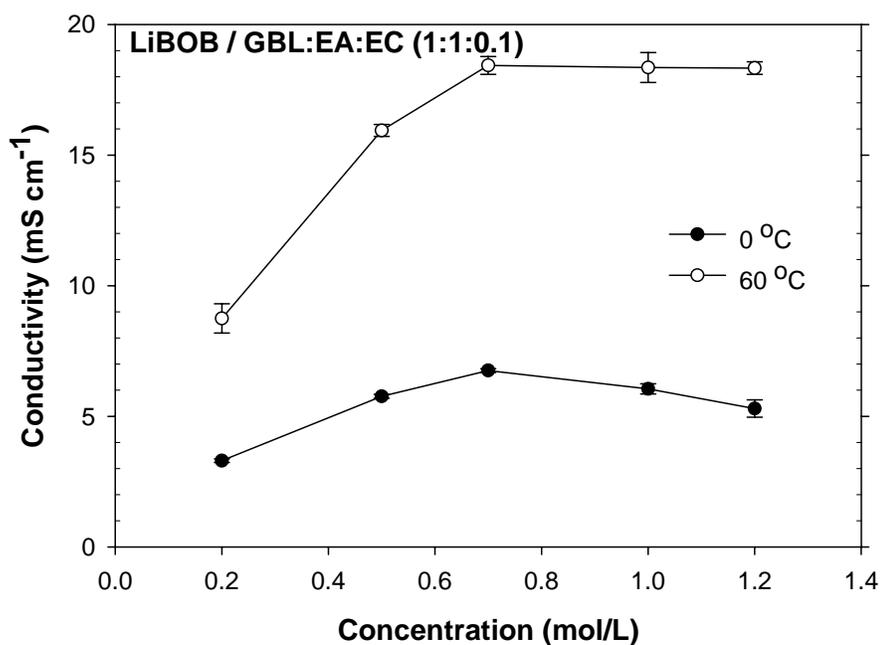
To eliminate the effect of free ions and their contribution to the conductivity, the molar conductivity is useful<sup>1</sup>. Figures 4.7-4.10 show the molar conductivity as a function of LiBOB concentration in GBL+ EA+ EC mixtures at 0 and 60 °C. Each figure is for a solvent

composition of GBL+EA+EC of 1:1:0, 1:1:0.1, 1:1:0.5, and 1:1:1, respectively. The molar conductivity monotonically decreases with salt concentration. To enable a more direct comparison of these results, molar conductivities for all compositions 0 and 60 °C are plotted in Figures 4.11 and 4.12, respectively.

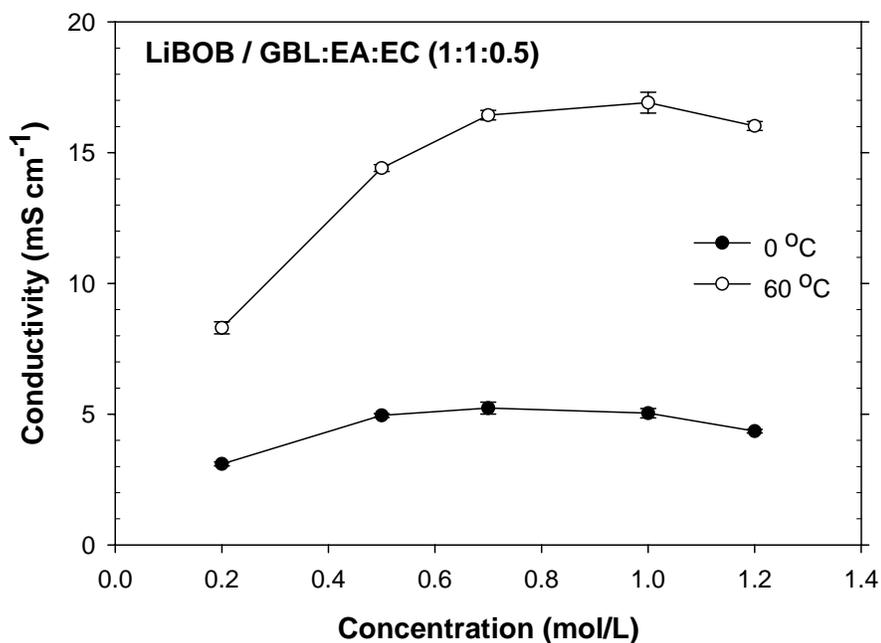
The viscosity of GBL+EA+EC solvents at 1:1:0.1 as a function of LiBOB concentration at 5 and 25 °C is plotted in Figure 4.13. The viscosity increases with salt concentration and decreases with lowering temperature.



**Figure 4.1. Concentration dependence of conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0 composition at 0 and 60 °C**



**Figure 4.2.** Concentration dependence of conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0.1 composition at 0 and 60 °C



**Figure 4.3.** Concentration dependence of conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0.5 composition at 0 and 60 °C

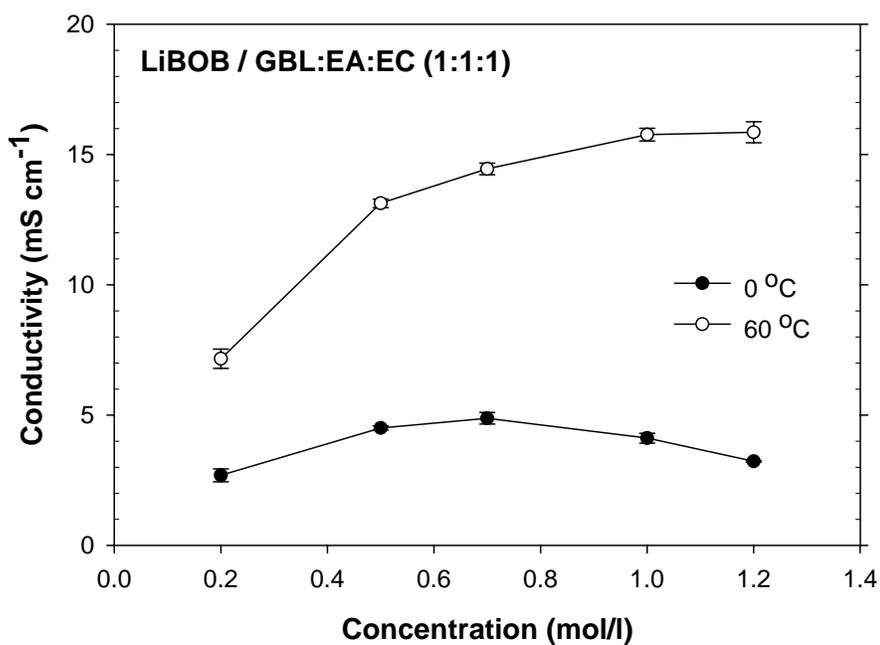


Figure 4.4. Concentration dependence of conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:1 composition at 0 and 60 °C

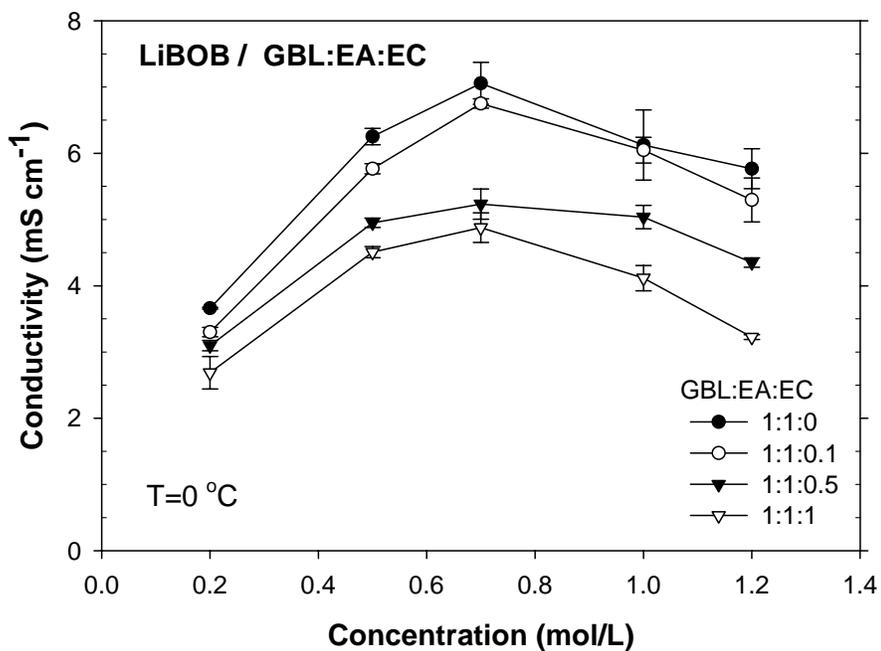


Figure 4.5. Concentration dependence of conductivity of electrolyte containing LiBOB in various solvent compositions of GBL+EA+EC at 0 °C

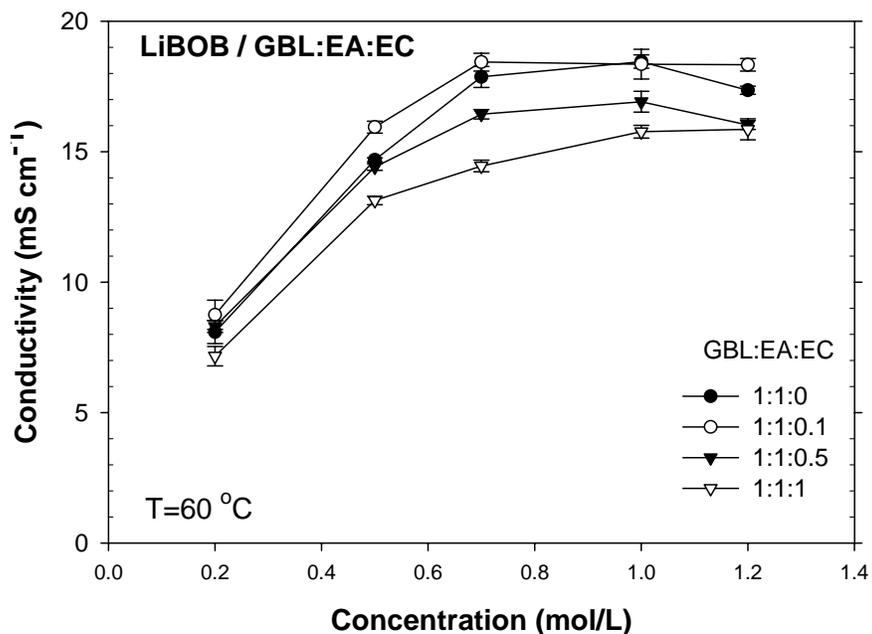


Figure 4.6. Concentration dependence of conductivity of electrolyte containing LiBOB in various solvent compositions of GBL+EA+EC at 60 °C

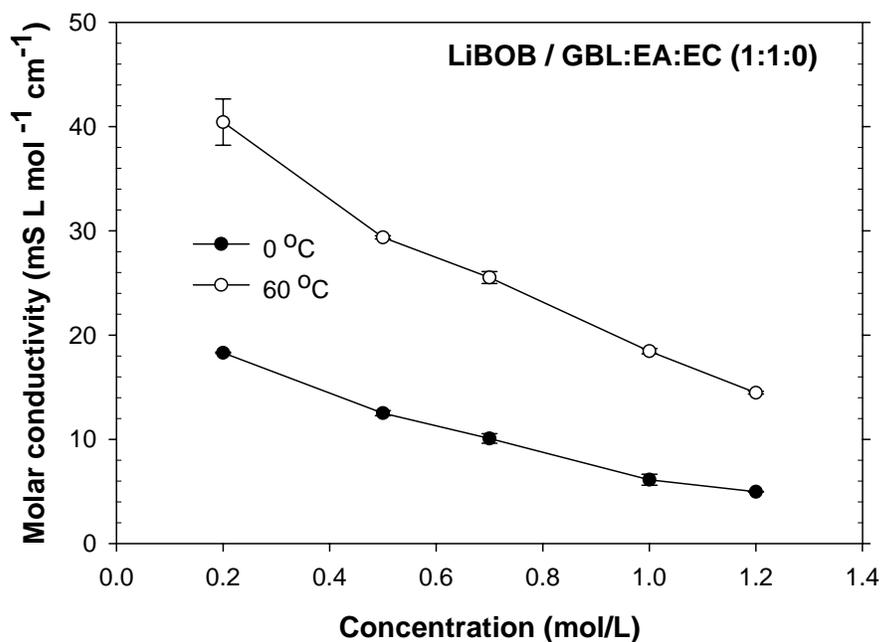
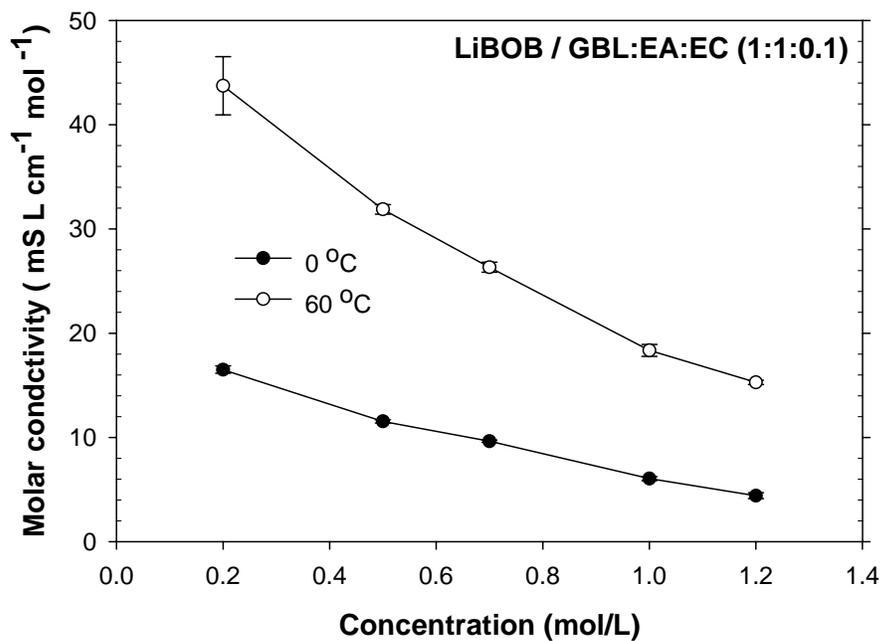
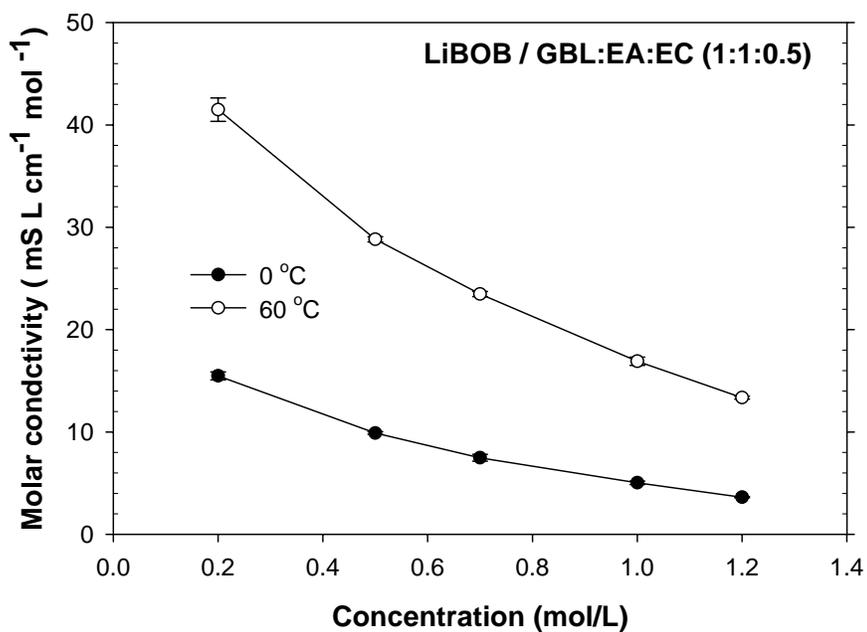


Figure 4.7. Concentration dependence of molar conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0 composition at 0 and 60 °C



**Figure 4.8.** Concentration dependence of molar conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0.1 composition at 0 and 60 °C



**Figure 4.9.** Concentration dependence of molar conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:0.5 composition at 0 and 60 °C

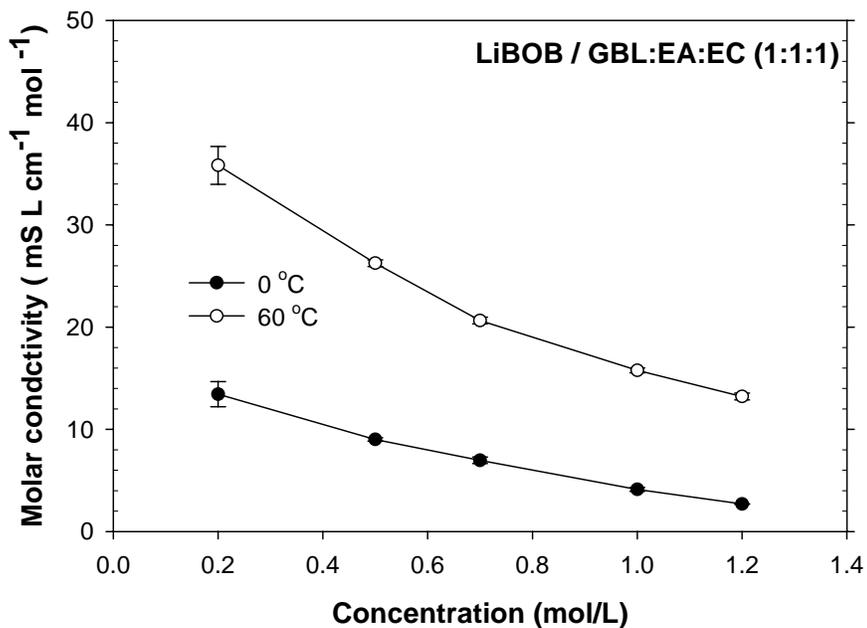


Figure 4.10. Concentration dependence of molar conductivity of electrolyte containing LiBOB in GBL+EA+EC of 1:1:1 composition at 0 and 60 °C

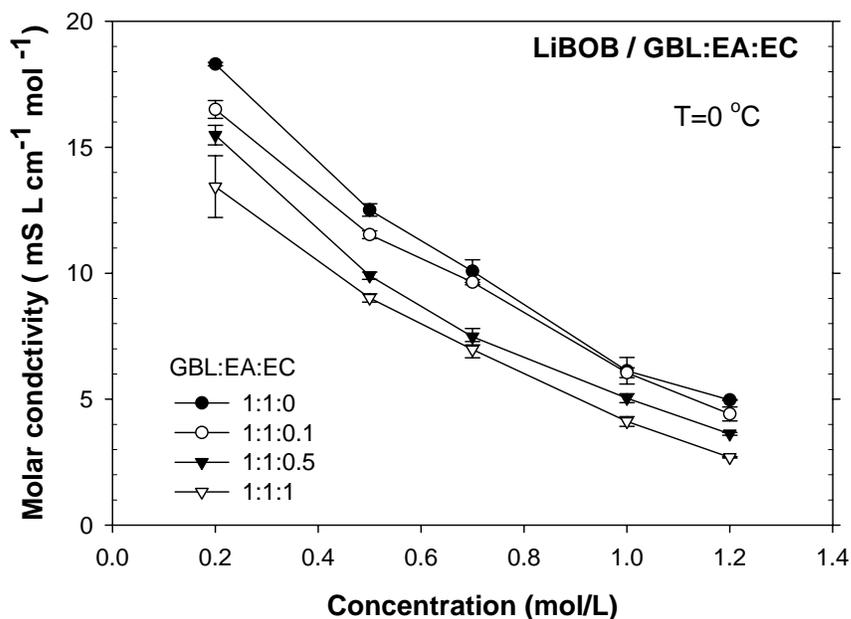
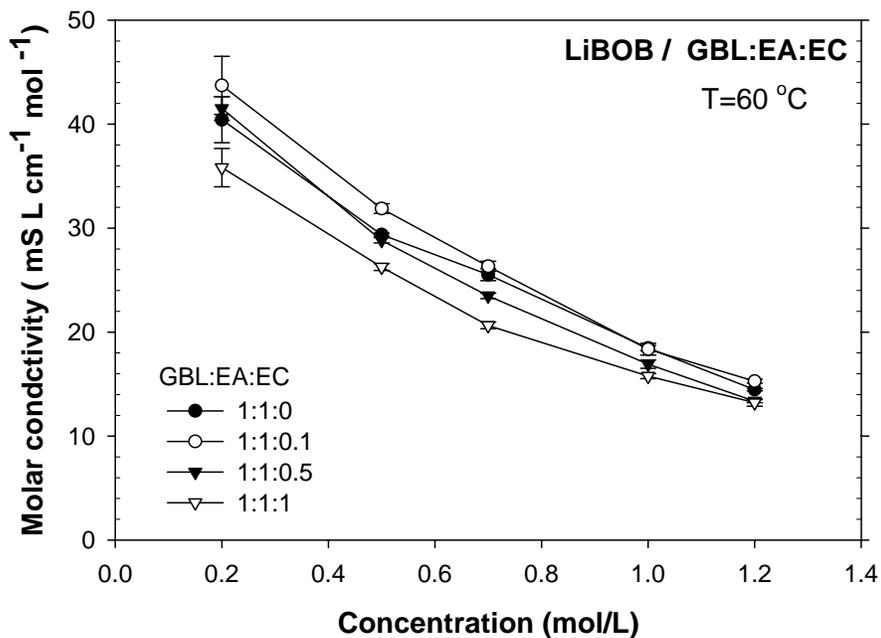
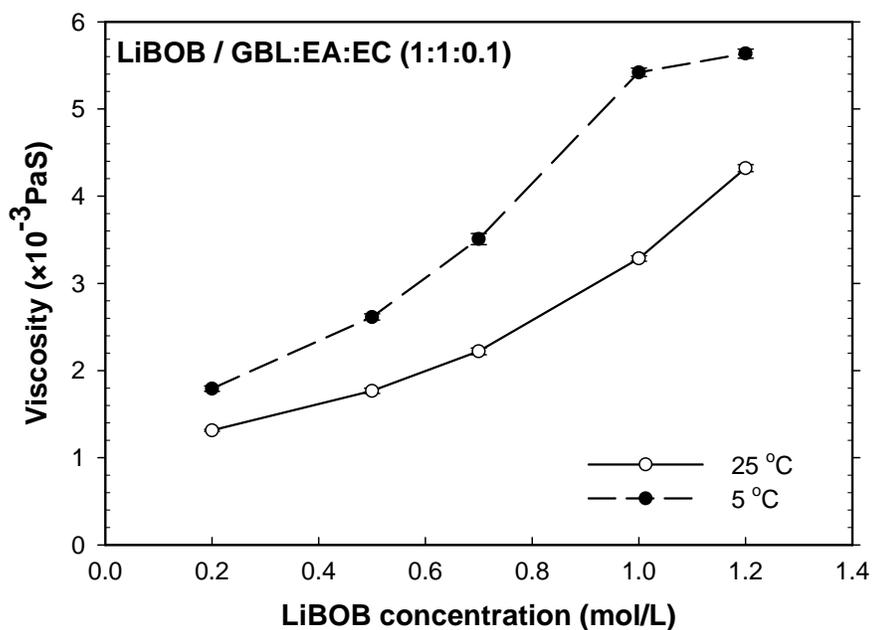


Figure 4.11. Concentration dependence of molar conductivity of electrolyte containing LiBOB in various solvent compositions of GBL+EA+EC at 0 °C



**Figure 4.12.** Concentration dependence of molar conductivity of electrolyte containing LiBOB in various solvent compositions of GBL+EA+EC at 60 °C

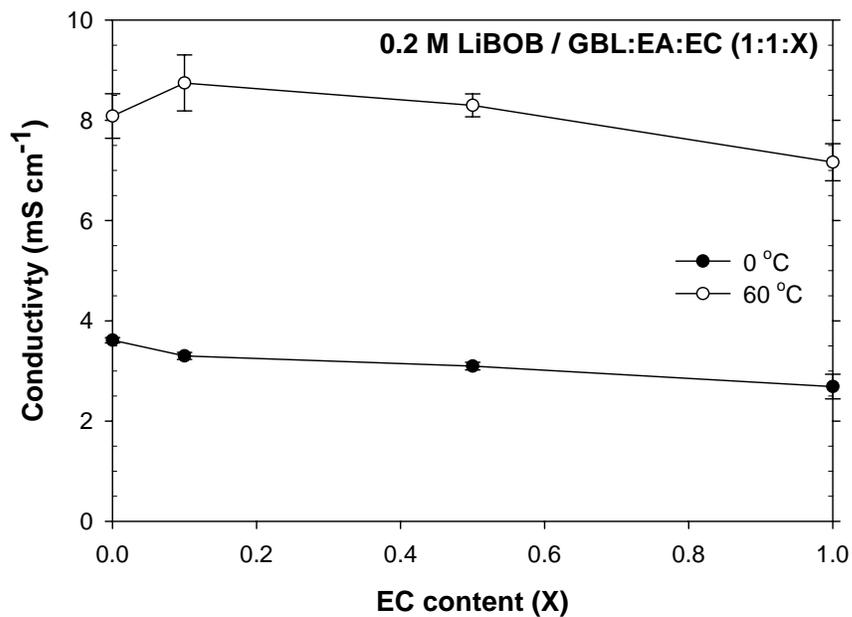


**Figure 4.13.** Concentration dependence of viscosity of electrolyte containing LiBOB in GBL+EA+EC composition of 1:1:0.1 at 5 and 25 °C

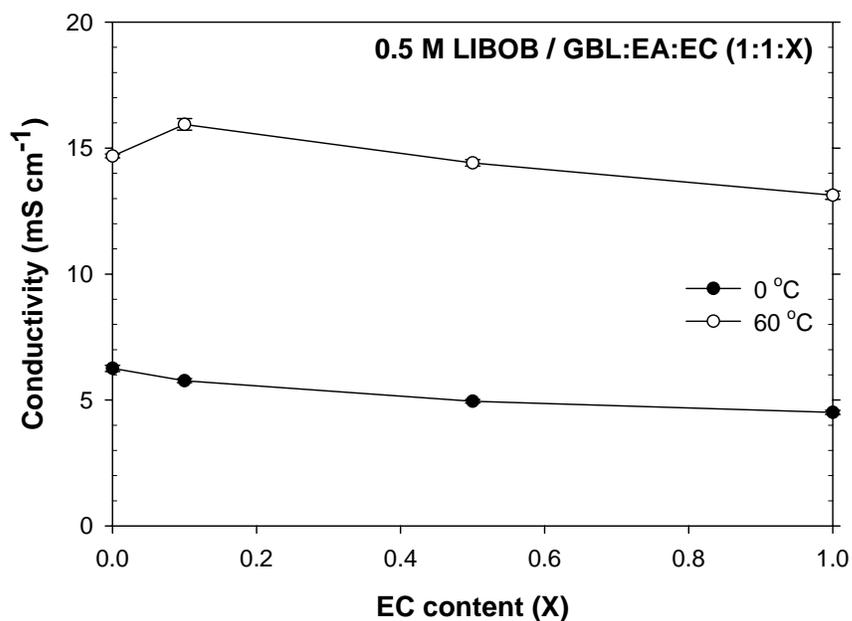
#### **4.1.2. Effect of EC content on conductivity and viscosity**

Conductivity was measured as a function of EC content in the three-component solvent mixture at 0 and 60 °C, as shown in Figures 4.14-4.18. Each figure is for one salt concentration of 0.2, 0.5, 0.7, 1, and 1.2 M, respectively. At 0 °C the conductivity decreases with increase in EC content; however, at 60 °C the conductivity reaches a maximum with EC content. This behavior was common for all LiBOB concentrations studied. To enable a direct comparison of these results, conductivities as function of EC content for all salt concentrations at 0 and 60 °C are plotted in Figures 4.19 and 4.20, respectively.

The viscosity of the electrolyte at fixed salt concentration and different EC content was measured at 10 and 25 °C and these results are plotted in Figure 4.21. We see that the viscosity increases with increasing EC content.



**Figure 4.14.** Dependence of conductivity on EC content in 0.2 M LiBOB in GBL+EA+EC at 0 and 60 °C



**Figure 4.15.** Dependence of conductivity on EC content in 0.5 M LiBOB in GBL+EA+EC at 0 and 60 °C

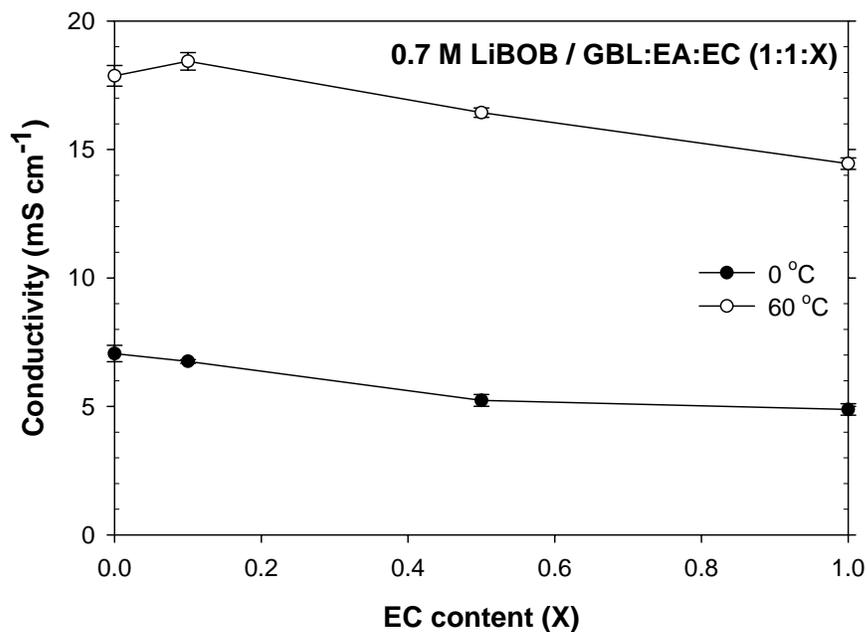


Figure 4.16. Dependence of conductivity on EC content in 0.7 M LiBOB in GBL+EA+EC at 0 and 60 °C

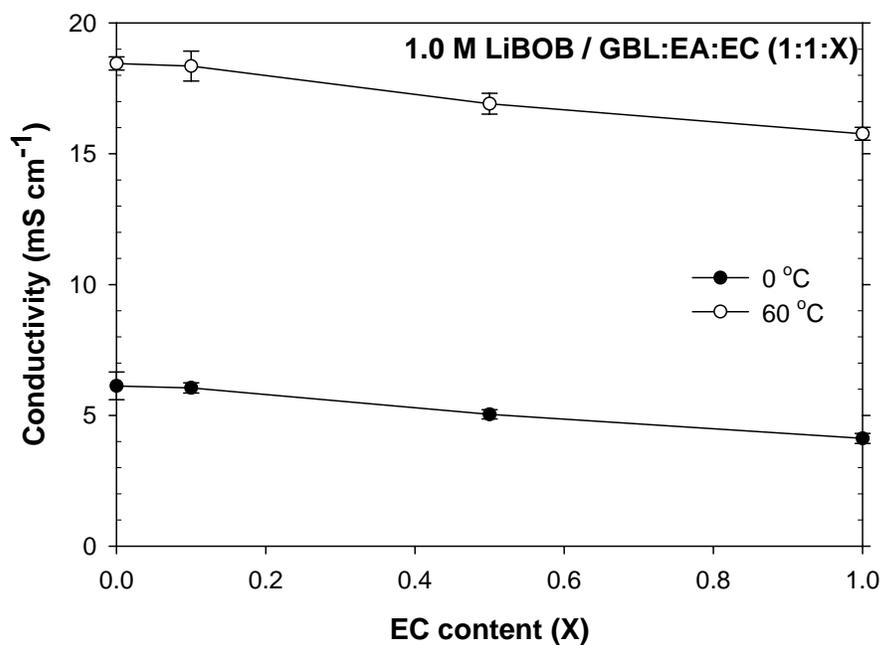


Figure 4.17. Dependence of conductivity on EC content in 1 M LiBOB in GBL+EA+EC at 0 and 60 °C

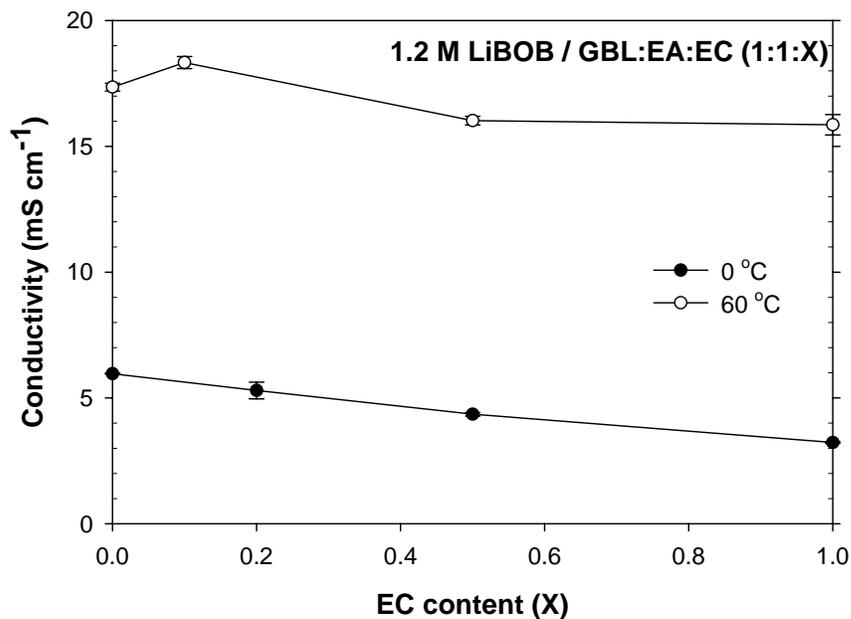


Figure 4.18. Dependence of conductivity on EC content in 1.2 M LiBOB in GBL+EA+EC at 0 and 60 °C

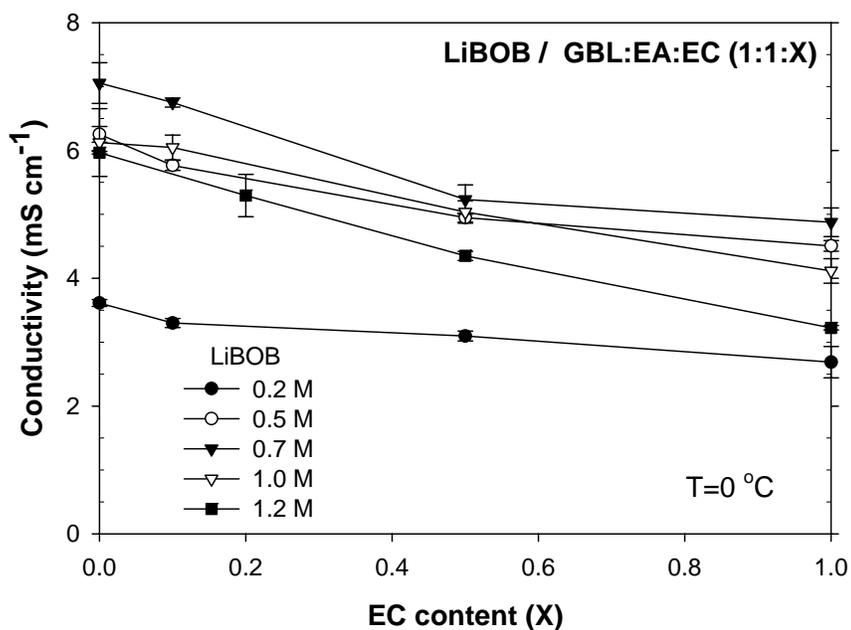


Figure 4.19. Dependence of conductivity on EC content in LiBOB in GBL+EA+EC at 0 °C at various LiBOB concentrations

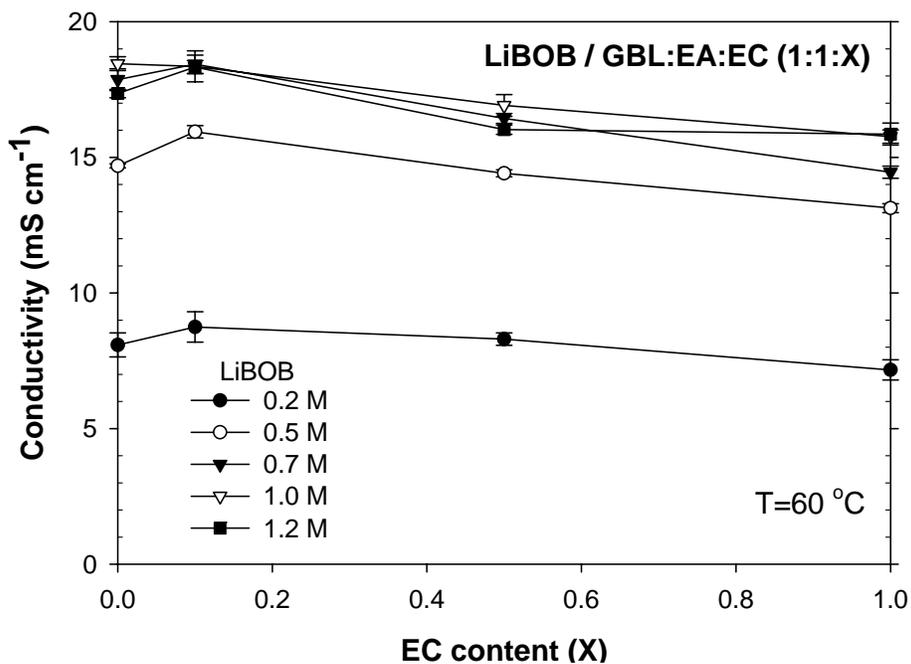


Figure 4.20. Dependence of conductivity on EC content in LiBOB in GBL+EA+EC at 60 °C at various LiBOB concentrations

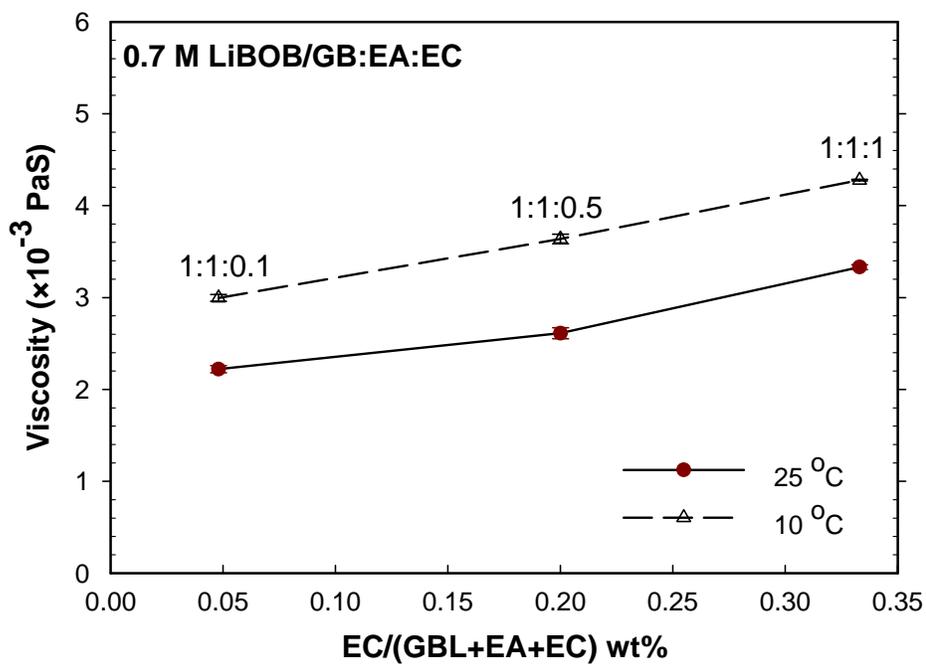


Figure 4.21. Dependence of viscosity on EC content in 0.7 M LiBOB in GBL+EA+EC at 10 and 25 °C

### 4.1.3. Effect of temperature on conductivity

Electrolyte conductivity for different salt concentrations was measured from -3 °C to 74 °C; however, only conductivity between 0 and 60 °C are plotted in Figures 4.22-4.30 because not all cells in the multi-cell thermostat reached the extrema in temperature. Figures 4.22-4.26 show the temperature dependence of conductivity for LiBOB in GBL+ EA+EC mixtures at different EC content. Each figure is for one salt concentration of 0.2, 0.5, 0.7, 1, and 1.2 M, respectively. The conductivity increases with temperature for all salt concentrations and solvent compositions. As the temperature decreases, the difference in conductivity between electrolytes with different EC content becomes more pronounced, as seen in Figure 4.26. The electrolyte composition with the highest conductivity at high temperature does not necessarily have the highest conductivity at low temperature. For example in Figure 4.26, at 60 °C the electrolyte with GBL: EA: EC composition of 1:1:0.1 is the best while the electrolyte with composition of 1:1:0 has a lower conductivity. At 0°C, however, the trends are reversed.

Figures 4.27-4.30 show the temperature dependence of molar conductivity for LiBOB in GBL+EA+EC solvent mixtures at different salt concentrations. Each figure is for one solvent composition varying from 1:1:0 to 1:1:1. The molar conductivity decreases with decrease in temperature for all solvent compositions and salt concentrations.

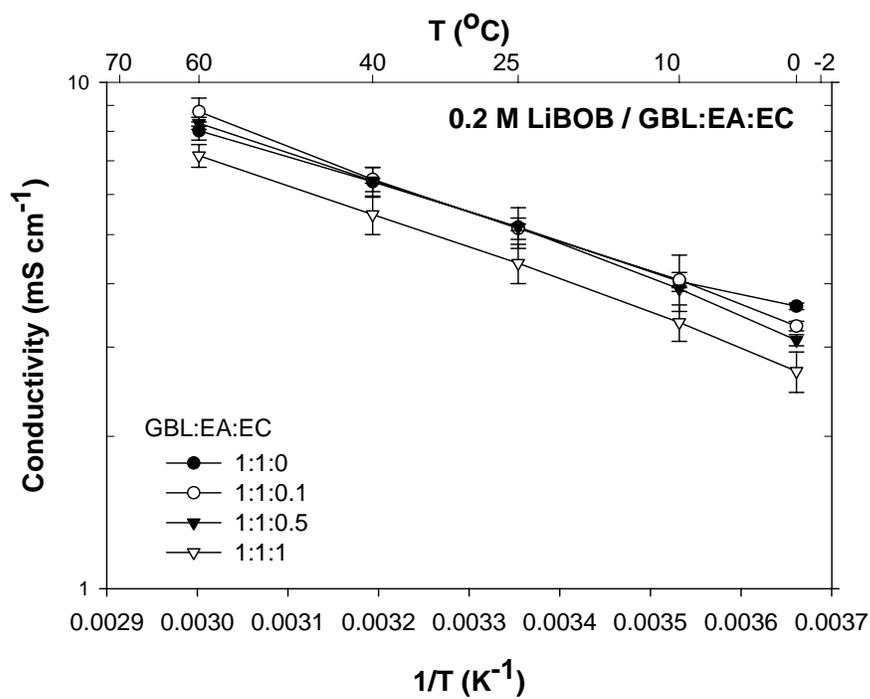


Figure 4.22. Temperature dependence of conductivity of 0.2 M LiBOB in a GBL+EA+EC solvent mixture of varying EC content

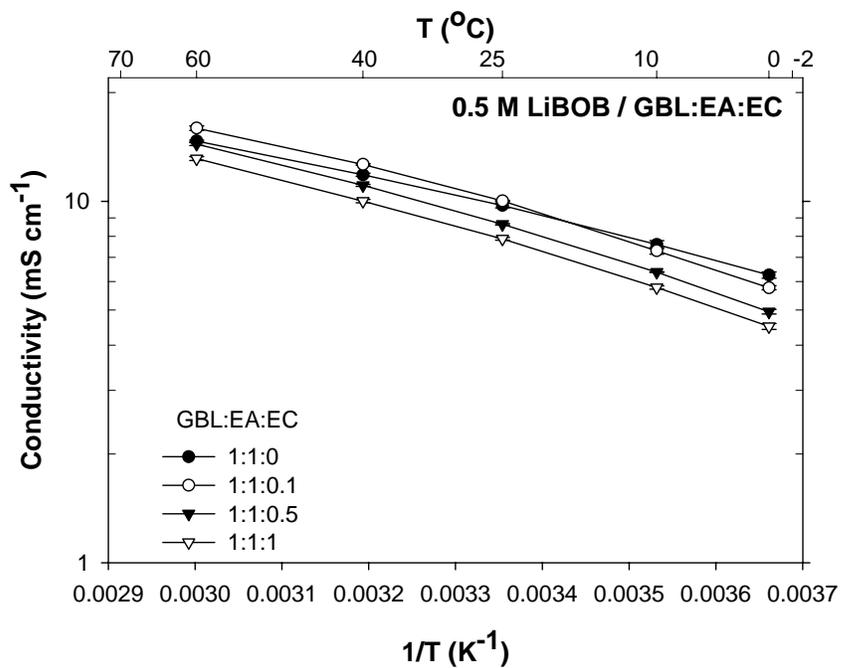


Figure 4.23. Temperature dependence of conductivity of 0.5 M LiBOB in a GBL+EA+EC solvent mixture of varying EC content

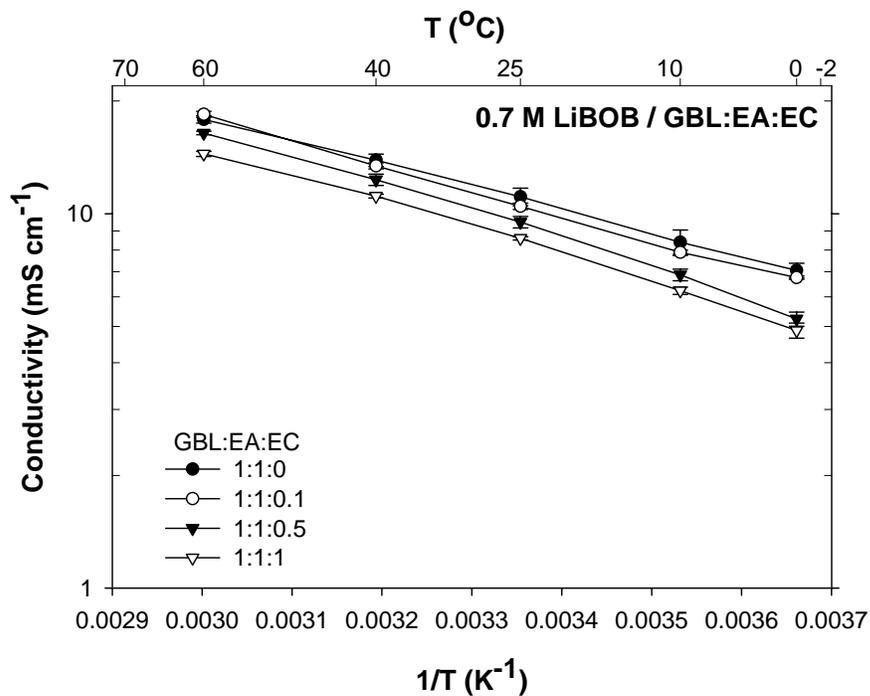


Figure 4.24. Temperature dependence of conductivity of 0.7 M LiBOB in a GBL+EA+EC solvent mixture of varying EC content

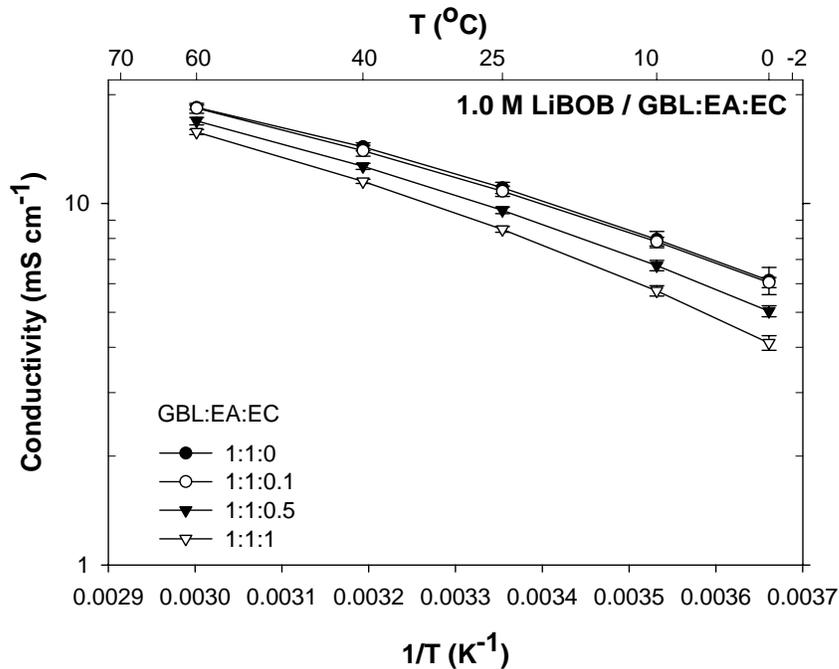


Figure 4.25. Temperature dependence of conductivity of 1.0 M LiBOB in a GBL+EA+EC solvent mixture of varying EC content

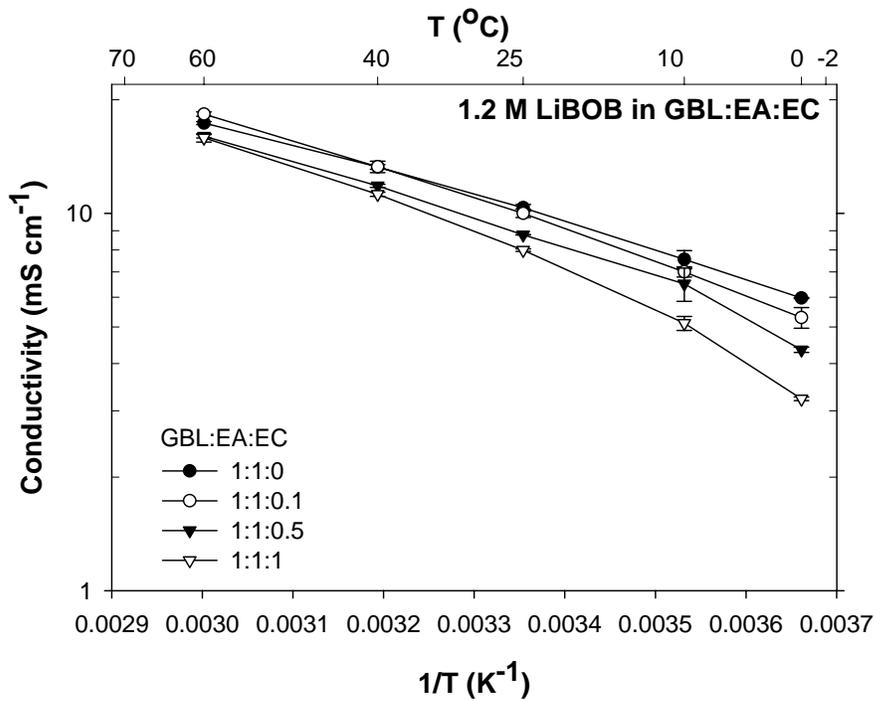


Figure 4.26. Temperature dependence of conductivity of 1.0 M LiBOB in a GBL+EA+EC solvent mixture of varying EC content

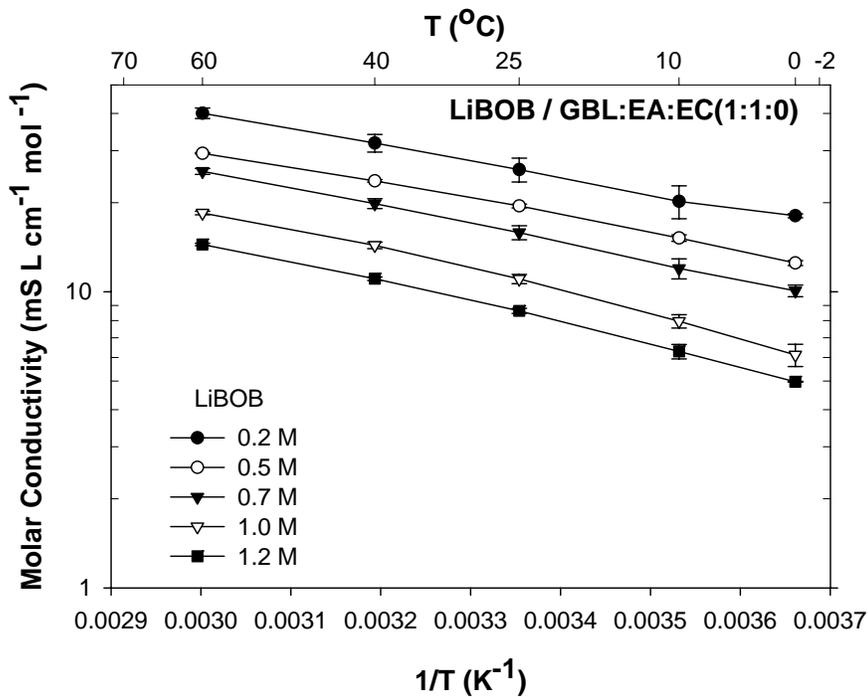


Figure 4.27. Temperature dependence of molar conductivity of LiBOB in a solvent composition of GBL+EA of 1:1 at different LiBOB concentration

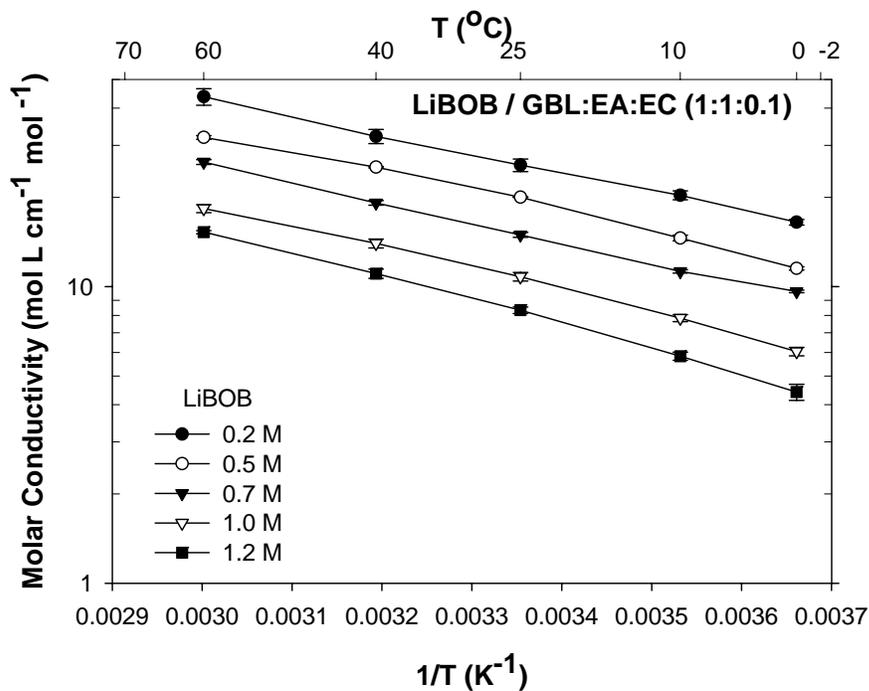


Figure 4.28. Temperature dependence of molar conductivity of LiBOB in a solvent composition of GBL+EA+EC of 1:1:0.1 at different LiBOB concentration

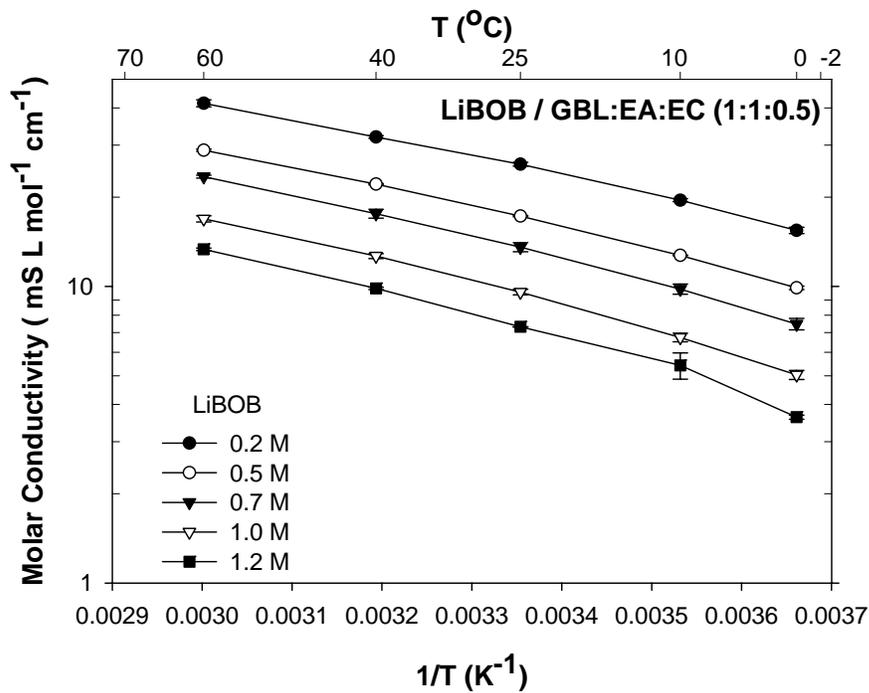
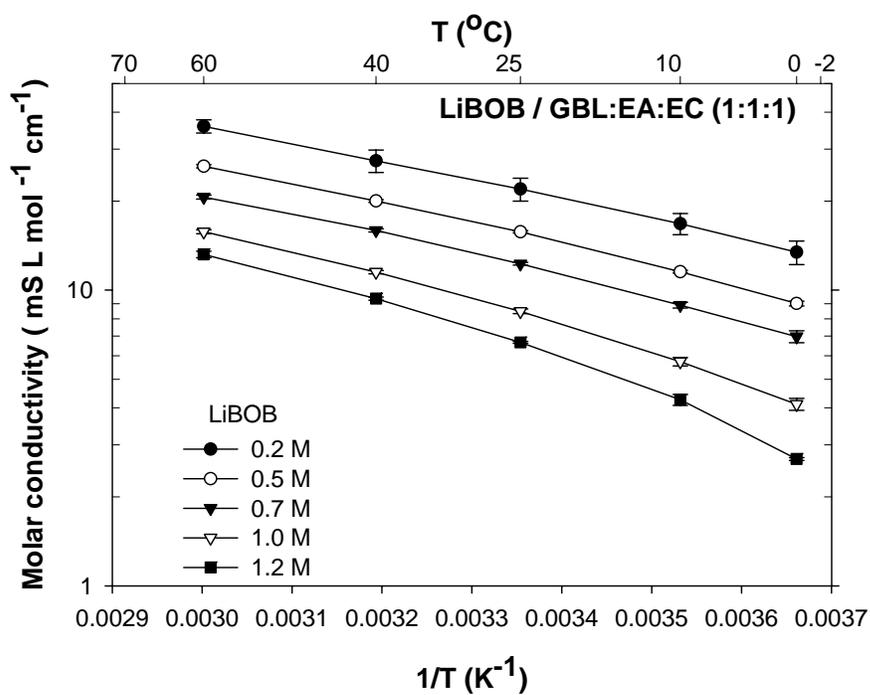


Figure 4.29. Temperature dependence of molar conductivity of LiBOB in a solvent composition of GBL+EA+EC of 1:1:0.5 at different LiBOB concentration



**Figure 4.30. Temperature dependence of molar conductivity of LiBOB in a solvent composition of GBL+EA+EC of 1:1:1 at different LiBOB concentration**

## 4.2. Discussion

The basic function of an electrolyte is to conduct ions, and in liquid electrolytes the transport of ions occurs through two steps:

1. Dissociation and solvation of the ionic compound
2. Migration of ions in the electrolyte media

The dissociation of an ionic compound is related to the physicochemical nature of the compound (e.g., how strongly it coordinates with the solvent) and by the dielectric constant of the solvent. The dielectric constant is important because it determines how effectively a solvent can shield an ion and prevent it from forming an ion pair with its counter ion. For ion-pair formation to occur, the distance between the two ions should be less than Bjerrum critical distance ( $q$ )<sup>2,3</sup>. The critical distance  $q$  for ion pair formation is given by equation 1:

$$q = \frac{|z_i z_j|}{8\pi\epsilon_0 \epsilon kT} e^2 \quad (1)$$

where  $z$ ,  $\epsilon_0$ ,  $k$ ,  $e$ , and  $T$  are the ion-valence order, dielectric constant of vacuum, Boltzmann's constant, electronic charge, and temperature, respectively. As the dielectric constant increases, the required distance  $q$  for ion-pair formation decreases, and thereby for a given salt concentration, the probability of ion-pair formation decreases.

For the second step, when ions migrate within the electrolyte they face an opposing drag force applied by the surrounding solvent molecules, which is affected by the solution

viscosity. For a solvent with a high viscosity, it is difficult for ions to migrate within the electrolyte which lowers the conductivity. The relationship between viscosity ( $\eta$ ) and ion mobility ( $\mu_i$ ), as given by Stokes-Einstein relation, is shown in equation 2<sup>2</sup>:

$$\mu_i = \frac{|z_i|e}{6\pi\eta r_i} \quad (2)$$

where  $\eta$ ,  $\mu_i$ ,  $e$ ,  $z_i$ , and  $r_i$  are the viscosity of the solution, ion mobility, electronic charge, valence order, and radius of the ion, respectively. As seen in equation 2, ion mobility decreases as viscosity increases. Hence, low-viscosity solvents are ideal candidates for electrolyte application; however, their use as a practical electrolyte for lithium-ion cells is restricted because of their low-dielectric constants (Tables 2.1 and 2.2), which limits their ability to dissociate ions effectively to prevent ion pairing. The net effect of these two steps is seen in the ionic conductivity  $\sigma$ , as shown in equation 3.

$$\sigma = F \sum_i |z_i| \mu_j C_i \quad (3)$$

where  $z_i$ ,  $C_i$ ,  $\mu_i$ , and  $F$  are the valence order of ionic species  $i$ , ion concentration of species  $i$ , the ionic mobility, and Faraday constant, respectively.

In summary, ionic conductance is affected by three major factors: number density of free ions; dielectric constant of the solvent; and viscosity of the electrolyte. The conductivity behavior of our system electrolyte system with changes in salt concentration, EC content, and temperature can be understood by these three factors. A brief discussion about these factors is given below:

### 1. The number density of free ions

If we keep all other variables constant, as the number density of free ions increases, the conductivity of the electrolyte follows likewise. The number density of free ions depends on salt concentration and temperature. For example, if all variables are constant except temperature, as the temperature increases the number of free ions will increase asymptotically until complete dissociation of salt occurs. This is because increasing temperature adds thermal agitation which weakens the pairing between ions and decrease the required distance  $q$  for ion pairing, as shown in equation 1<sup>4</sup>.

### 2. Dielectric constant of the solvents

A solvent with high-dielectric constant is able to shield ions from attraction of ions of opposite charge. So, solvents with high-dielectric constant are able to decrease ion association in the electrolyte. As temperature increases, thermal energy is added to the system that disrupts the alignment of solvent molecules to the applied electrical field<sup>5-7</sup> and hence, the dielectric constant decreases.

### 3. Viscosity

As viscosity increases, keeping all other variables constant, the conductivity decreases because the resistance for movement of ions becomes larger. As the temperature increases the viscosity decreases. The viscosity also increases with increase in EC content<sup>4, 7-10</sup> and salt concentration<sup>11-13</sup>

Using these three factors, we can rationalize the trend in conductivity of our electrolyte with temperature, LiBOB concentration, and EC content.

#### **4.2.1. Salt effect on conductivity and viscosity**

As we see from Figures 4.1-4.4, conductivity increases with salt concentration at low-salt concentrations. This occurs because the number of free ions increases with salt concentration. From equation 3, as the number of free ions increases, the conductivity increases. This is understandable since more free ions can carry more charge through the electrolyte. Consequently, ion conductivity increases with salt concentration until it peaks at a certain concentration. After achieving the maximum conductivity, any increase in salt concentration results in higher ion aggregation and higher viscosity of the solution, which reduces the free-ion number and the ionic mobility, respectively. It is a universal phenomenon to have a maximum in conductivity at a certain concentration for liquid electrolytes, and it has been reported for many electrolytes of lithium salts<sup>13-17</sup>.

The concentration at which maximum conductivity occurs is affected by the dielectric constant of the solvent and temperature. With all things remaining equal, with a high-dielectric constant ion pairing occurs at higher salt concentration, and as the temperature increases the viscosity of the solution decreases and ion disassociation increases. The result of both effects is to shift the maximum conductivity to higher salt concentrations. For our system, the maximum conductivity was  $\sim 0.7$  M LiBOB at  $0^\circ\text{C}$  for all solvent compositions studied. At  $60^\circ\text{C}$  the system with GBL: EA: EC at 1:1:0 shows a broad maximum around 1.0 M in LiBOB. For the system with solvent composition of 1:1:0.1, the maximum in conductivity occurs between 0.7 and 1.2 M LiBOB. The system with GBL: EA: EC at

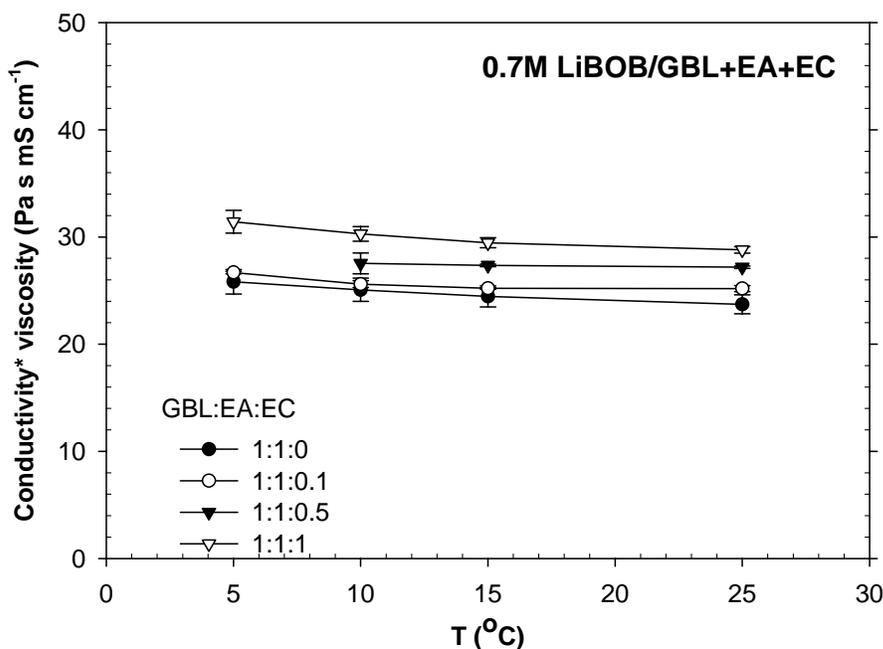
1:1:0.5, the maximum conductivity occurs around 1.0 M LiBOB, and finally for the system with solvent composition of 1:1:1, there is no maximum in the studied range of salt concentration. As seen in equation 1, the required distance  $q$  for ion-pair formation decreases as temperature increases. The decrease in  $q$  means that more salt can be dissolved without ion pairing, which will shift the maximum conductivity to a higher salt concentration than the same electrolyte at lower temperature. At high temperature (60°C), the maximum conductivity occurs at higher salt concentration as the EC content increases because more EC content means a higher dielectric constant of the solvent mixture. For the system GBL: EA: EC at 1:1:0.5, the maximum conductivity occurs at a lower salt concentration than that in the system with lower EC content (1:1:0.1) since at the former solvent composition, the higher EC content increases the viscosity which dominates over the dielectric-constant effect. The maximum conductivity at 0 °C occurs around 0.7 M LiBOB irrespective of EC content. Although more EC increases the solvent dielectric constant, the high viscosity of EC decreases the conductivity; that is, at low temperature the viscosity effect dominates over the dielectric-constant effect.

We eliminate the effect of salt concentration on the number of free ions in Figures 4.1-4.4 by dividing conductivity by the LiBOB concentration. The resulting molar conductivity  $\Lambda$  is plotted against concentration in Figures 4.7-4.10. The molar conductivity decreases with increase of salt concentration because of the two negative factors (viscosity and ion association). That is, as the salt concentration increases, the viscosity and ion association increases. As seen in equation 1, the conductivity decreases when the ion

mobility decreases as a result of viscosity increase. When ion association increases, the number density of free ions decreases, which also decreases the ion conductivity.

We can see the relation between the viscosity and the salt concentration in Figure 4.13. As the salt concentration increases so does the viscosity because of the increasing intermolecular force between ions and molecules.

Figure 4.31 shows the product of conductivity and viscosity as a function of temperature for all solvent compositions studied. The product of conductivity and



**Figure 4.31. Product of viscosity and conductivity for 0.7 M LiBOB/GBL+EA+EC as a function of temperature for various solvent compositions**

viscosity is nearly temperature independent, although there is a slight increase at the lowest temperature shown. Increasing values of the product  $\sigma\eta$  indicate increasing ion

disassociation.<sup>18</sup> Figure 4.31 shows that the highest  $\sigma\eta$  value is for GBL: EA: EC of 1:1:1 and smallest value is for solvent composition of 1:1:0. The increase of  $\sigma\eta$  product is due to the increase of EC content, which leads to the increase of dielectric constant, in turn leading to an increase of ion disassociation. Although the solvent composition of 1:1:1 should have the highest ion disassociation, its conductivity is the lowest as shown in Figures 4.5 and 4.6. This is because of the high viscosity of EC. From Figure 4.31 we can deduce that viscosity is the dominate factor in our electrolyte.

#### 4.2.2. Effect of EC content on conductivity and viscosity

At fixed temperature and salt concentration, solvent composition has an effect on conductivity. The effect of solvent composition is expected through its influence on viscosity and dielectric constant. Mixing rules for viscosity and dielectric constant of a solvent mixture are given in equations 4 and 5, respectively<sup>19</sup>:

$$\log \eta_m = x_1 \log \eta_1 + x_2 \log \eta_2 + \dots \quad (4)$$

$$\varepsilon_m = y_1 \varepsilon_1 + y_2 \varepsilon_2 + \dots \quad (5)$$

where  $x_i$  is the mole fraction of solvent  $i$  and  $\eta_i$  is the viscosity of the component  $i$ ,  $y_i = x_i V_i / V_m$  = volume fraction of component  $i$ ,  $V_i$  is the molar volume fraction of component  $i$ , and  $V_m$  is the molar volume of mixture

$$V_m = x_1 V_1 + x_2 V_2 + \dots \quad (6)$$

These equations are derived from ideal or nearly ideal solution theory<sup>20</sup>, however, they predict properties of practical mixtures for solvents of interest for lithium batteries within a

few percent <sup>20</sup>. For example, equation 6 is accurate within 1% for system of interest (lithium-batteries solvents) <sup>19</sup>. Since dielectric constant is a volume-related property, the dielectric constant of an ideal mixture of solvents can be written as equation 5. The accuracy of equation 5 is within 5% for solution of interest for lithium batteries <sup>19</sup>. Equation 4 accuracy is about 8% for solvent of interest for lithium batteries.<sup>19</sup> As a measure to test equation 4, we measured the viscosity of EA, GBL, and their mixtures at a 1:1 composition for temperatures between 10 and 25 °C. The results are presented in Table 4.1, which shows how well equation 4 applies to this binary system.

**Table 4.1. Measured and calculated viscosity for GBL, EA and mixture of 1:1 composition**

<b>Temp. (°C)</b>	<b>GBL viscosity (cP)</b>	<b>EA viscosity (cP)</b>	<b>Measured viscosity for GBL:EA (cP)</b>	<b>Calculated viscosity (eqn 4) for GBL:EA (cP)</b>	<b>% error</b>
25	1.993	0.542	1.005	1.047	4.00
20	2.143	0.568	1.080	1.112	2.88
15	2.340	0.593	1.163	1.187	2.02
10	2.533	0.629	1.263	1.273	0.79

As seen in equations 4 and 5, the solvent viscosity and dielectric constant change with composition of the mixture, which affects the conductivity of the electrolyte through its dependence on viscosity and dielectric constant; however, the temperature and salt

concentration influence the degree of the effect. For example, at 0.2 M LiBOB and 0 °C (Figure 4.14), the conductivity decreases as EC content increases. The conductivity decrease is due to the dominant role of viscosity over dielectric constant at low temperature. In comparison at 60 °C, initially the conductivity increases with EC content and reaches a maximum at 1:1:0.1 (GBL: EA: EC); at higher EC content it decreases. The initial increase of conductivity with EC content occurs because the number of free ions increases upon addition of the high-dielectric constant EC ( $\epsilon \sim 89.6$ ). At the same time, however, the viscosity of system increases because of the high viscosity of EC (Figure 4.21). At the combination condition of low-EC content, low-salt concentration, and high temperature, the effect of free ions dominates over the viscosity effect. However, as the EC content increases the viscosity of the electrolyte increases and the viscosity effect dominates.

Similarly, salt concentration also affects the dependence of conductivity on solvent composition. For example, at 60 °C and 0.2 M LiBOB (Figure 4.14), conductivity increases with EC content up to a GBL:EA:EC composition of 1:1:0.1 but decreases at higher EC content. For 1.2 M LiBOB at 60 °C (Figure 4.18), the conductivity increases with increasing EC content up to solvent composition of 1:1:0.1 but decreases more slowly at higher EC content. At low-salt concentration, the positive effect of EC is effective only for low-EC content since the low-salt concentration does not need high-dielectric constant to disassociate the salt. This is because the distance between ions in the electrolyte is already large, which reduces the effect of dielectric constant on ion disassociation. So, as the EC content increases, its effect on ion dissociation will not be significant; however, the viscosity increases with EC content (Figure 4.21) till it reaches a point where the viscosity effect is

more important than the free-ion effect. In the case of high-salt concentration (1.2 M), the conductivity initially increases with EC content till it reaches the point where it decreases because the viscosity effect becomes dominant over the number density of free ions; however, as the EC content continues to increase, the number-of-free-ions effect counters the effect of viscosity so the two effects counter one another and conductivity levels off at high-salt concentration. For low temperature, the viscosity effect of EC is always more important than the effect of free ions generated by adding more EC.

From Figures 4.14-4.18, we see that the best solvent composition and salt concentration for the low temperature (0°C) is the system with GBL: EA: EC composition of 1:1:0 and 0.7 M LiBOB. For high temperature (60 °C), the best solvent composition and salt concentration is the system with GBL: EA: EC composition of 1:1:0.1 and 0.7 -1.2 M LiBOB.

### **4.2.3. Effect of temperature on conductivity**

Keeping the salt concentration and solvent composition fixed, the conductivity of LiBOB-containing electrolytes increases with temperature, as shown in Figures 4.22-4.26. As the temperature increases, the viscosity decreases and dielectric constant decreases. In the studied temperature range, the effect of viscosity outweighs the effect of dielectric constant. However, at temperatures much higher than 60 °C (not performed in this study) the dielectric constant is anticipated to take over viscosity and ionic conductivity should decrease. Such high temperatures are usually beyond the range of practical interest<sup>1, 21</sup>. Although the dielectric constant increases with a decrease in temperature, at low temperature, ion

conductivity is predominately determined by electrolyte viscosity. As the salt concentration increases, the drop in conductivity with decreasing temperature increases since the increasing salt concentration contributes to a higher viscosity. The combined effect of higher viscosity and low temperature is shown by the steeper curves at higher concentration in Figures 4.24-4.26.

Solvent composition also has an influence on the temperature dependence of ion conductivity. From Figures 4.22-4.26, we see that the rate of change of conductivity with temperature increases as the EC content increases.<sup>1</sup>

To see the effect of the temperature on the ionic conductivity more clearly, the molar conductivity is plotted against the inverse of temperature and the results are shown on Figures 4.27-4.30. These Figures clearly show that the rate of change in conductivity at low temperatures increases as concentration and EC content increase, as described on page 96.

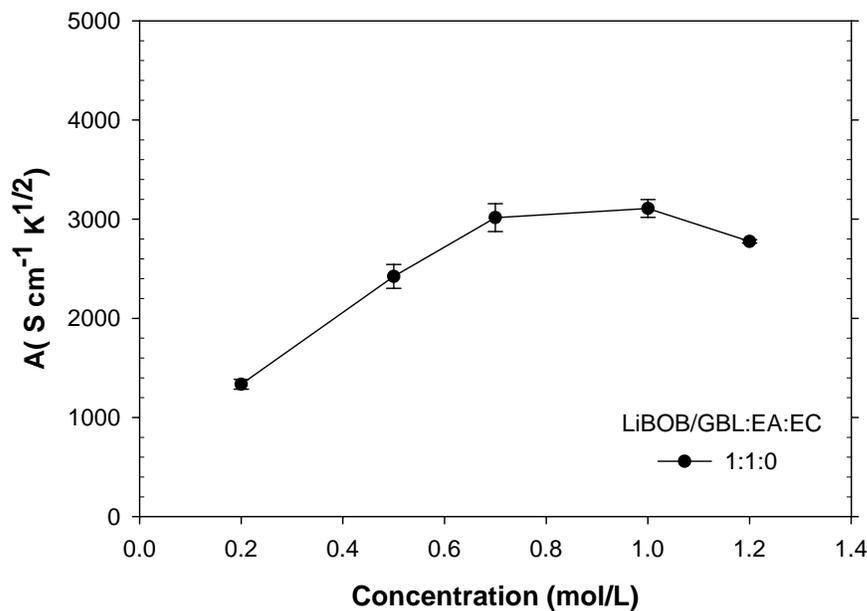
Figures 4.22-4.26 demonstrate that the conductivity behavior with temperature is non-Arrhenius, but it can be fitted to the Vogel-Tamman-Fulcher (VTF) equation:

$$\sigma = \frac{A \exp[-B / R(T - T_o)]}{\sqrt{T}} \quad (7)$$

where  $A$ ,  $B$ , and  $T_o$  are constants determined through data fitting. The constant  $A$  is a pre-exponential factor which is related to ion mobility and ion association<sup>22</sup>. The constant  $B$  is an apparent activation energy<sup>22</sup>. The constant  $T_o$  is the temperature at which conductivity would completely vanish, and thus is sometimes called vanishing conductivity temperature.<sup>23-26</sup>

The  $T_0$  are closely related to the glass transition temperatures of the solutions, which agrees with general knowledge that ion transport in liquids or any noncrystalline polymer media is coupled with solvent movement.<sup>21,27,28</sup> The glass transition temperature is a characteristic temperature at which material in the state of supercooled liquid changes its behavior from that of a liquid to solid during cooling without undergoing crystallization. Generally, the higher is the viscosity of a liquid, the higher is the glass transition temperature.

Figures 4.32-4.34 show the concentration dependence of  $A$ ,  $B$ , and  $T_0$ , respectively, from fit of the data in Figures 4.22-4.26. The results in Figures 4.32-4.34 agree with trends for these parameters reported in the literature.<sup>22</sup> In Figure 4.32 we see that  $A$  increases



**Figure 4.32. Concentration dependence of constant  $A$  for GBL: EA: EC composition of 1:1:0**

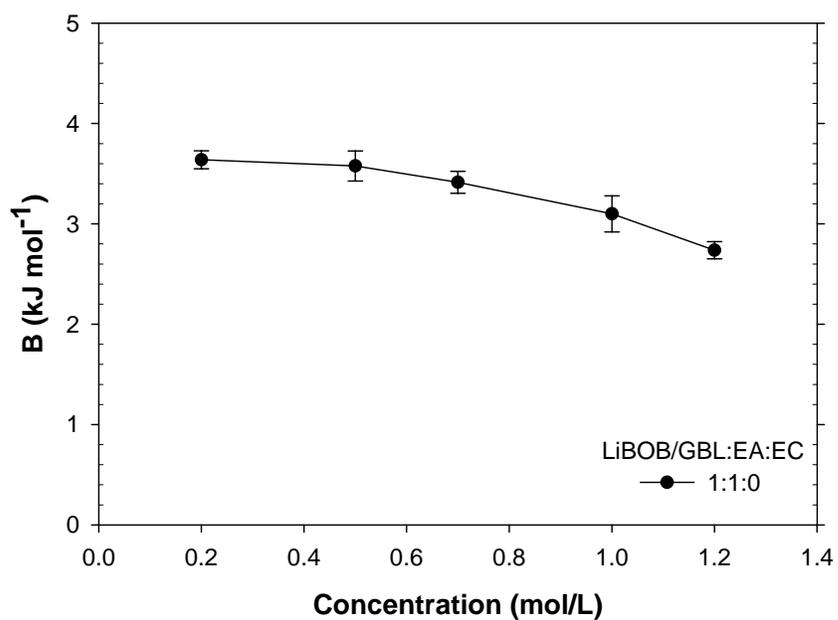


Figure 4.33. Concentration dependence of constant  $B$  for GBL: EA: EC composition of 1:1:0

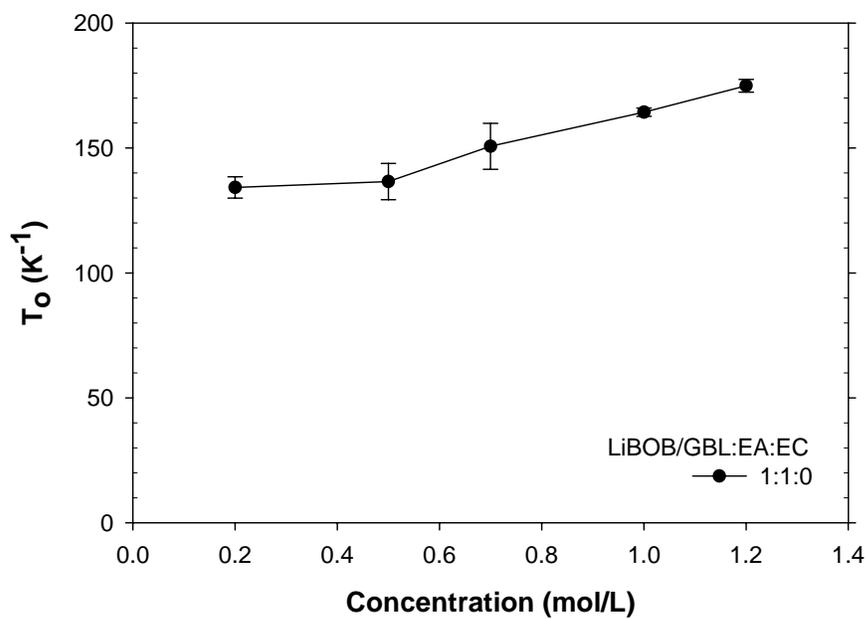


Figure 4.34. Concentration dependence of constant  $T_0$  for GBL: EA: EC composition of 1:1:0

then decreases with salt concentration which supports the supposition that  $A$  is related to the mobility and association of ions. In Figure 4.33,  $B$  decreases with salt concentration, which can be rationalized from Debye-Huckel theory. As salt concentration increases the Debye length, which is defined as the effective radius of the ionic cloud that surrounds the reference ion, decreases. We can see the relation between Debye length and salt concentration in equation 8:

$$\kappa^{-1} = \left( \frac{\epsilon k T}{4\pi \sum_i n_i^o z_i^2 e^2} \right)^{1/2} \quad (8)$$

where  $\kappa^{-1}$ ,  $z_i$ ,  $n_i^o$ ,  $\epsilon$ , and  $e$  are the Debye length, valence order of ionic species  $i$ , bulk concentration of species ionic  $i$ , dielectric constant, and the electron charge, respectively. In dilute solution for a 1:1 electrolyte, the potential at distance  $r$  ( $\psi_r$ ) is given by equation 9.<sup>2</sup>

$$\psi_r = \frac{z_i e}{\epsilon r} - \frac{z_i e}{\epsilon \kappa^{-1}} \quad (9)$$

As the Debye length decreases, the potential decreases. This mean that the energy required to move an ion is less, which explains why  $B$  decreases with increase of salt concentration. Figure 4.34 shows that as the LiBOB concentration increases,  $T_o$  increases. Since  $T_o$  is related to the glass transition temperature of the solution, any increase in glass transition temperature will increase  $T_o$ . The increase of the salt concentration leads to an increase in viscosity which in turn increases the glass transition temperature<sup>29-32</sup>.

### 4.3. Summary

The trends observed in this study in the conductivity with changing salt concentration, solvent composition, and temperature can be interpreted in terms of the change in dielectric constant and viscosity with these same variables. Since these factors and their effect on ion conductivity are not unique to the LiBOB/GBL+EA+EC system, these trends provide a general guidance to how ion conductivities of other electrolyte systems with similar solvent compositions would change with these same variables, and they should constitute a useful database for the understanding of more complex systems, such as quaternary mixtures.

The electrolyte conductivity depends on the solvent composition (GBL:EA:EC ratio), LiBOB concentration and temperature. For example for high-temperature application, the best electrolyte is that which contains 1 M LiBOB in GBL+EA+EC of composition 1:1:0.1. The EC improves the dielectric constant of the electrolyte which decreases ion association. For low-temperature applications, the best electrolyte is that which contains 0.7 M LiBOB in GBL+EA+EC of composition 1:1:0. The EC is not recommended at low temperature because its high viscosity and melting point affects the ion mobility and decreases conductivity.

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## CHAPTER 5: CONCLUSIONS AND RECOMENDATIONS

### 5.1. Conclusions

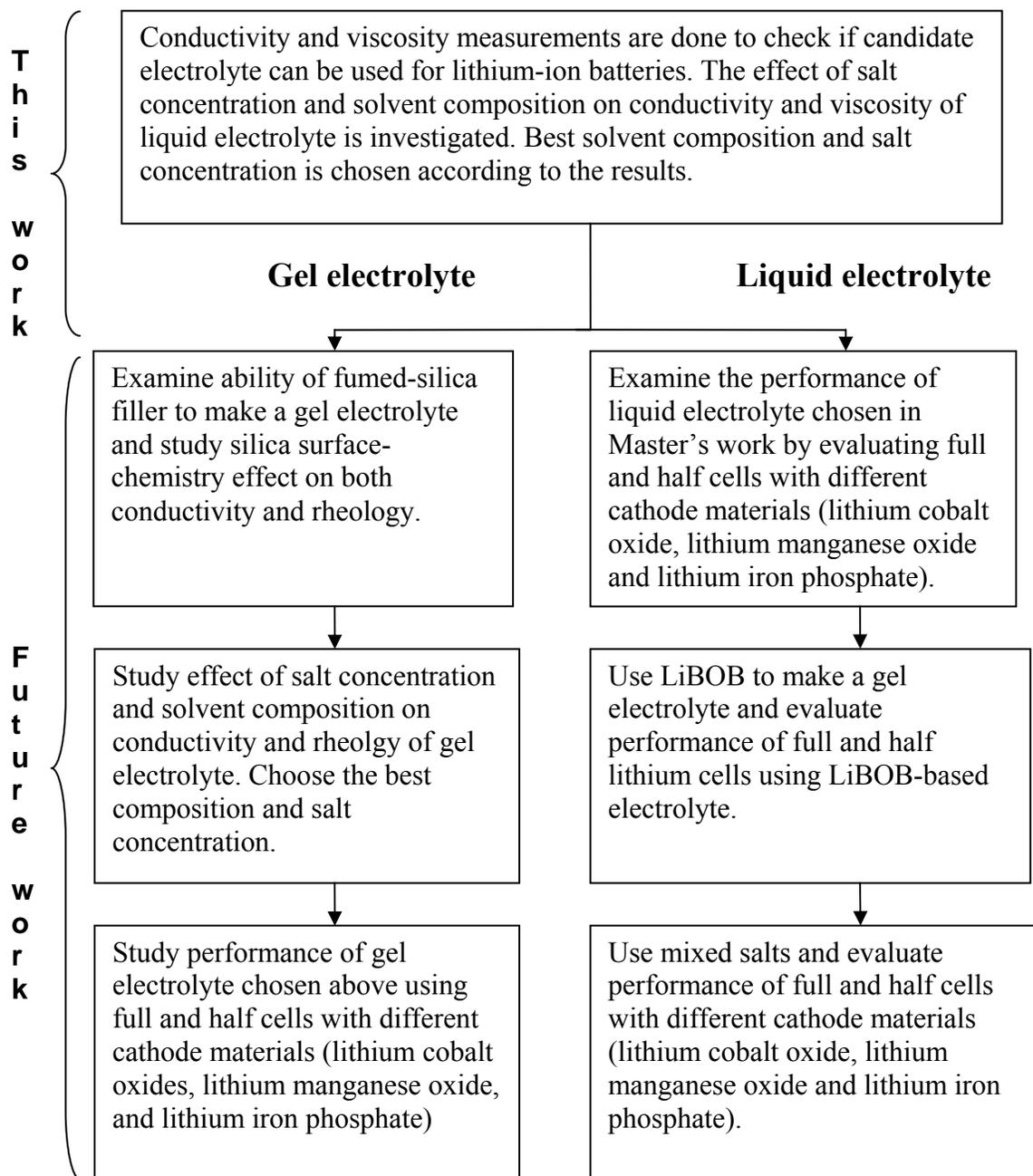
This work is a first step towards making and characterizing a gel electrolyte for lithium-ion cells using LiBOB salt in organic solvent and nanoparticulate fumed silica as filler. The full plan to achieve this final goal is schematically illustrated in scheme 5.1, which shows our approach to formulate and characterize LiBOB-based liquid and gel electrolytes for use in lithium-ion and lithium cells.

This work demonstrated that electrolytes based on LiBOB in GBL+EA+EC have a good conductivity in a wide temperature range. For example, LiBOB based-electrolyte with a salt concentration of 0.7 M LiBOB in a GBL: EA: EC composition of 1:1:0 (wt) has a conductivity  $\sim 6 \text{ mS cm}^{-1}$  at  $-3 \text{ }^\circ\text{C}$ , and at 1 M LiBOB in solvent composition of 1:1:0.1, the conductivity is  $\sim 22 \text{ mS cm}^{-1}$  at  $74 \text{ }^\circ\text{C}$ .

The effect of solvent composition and salt concentration was studied. For low temperature, the conductivity decreases as EC content increases because of the high viscosity imparted to the mixture by the EC. At high temperature, the conductivity increases as EC content increases till it reaches a maximum at solvent composition of GBL: EA: EC of 1:1:0.1. The maximum occurs due to two counter effects of viscosity and ion dissociation. The best salt concentration was between 0.7-1 M: a higher salt concentration leads to ion association and higher electrolyte viscosity which reduces the conductivity, and a lower salt

concentration dose not provide sufficient number of free ions for transport which lowers the conductivity.

Temperature affects the effect of solvent composition and salt concentration on conductivity. As temperature increases, the salt concentration at maximum conductivity increases. As temperature increases, the negative effect of EC viscosity on conductivity decreases and the positive effect of free ion concentration increases. According to this work, the best electrolytes are 0.7-1 M LiBOB in a GBL+EA+EC mixture of composition of 1:1:0 and 1:1:0.1.



**Scheme 5.1. Future-work plan.**

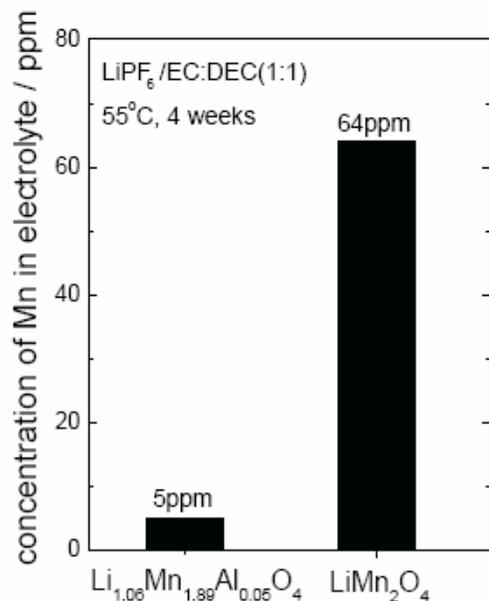
## 5.2. Recommendations

The good transport properties of LiBOB-based electrolytes motivate us to continue using this salt in future work and perform more extensive studies with it. The following recommendations for these studies are divided into three sections: liquid-electrolyte system, gel-electrolyte system, and Li metal system.

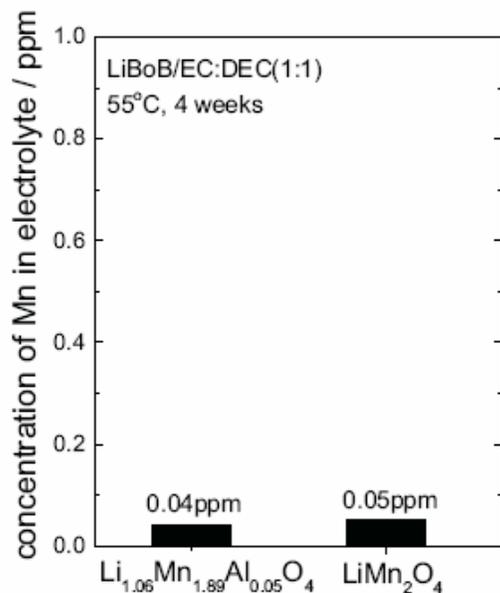
### 5.2.1. Liquid electrolyte

The work so far has focused on the transport properties of LiBOB-based electrolytes, but more work needs to be done to check the performance of lithium-ion cells using LiBOB-based electrolytes. So the next step, in the PhD work, is to test the performance of full and half cells using the chosen electrolytes (0.7 M-1 M LiBOB/GBL+EA+EC of solvent composition of 1:1:0 and 1:1:0.1). For these studies, full and half cells will be made using three types of metal-oxide cathode: lithium cobalt oxide, lithium manganese oxide, and lithium iron phosphate. Lithium cobalt oxide, which is used in most commercial lithium-ion cells, is chosen because of its excellent electrochemical performance. LiBOB has been shown to improve the performance of lithium cobalt oxide (e.g. improved capacity retention when LiBOB-based electrolyte is cycled at 4.5 V).<sup>1</sup> Lithium manganese oxide is chosen because of its cost advantage and the ability of LiBOB to improve the performance of manganese oxide by decreasing Mn dissolution as shown in Figures 5.1 and 5.2<sup>2</sup>, which show Mn dissolution after four weeks storage at 55 °C in LiPF<sub>6</sub>/EC+DEC (1:1) based electrolyte and 1 M LiBOB/EC+DEC (1:1), respectively. Figure 5.3<sup>2</sup> shows the discharge capacity

LiBOB/EC+DEC (1:1), respectively. Figure 5.3 <sup>2</sup> shows the discharge capacity characteristic

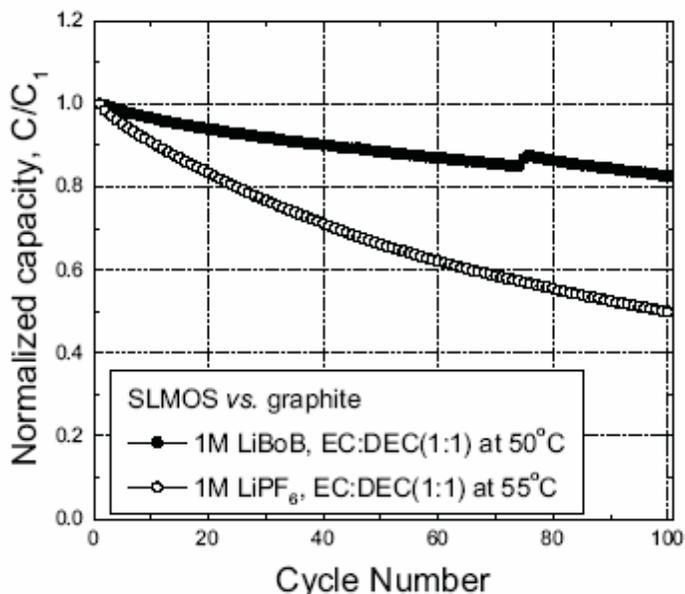


**Figure 5.1. Concentration of Mn dissolved from stabilized lithium manganese oxide spinel (SLMOS) and  $\text{LiMn}_2\text{O}_4$  powders stored in  $\text{LiPF}_6/\text{EC}:\text{DEC}$  (1:1) electrolyte at 55 °C for 4 weeks.<sup>2</sup>**



**Figure 5.2. Concentration of Mn dissolved from stabilized lithium manganese oxide spinel (SLMOS) and  $\text{LiMn}_2\text{O}_4$  powders stored in 1M  $\text{LiBOB}/\text{EC}:\text{DEC}$  (1:1) electrolyte at 55 °C after 4 weeks.<sup>2</sup>**

of a lithium manganese oxide/graphite cell using 1M LiBOB/EC+DEC (1:1) and LiPF<sub>6</sub>/EC+DEC at 50 °C. From Figure 5.3 we see that the LiBOB-based electrolyte improved

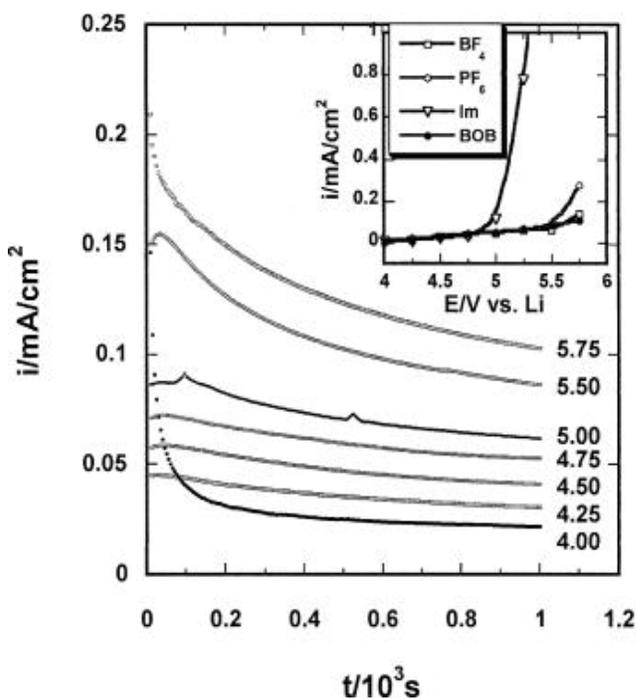


**Figure 5.3. Normalized discharge capacity against cycle number of SLMOS/graphite cells using 1M LiBOB/EC: DEC (1:1) electrolyte (closed circles) and using 1M LiPF<sub>6</sub>/EC: DEC (1:1) electrolyte (open circles). C<sub>1</sub> denotes the first discharge capacity.<sup>2</sup>**

the cycle performance of lithium manganese oxide cathode, which is attributed to the absence of fluorine in the chemical structure of LiBOB.<sup>2</sup> The cycleability and thermal stability of all three cathode materials using LiBOB in GBL+EA+EC will be evaluated and compared with cells using LiPF<sub>6</sub> as a salt.

A mixed-salt system will also be investigated. By using a mixed-salt system we hope to combine the positive effects of both salts so that the shortcoming of one salt will be overcome by the other. For example, we plan to use LiBOB with LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>. The

problem with  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  is it causes severe corrosion at the Al cathode current collector<sup>3</sup>, as illustrated in the inset of Figure 5.4<sup>4</sup>. The figure also shows that LiBOB passivates Al. Since LiBOB has the ability to protect Al in lithium-ion batteries, we hypothesize that by mixing LiBOB with  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , LiBOB can form a passivation film on the Al cathode current collector and prevent its corrosion<sup>4,5</sup>.



**Figure 5.4.** Current density obtained on an Al electrode at various potentials vs. Li in electrolyte containing 1.0 M LiBOB in an EC/EMC (1:1) mixture. Inset: Dependence of steady-state current density on applied potential on an Al electrode in electrolytes containing various Li-salts.<sup>4</sup>

### 5.2.2. Gel electrolyte

In the context of this thesis, a gel electrolyte is defined as a composite consisting of a liquid electrolyte + fumed-silica particles. The mixture exhibits a frequency-independent elastic modulus  $G'$  and its elastic modulus is larger than its viscous modulus  $G''$ . Fumed

silica is a filler that is used to modify the rheology of a variety of systems. The procedure to prepare gel electrolyte is described in Appendix A. The long-term objective of this study is to formulate and study fumed-silica gel electrolytes using LiBOB salt and use this electrolyte in lithium-ion cells. Gel electrolytes can improve the safety of lithium-ion batteries by preventing electrolyte leakage. To achieve the above objective, more work needs to be done on gel electrolyte systems. A first step in our efforts is to examine the ability of the LiBOB-containing liquid electrolyte to form a gel. Two types of fumed silica are chosen: R805 and A200 (Degussa). The R805 fumed silica contains octyl surface group at 48% coverage and silanol surface group at 52% coverage, and the A200 fumed silica contains only native silanol on the surface. These two silica types are chosen to examine the effect of surface chemistry of the fumed-silica particulates on conductivity and rheology of the gel electrolytes. The ability to form gel electrolytes using fumed-silica particulates was tested in mixtures of GBL+EA+EC. The conductivity and rheology of some representative mixtures are shown in Figures 5.5-5.16. These Figures represent preliminary results for some samples of gel electrolyte.

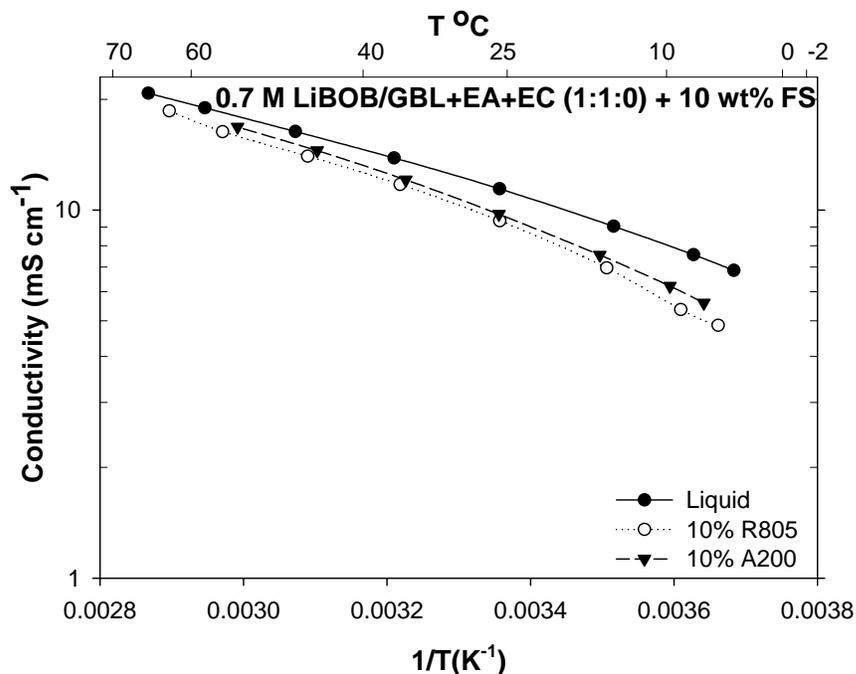


Figure 5.5. Temperature dependence of conductivity for 0.7 M LiBOB in mixture of GBL+EA+EC of 1:1:0 composition for liquid electrolyte with and without 10% fumed silica (R805 and A200)

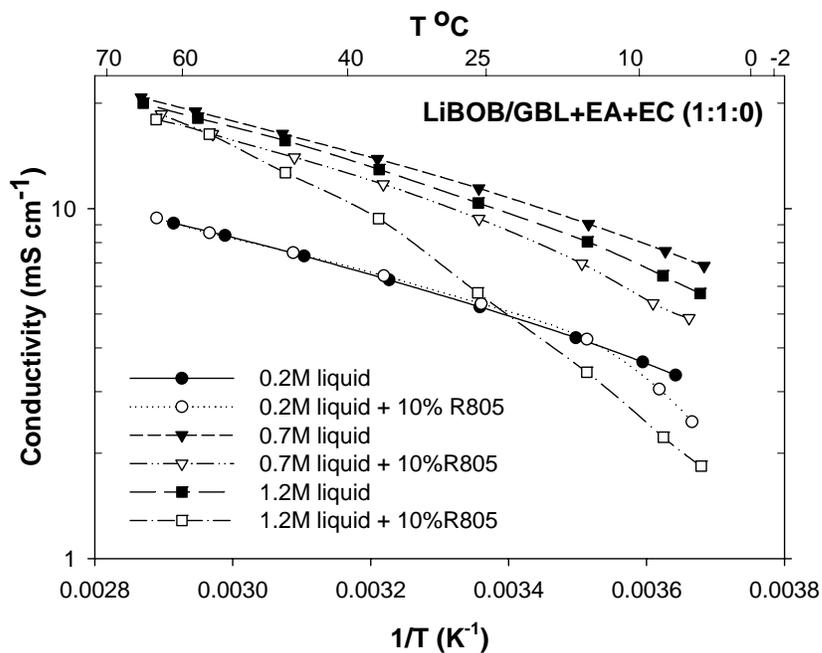


Figure 5.6. Temperature dependence of conductivity for different concentrations of LiBOB in mixture of GBL+EA+EC of 1:1:0 composition for liquid electrolyte with and without 10% fumed silica (R805)

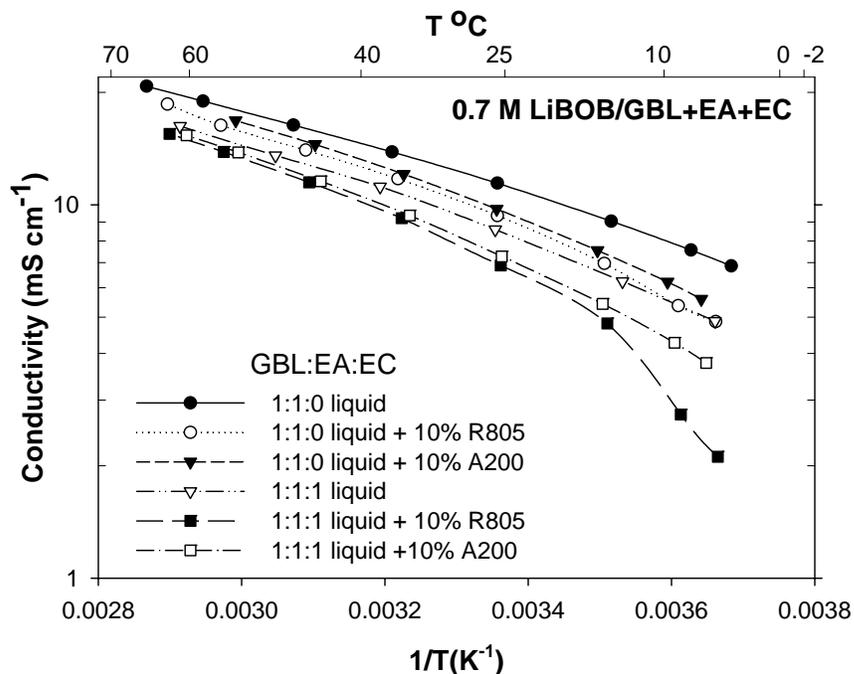


Figure 5.7. Temperature dependence of conductivity for 0.7 M LiBOB in GBL+EA+EC mixture of varying EC content with and without 10% fumed silica (R805 and A200)

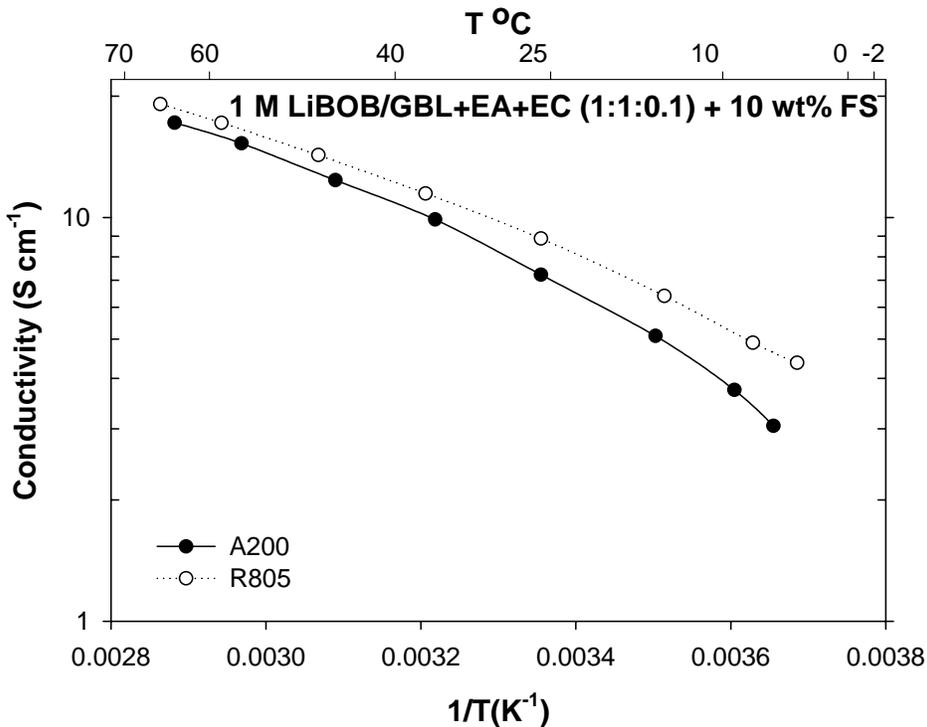
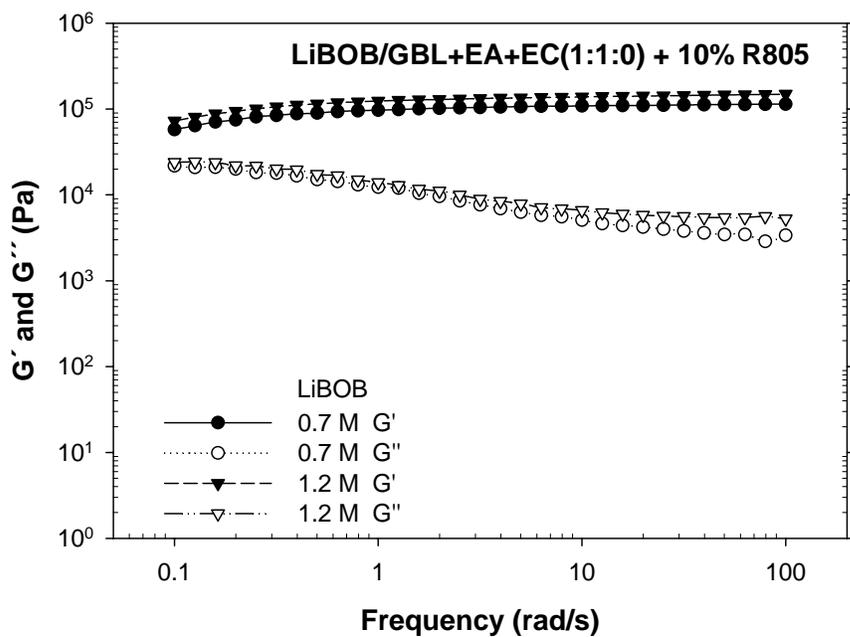
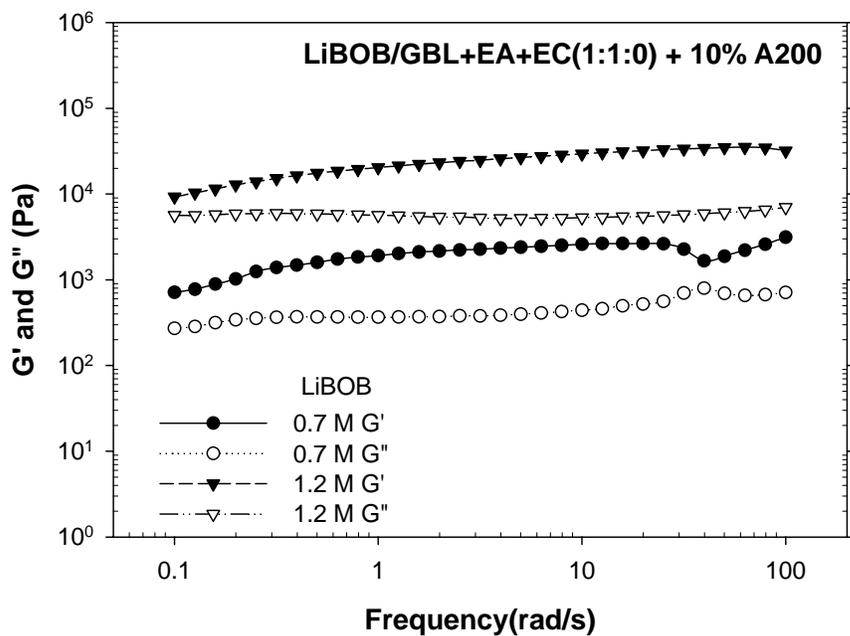


Figure 5.8. Temperature dependence of conductivity for 1 M LiBOB in mixture of 10% fumed silica and GBL+EA+EC of 1:1:0.1 composition



**Figure 5.9. Effect of salt concentration on  $G'$  and  $G''$  for LiBOB in mixture of 10% fumed silica (R805) and GBL+EA+EC of 1:1:0 composition**



**Figure 5.10. Effect of salt concentration on  $G'$  and  $G''$  for LiBOB in mixture of 10% fumed silica (A200) and GBL+EA+EC of 1:1:0 composition**

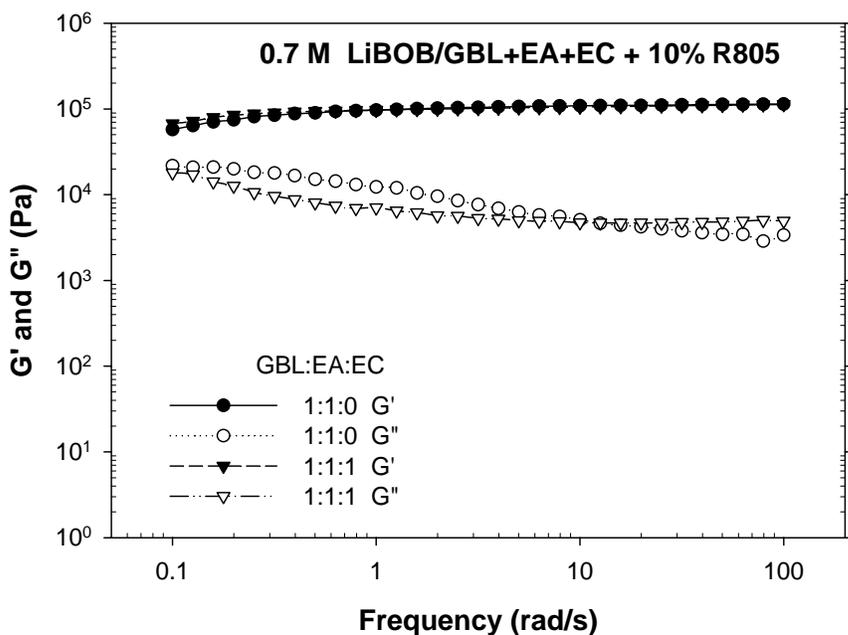


Figure 5.11. Effect of EC content on  $G'$  and  $G''$  for 0.7 M LiBOB in mixture of GBL+EA+EC for liquid electrolyte with 10% fumed silica (R805)

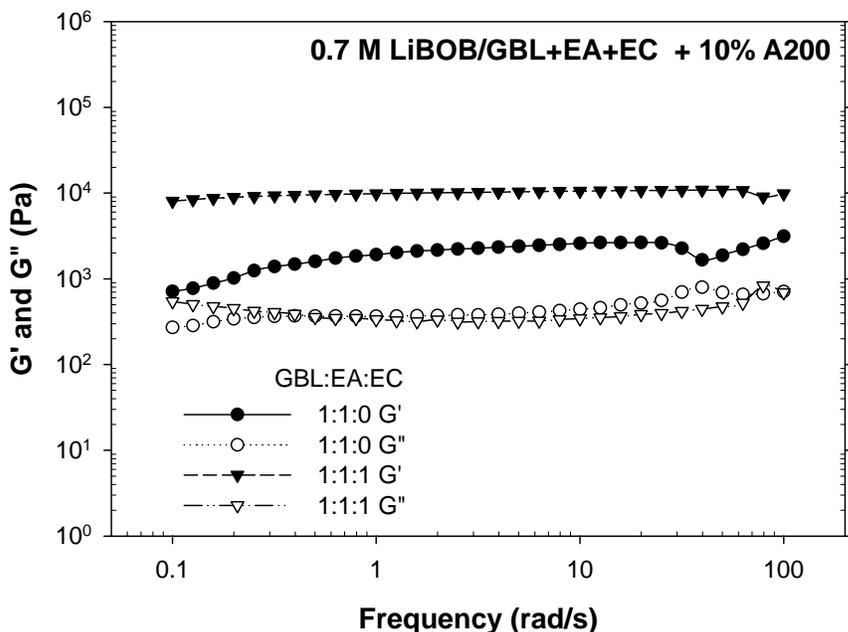


Figure 5.12. Effect of EC content on  $G'$  and  $G''$  for 0.7 M LiBOB in mixture of GBL+EA+EC for liquid electrolyte with 10% fumed silica (A200)

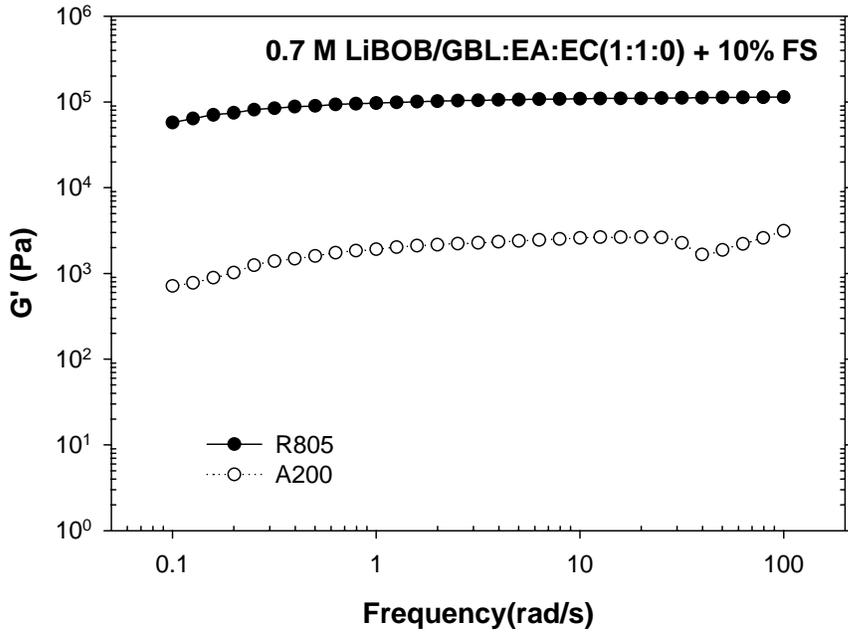


Figure 5.13.  $G'$  for 0.7 M LiBOB in mixture of GBL+EA+EC of 1:1:0 composition with 10% fumed silica (R805 and A200)

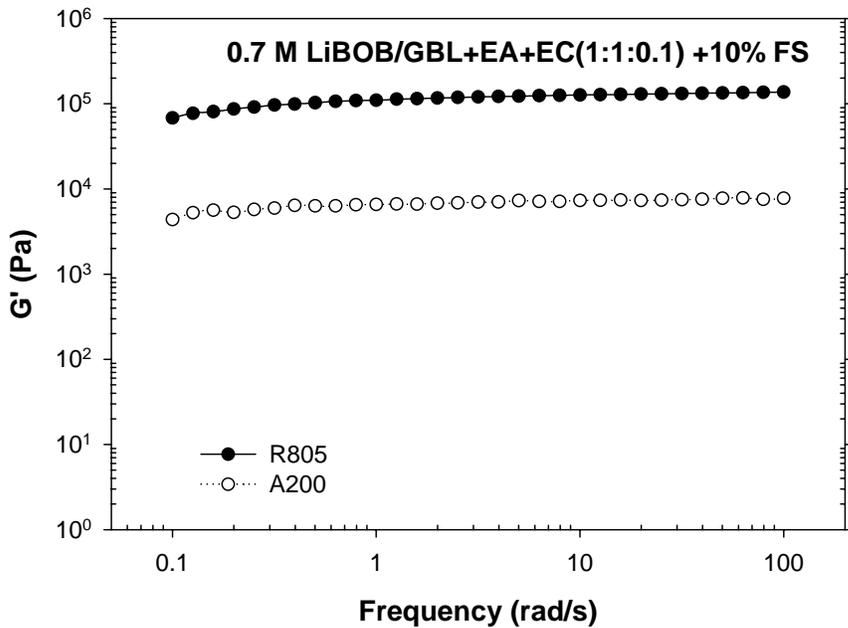
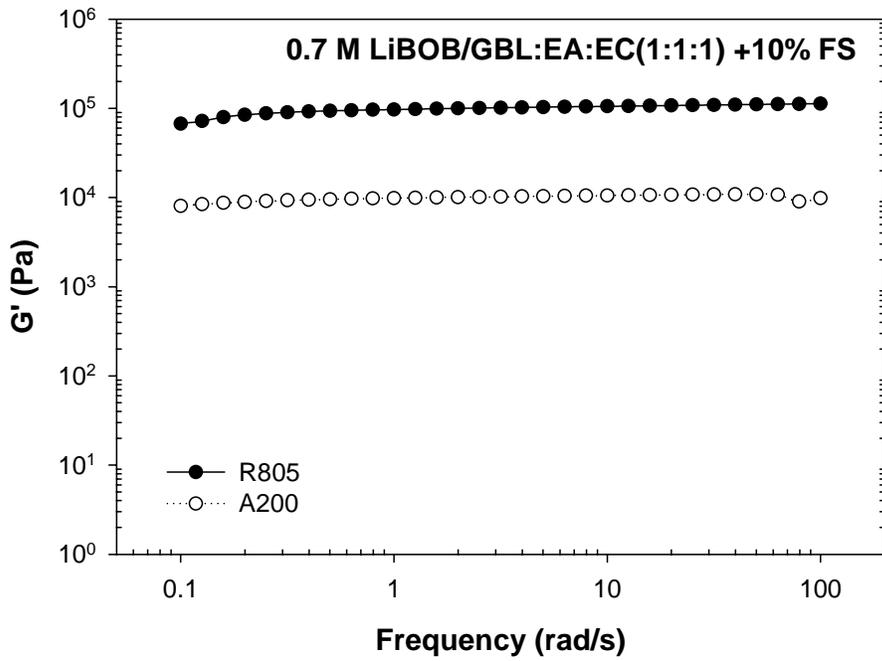
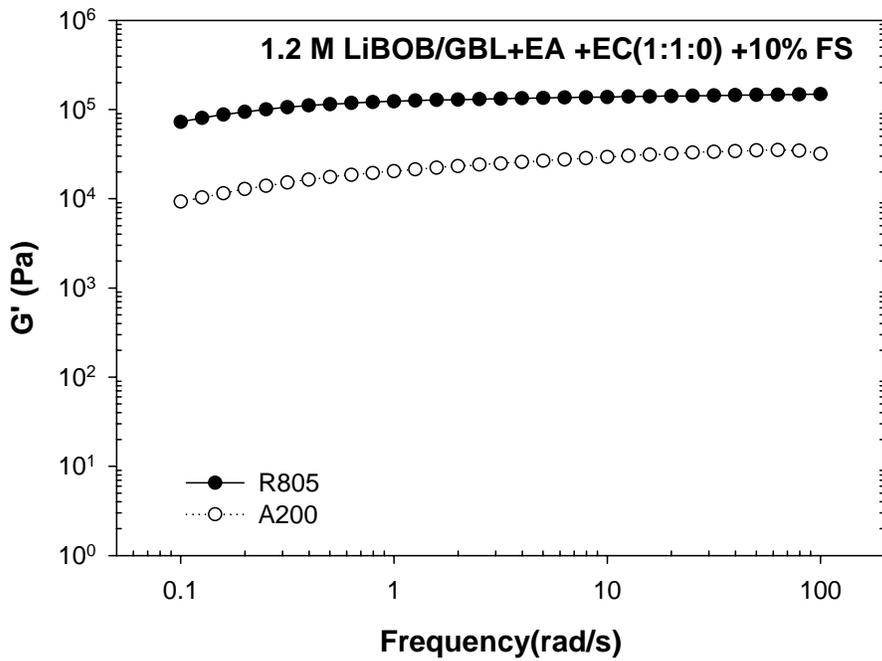


Figure 5.14.  $G'$  for 0.7 M LiBOB in mixture of GBL+EA+EC of 1:1:0.1 composition with 10% fumed silica (R805 and A200)



**Figure 5.15.  $G'$  for 0.7 M LiBOB in mixture of GBL+EA+EC of 1:1:1 composition with 10% fumed silica (R805 and A200)**



**Figure 5.16.  $G'$  for 1.2 M LiBOB in mixture of GBL+EA+EC of 1:1:0 composition with 10% fumed silica (R805 and A200)**

From Figures 5.5-5.16, we see that the surface chemistry, salt concentration, and EC content have an effect on conductivity. The effect of surface chemistry on conductivity is surprising since it was found in prior work from our group that there was no effect of silica surface chemistry<sup>6-8</sup>, albeit for a different salt and solvent. According to our knowledge, this is the first time that an effect of surface chemistry of fumed silica on conductivity has been reported. We notice that there is little effect of EC content on the rheology properties of mixtures containing R805; however there is an effect of EC content on the rheology properties of mixtures containing A200. We notice that salt concentration has an effect on the rheology properties of mixtures containing R805 and A200. Since these are preliminary results, more work must be done to determine why the surface chemistry, salt concentration and solvent composition affect the conductivity and rheology of the gel electrolyte.

The concentration of fumed silica in gel electrolyte systems will be varied to examine the effect of fumed silica content on conductivity and rheology of the gel system. This study will allow us also to determine the maximum concentration of fumed silica that can be dispersed in the liquid-electrolyte system. From these results, the best solvent composition, salt concentration and fumed silica percentage in the electrolyte will be determined.

In order to determine if we can use the gel electrolyte in lithium-ion cells, we intend to evaluate the performance of the gel electrolyte with full and half cells studies using three types of cathode (lithium cobalt oxide, lithium manganese oxide, and lithium iron phosphate). The cycleability and thermal stability of the all these cells will be evaluated and compared with the LiBOB-based liquid electrolyte.

A mixed-salt system for gel electrolyte will also be investigated. By using a mixed-salt system we hope to combine the positive effects of both salts so that the shortcoming of

one salt will be overcome by the other. We plan to use LiBOB with  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  to eliminate the corrosion at the Al cathode current collector caused by  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ .

### **5.2.3. Lithium batteries**

We are planning to make electrolytes that can be used with lithium batteries. To solve the dendrite problem of lithium batteries, we will use a gel-electrolyte system that can hinder dendrite formation. The solvent here will differ from the GBL: EA: EC solvent because of known reactivity of EA with lithium <sup>9</sup>. Currently we have not identified the specific composition of the electrolyte; however PEGdm probably will be one component. We will use LiBOB salt since it was reported that LiBOB has hindered dendrite formation <sup>10</sup>.

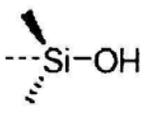
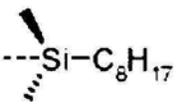
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## Appendix A: GEL ELECTROLYTE PREPARATION

A gel electrolyte is a composite consisting of a liquid electrolyte + nanoparticulate fumed-silica. The mixture exhibits a frequency-independent elastic modulus  $G'$  and its elastic modulus is larger than its viscous modulus  $G''$ . Fumed silica is a filler that is used to modify the rheology of a variety of systems. Fumed silica is supplied by Degussa Corporation (Akron, OH) and are denoted by the manufacturer as Aerosil A200 (silanol, -OH groups) and Aerosil R805 (octyl, -C<sub>8</sub>H<sub>17</sub> groups). A200 silica is the native, unmodified fumed silica with a surface covered with silanol (Si-OH) groups. R805 silica is modified silica which has 48% of the native silanol groups replaced with octyl groups. A summary of the properties of A200 and R805 fumed silica is shown in Table 1.

**Table A.1. Properties of A200 and R805**

Fumed silica	Dominant surface group	Particle Size (nm)	Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Fraction of surface substituted (mol%)	Fraction of unreacted Si-OH (mol%)	OH-Density per nm <sup>2</sup>
A200	 silanol	12	200	0	100	2.50
R805	 octyl	12	150	48	52	1.66

Both A200 and R805 form gels in EA+GBL or EA+GBL+EC with a salt concentration of 0.7 M LiBOB or higher. At lower concentration (0.2 and 0.5 M) only R805 forms a gel electrolyte.

Gel electrolytes are prepared in an argon-filled glove box by adding appropriate amounts of LiBOB-based liquid electrolyte to a known amount of fumed silica. Fumed silica is dried at 120°C under vacuum (~ 1 kPa) for one week to remove residual water. The fumed silica weight percent is based on the amount of total liquid electrolyte (solvent + salt). The gel is mixed by hand until homogeneity is reached, as assessed by visual observation, and then mixed by a high-shear mixer (Tissue Tearor, Model 398, BioSpec Products, Inc.). The entrained air bubbles are removed using centrifugation (IEC HN-SII centrifuge, Damon/IEC Division) at 2000 rpm for 20 minutes.