

**Improvement of lithium-ion battery
performance by control of electrode
electrolyte interface**

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1. General Introduction

1.1. Background

As the world's energy demand increases, promoting the efficient use of energy has become an important and urgent issue on a global scale. In recent years, the cost of lithium ion secondary batteries having enough energy density and power density has been lowered, so lithium ion secondary batteries are adopted as a drive train power source for automobiles, and electric vehicles are spreading worldwide. On the other hand, lithium ion secondary batteries life is still very short compared to other electronic devices, and there is always a risk of fire. As a result, safer and longer-life lithium ion secondary battery is required. Although several rechargeable batteries have been developed until now, lithium-ion batteries outperform competing devices such as nickel (Ni)-metal hydride or lead (Pb)-acid in terms of delivered energy while providing high specific power (Figure 1).[1] Therefore, many researchers make a lot of effort to enhance the performance of lithium-ion batteries to meet the above demands.

1.2. History of Lithium-Ion Batteries

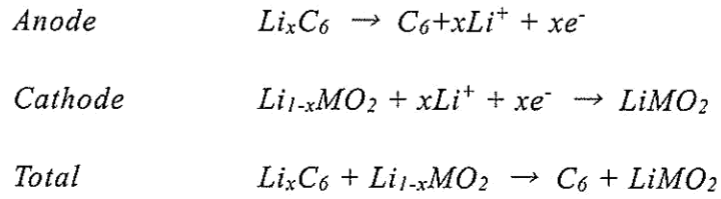
In 1976, Whittingham discovered that lithium ions are inserted/extracted reversibly in TiS_2 with the electrochemical reaction in Li/TiS_2 system.[2,3]

This discovery is a basic concept of lithium ion batteries in which topotactic reactions are used.[4] In 1980, Lazzari and Scrosati developed $\text{Li}_x\text{WO}_2/\text{TiS}_2$ system consisting of two insertion electrodes by choosing Li_xWO_2 as an anode, which was obtained by inserting lithium ions electrochemically to WO_2 . [5] Mizushima *et al.* reported that LiCoO_2 having layered rock salt structure shows reversible insertion/extraction reaction of lithium ions and that the open-circuit voltages of the Li_xCoO_2 after extraction reaction of lithium ions were approximately 4 V with respect to lithium metal in that year.[6] In 1983, the insertion/extraction reaction of lithium ions in graphite can be reversibly performed by an electrochemical method using a solid organic electrolyte.[7] In 1987, Auborn and Barberio proposed $\text{LiCoO}_2/\text{MoO}_2$ and $\text{LiCoO}_2/\text{WO}_2$ systems as lithium ion intercalation cells without metallic lithium.[8] 15 years later from Whittingham's discovery, the lithium-ion battery, which was LiCoO_2 /graphite system developed by Yoshino of the Asahi Kasei Corporation, was first commercialized by Sony Corporation in 1991.[9]

1.3. Mechanism of Lithium-Ion Batteries

The schematic view of lithium-ion batteries is shown in Figure 2.[1] Lithium ion battery is composed of a cathode, an anode, an electrolyte (which is in separator) and current collectors. The cathode and anode are separated by the electrolyte. In the typical LiMO_2 /graphite cell as shown in Figure 2, the operating principle is explained as the following. In the discharge process,

lithium ions are simultaneously extracted from the graphite and solvated with solvents in the electrolyte. The solvated-lithium ions transfer to the LiMO_2 side, and then the lithium ions are simultaneously dissolved and inserted into the LiMO_2 . When the LiMO_2 receives the lithium ions from the electrolyte, it receives electrons from the external circuit. In the discharge process, each electrode reaction and total reaction are expressed as the following equations;



In the charging process, the reverse reaction occurs.

Although modern lithium-ion batteries hold more than twice as much energy by weight as the first commercial systems sold by Sony in 1991,[10] it is necessary to understand the mechanism of reactions occurring inside lithium-ion battery cells for further improvement of the performance. The reactions in the battery cells are classified into three groups according to time and space scale as shown in Figure 3. The reaction in the largest scale occurs in composite electrodes. The composite electrodes consist of active materials, electroconductive additives (carbon) and binders, forming a complex structure. In the composite electrodes, there are many internal resistances concerning

electronic conductivity and ionic conductivity. Because the electrode reaction occurs preferentially in the regions with lower resistance, reaction distribution is generated within the composite electrodes.[11-14] The reaction distribution affects largely the battery performance such as safety and cyclability. The reaction in the second largest scale occurs in active materials. There are many active materials with various crystal structures.[15-17] The crystal structures change with lithium extraction/insertion reaction, leading to phase transition.[18,19] The battery performance such as the energy density or durability is largely influenced by the crystal structure and/or the phase transition behavior of the active materials.[15,16,20-22] The reaction in the smallest scale occurs at an electrode/electrolyte interface. At the interface, charge transfer reaction occurs when lithium ions insert in or extract from the active material. The interfacial reaction is the starting point in all reaction occurring in the battery, which affects largely the performance such as power density or durability. [23,24] In order to improve the performance of lithium-ion batteries, the reaction mechanism of each scale is fundamentally understood. In this study, understanding the interfacial reaction is focused on.

1.4. Electrode/Electrolyte Interfacial Structure and Reaction [25,26]

Because an electrode and an electrolyte have different inner potentials each other, the gap between the two potentials is compensated around the

interface. This region that potential compensation occurs is called an electrical double layer at the electrolyte side and a space charge layer at the electrode side, respectively. The electrical double layer consists of the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP) and the diffuse layer. The potential profiles in the region of the electrical double layer and space charge layer are classically written down as the following.

- The potential profile of the electrical double layer

When the electrode has an excess charge on its surface, the counter-charge in solution resides as an OHP at the surface. Such a structure is equivalent to a parallel-plate capacitor. Hence, the potential profile (ψ_{OHP}) from the electrode to the OHP is

$$\psi_{OHP} = \frac{d}{\epsilon\epsilon_0} q_s \quad (1)$$

where d is the distance between the electrode and the OHP, ϵ is the dielectric constant of solution, ϵ_0 is the permittivity of free space, and q_s is the entire excess charge density.

The potential profile through the diffuse layer (ψ_{dif}) is expressed as the following. The ionic distribution from electrode to electrolyte is expressed by Boltzmann equation:

$$c_i = c_i^0 \exp \left(\frac{-z_i e \psi}{kT} \right) \quad (2)$$

where k is the Boltzmann constant and T is the absolute temperature. The total charge density $\rho(x)$ on any electrolyte lamina parallel to the electrode is then

$$\rho(x) = \sum_i c_i z_i e = \sum_i c_i^0 z_i e \exp \left(\frac{-z_i e \psi}{kT} \right) \quad (3)$$

where i runs overall ionic species. From electrostatics, $\rho(x)$ is related to the potential at distance x by the Poisson equation:

$$\rho(x) = -\epsilon \epsilon_0 \frac{d^2 \psi}{dx^2} \quad (4)$$

hence (3) and (4) can be combined to yield the Poisson-Boltzmann equation as the following:

$$\frac{d^2 \psi}{dx^2} = -\frac{e}{\epsilon \epsilon_0} \sum_i c_i^0 z_i \exp \left(\frac{-z_i e \psi}{kT} \right) \quad (5)$$

Equation (5) is treated by noting that

$$\frac{d^2 \psi}{dx^2} = -\frac{1}{2} \frac{d}{d\psi} \left(\frac{d\psi}{dx} \right)^2 \quad (6)$$

hence,

$$d \left(\frac{d\psi}{dx} \right)^2 = - \frac{2e}{\varepsilon \varepsilon_0} \sum_i c_i^0 z_i \exp \left(\frac{-z_i e \psi}{kT} \right) d\psi \quad (7)$$

Integration gives

$$\left(\frac{d\psi}{dx} \right)^2 = \frac{2kT}{\varepsilon \varepsilon_0} \sum_i c_i^0 \exp \left(\frac{-z_i e \psi}{kT} \right) + \text{constant} \quad (8)$$

and the constant is evaluated by recognizing that at distances far from the electrode $\psi = 0$ and $(d\psi/dx) = 0$. Thus,

$$\left(\frac{d\psi}{dx} \right)^2 = \frac{2kT}{\varepsilon \varepsilon_0} \sum_i c_i^0 \left[\exp \left(\frac{-z_i e \psi}{kT} \right) - 1 \right] \quad (9)$$

When the model is specialized to a system containing only asymmetrical electrolyte such as NaCl, $(d\psi/dx)^2$ is

$$\begin{aligned}
\left(\frac{d\psi}{dx}\right)^2 &= \frac{2kT}{\varepsilon\varepsilon_0} \sum_i c_i^0 \left[\exp\left(\frac{-z_i e\psi}{kT}\right) - 1 \right] \\
&= \frac{2kT}{\varepsilon\varepsilon_0} c_{cation}^0 \left[\exp\left(\frac{-|z_{cation}|e\psi}{kT}\right) - 1 \right] + \frac{2kT}{\varepsilon\varepsilon_0} c_{anion}^0 \left[\exp\left(\frac{|z_{anion}|e\psi}{kT}\right) - 1 \right] \\
&= \frac{2kT}{\varepsilon\varepsilon_0} c^0 \left\{ \exp\left(\frac{ze\psi}{kT}\right) + \exp\left(\frac{-ze\psi}{kT}\right) - 2 \right\} \quad \because c_{cation}^0 = c_{anion}^0 \\
&= c^0 \text{ and } |z_{cation}| = |z_{anion}| = z \\
&= \frac{2kT}{\varepsilon\varepsilon_0} c^0 \left\{ \exp\left(\frac{ze\psi}{2kT}\right) - \exp\left(\frac{-ze\psi}{2kT}\right) \right\}^2 \\
&= \frac{2kT}{\varepsilon\varepsilon_0} c^0 \left\{ 2\sinh\left(\frac{ze\psi}{2kT}\right) \right\}^2 \\
&= \frac{8kT}{\varepsilon\varepsilon_0} c^0 \left\{ \sinh\left(\frac{ze\psi}{2kT}\right) \right\}^2 \quad (10)
\end{aligned}$$

Hence,

$$\frac{d\psi}{dx} = - \left(\frac{8kTc^0}{\varepsilon\varepsilon_0} \right)^{1/2} \sinh\left(\frac{ze\psi}{2kT}\right) \quad (11)$$

Equation (11) can be rearranged and integrated in the following manner:

$$\int_{\psi_{OHP}}^{\psi_{dif}} \frac{d\psi}{\sinh(ze\psi/2kT)} = - \left(\frac{8kTc^0}{\varepsilon\varepsilon_0} \right)^{1/2} \int_{x_{OHP}}^x dx \quad (12)$$

where x_{OHP} is the location of the OHP. The result is

$$\frac{2kT}{ze} \ln \left[\frac{\tanh(ze\psi_{dif}/4kT)}{\tanh(ze\psi_{OHP}/4kT)} \right] = - \left(\frac{8kTc^0}{\varepsilon\varepsilon_0} \right)^{1/2} (x - x_{OHP}) \quad (13)$$

or,

$$\frac{\tanh(ze\psi_{dif}/4kT)}{\tanh(ze\psi_{OHP}/4kT)} = e^{-\kappa(x-x_{OHP})} \quad (14)$$

where

$$\kappa = \left(\frac{2c^0 z^2 e^2}{\varepsilon\varepsilon_0 kT} \right)^{1/2} \quad (15)$$

Equation (14) describes the potential profile in the diffuse layer in a general way. If ψ_{OHP} is sufficiently low that $(ze\psi_{OHP}/4kT) < 0.5$, then $\tanh(ze\psi_{dif}/4kT) \approx (ze\psi_{dif}/4kT)$ everywhere, and

$$\psi_{dif} = \psi_{OHP} e^{-\kappa x} \quad (16)$$

Hence, by combining ψ_{OHP} and ψ_{dif} , the potential profile of the whole electrical double layer (ψ_{EDL}) is

$$\psi_{EDL} = \psi_{OHP} + \psi_{OHP}e^{-\kappa x} \quad (17)$$

- The potential profile of the space charge layer

Given a layer of charge on the OHP of the electrolyte, the electrons and holes inside an electrode distribute themselves. In the electrolyte bulk, the excess-charge density in any volume element is zero because the numbers per unit volume of positive and negative charges are exactly equal; similarly, deep inside the electrode, the excess-charge density is zero because of the equality of the density of electrons n^0 and holes p^0 . Thus,

$$n^0 = p^0 \quad (18)$$

The charged electrode exerts an electric field on the positive and negative ions in the electrolyte; similarly, the sheet of charge on the OHP exerts an electric field on the holes and electrons in the electrode so that the charge density $\rho_{sc}(x)$ can be obtained by the application of Boltzmann distribution and Poisson's equation. From equation (3), Boltzmann distribution is

$$\begin{aligned}
\rho_{sc}(x) &= ep^0 \exp\left(-\frac{e\psi}{kT}\right) - en^0 \exp\left(\frac{e\psi}{kT}\right) \\
&= en^0 \exp\left(-\frac{e\psi}{kT}\right) - en^0 \exp\left(\frac{e\psi}{kT}\right) \quad \because n^0 = p^0 \\
&= -en^0 \left\{ \exp\left(\frac{e\psi}{kT}\right) - \exp\left(-\frac{e\psi}{kT}\right) \right\} \\
&= -2en^0 \sinh\left(\frac{e\psi}{kT}\right) \quad (19)
\end{aligned}$$

and Poisson's equation is

$$\rho_{sc}(x) = -\varepsilon\varepsilon_0 \frac{d^2\psi}{dx^2} \quad (20)$$

The two expressions for the charge density can be equated to give the Poisson-Boltzmann equation

$$\frac{d^2\psi}{dx^2} = \frac{2en^0}{\varepsilon\varepsilon_0} \sinh\left(\frac{e\psi}{kT}\right) \quad (21)$$

This differential equation for the space variation of the potential inside the electrode can be identified with that the space variation of the potential inside the diffuse layer of the electrolyte. The solution can, therefore, be borrowed from the diffuse-layer theory. From equation (11)

$$\frac{d\psi}{dx} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{e\psi}{2kT}\right) \quad (22)$$

Equation (22) can be rearranged and integrated in the following manner:

$$\int_{\psi_s}^{\psi_{sc}} \frac{d\psi}{\sinh(e\psi/2kT)} = - \left(\frac{8kTn^0}{\epsilon\epsilon_0} \right)^{1/2} \int_0^x dx \quad (23)$$

where ψ_s is the potential at the surface of the electrode. The result is

$$\frac{2kT}{e} \ln \left[\frac{\tanh(e\psi_{sc}/4kT)}{\tanh(e\psi_s/4kT)} \right] = - \left(\frac{8kTn^0}{\epsilon\epsilon_0} \right)^{1/2} x \quad (24)$$

or,

$$\frac{\tanh(e\psi_{sc}/4kT)}{\tanh(e\psi_s/4kT)} = e^{-\kappa x} \quad (25)$$

where

$$\kappa = \left(\frac{2n^0 e^2}{\epsilon\epsilon_0 kT} \right)^{1/2} \quad (26)$$

If ψ_s is sufficiently low that $(e\psi_s/4kT) < 0.5$, then $\tanh(e\psi_{sc}/4kT) \approx (e\psi_{sc}/4kT)$

everywhere, and

$$\psi_{sc} = \psi_s e^{-\kappa x} \quad (27)$$

In conclusion, the ideal potential profiles of the electrical double layer and space charge layer are

$$\psi_{EDL} = \psi_{OHP} + \psi_{OHP}e^{-\kappa x} \quad (17)$$

$$\psi_{SC} = \psi_s e^{-\kappa x} \quad (27)$$

However, the practical potential profiles probably become more complicated because of the following three reasons: (1) surface potential changes due to specific adsorption.[26] (2) The electronic structure in the bulk of active material changes with lithium ion insertion/extraction reaction [27-30] and (3) a protecting layer, which is called solid electrolyte interface (SEI), forms between the electrode and the electrolyte due to decomposition of electrolyte during the battery operating condition. [31-33] Because the inner potential around the electrode/electrolyte interface is different from the potential in the bulk as shown in Figure 4, specific phenomena occur at the interface as not seen in the bulk. In solid-state lithium-ion battery systems, in which the electrolyte is not a liquid state but solid state, Takada *et al.* have reported that the space charge layer affects largely the performance of the battery.[34-36] They also reported that the performance of the battery is enhanced by controlling the space charge layer.[37-41] Therefore, it is important to understand the interfacial phenomena and control them for the improvement of

the performance of lithium-ion batteries.

1.5. Previous Reports of Analyzing the Interfacial Phenomena between Electrode and Electrolyte

1.5.1. *Ex-Situ* Analysis

To clarify the interfacial phenomena, many types of research for the surface of active materials have been conducted via *ex-situ* methods. Okubo *et al.* researched surface effects on charge/discharge property in LiCoO₂ by preparing LiCoO₂ nanoparticles whose sizes are below 20 nm.[42-45] They reported that excess Li ions exist in the form of Li_{1+δ}Co^{II}_δCo^{III}_{1-δ}O₂ at the surface along the *c*-direction of the LiCoO₂ nanoparticles. The Li_{1+δ}Co^{II}_δCo^{III}_{1-δ}O₂ layer at the surface varies the charge/discharge property and the electronic structure from the LiCoO₂ bulk. Qian *et al.* reported that electronic spin state transitions occur on the surface of nanosized stoichiometric LiCoO₂. [46] Dedryvere *et al.* reported that surface reactivity to an electrolyte of LiFePO₄ is smaller than that of LiCoO₂ via x-ray photoelectron spectroscopy (XPS).[47] The same research group also investigated surface reactivity of LiCoO₂ with NH₃, SO₂ and CO₂ gaseous molecules and reported that the surface of LiCoO₂ was strong basicity as compared to common oxides.[48,49] Many investigations about SEI have been reported by many researchers.[31-33] These *ex-situ* studies are useful to

consider the interfacial phenomena but have not observed the real interface under battery operating condition (*in-situ*) where inner potential compensation between the electrode and electrolyte occurs as mentioned in section 1.4. Hence, in order to clarify the interfacial phenomena, it is pivotal to investigate directly the interface by *in-situ* measurements.

1.5.2. *In-Situ* Analysis

Although the importance of *in-situ* observation of the interfacial phenomena is described in section 1.5.1.1, the *in-situ* observation is quite difficult due to the following three restrictions.

(1) Construction of an ideal electrode/electrolyte interface

Composite electrodes, which are normally used for research of the lithium-ion batteries, cannot be used to investigate the interfacial phenomena. The reason is that because the composite electrodes have complicated morphology including many parameters, drawing only the information of the electrode/electrolyte interface from the reaction field is difficult. Therefore, in order to investigate the interfacial phenomena, it is necessary to construct an ideal electrode/electrolyte interface by using the thin-film electrode, which consists of only active material, as shown in Figure 5.

(2) Space resolution in a few nanometers

The scale of the space charge layer and the electrical double layer are approximately estimated from the Debye length (equation (15) in section 1.4). For example, when 1 M LiPF₆/propylene carbonate is considered as an electrolyte, the Debye length is estimated to be 0.28 nm at 25°C (the permittivity of propylene carbonate is 64.92.[50]) This length is under the ideal condition and the actual length of the electrical double layer is unknown. However, from this estimation, to investigate the interfacial structure, the analytical techniques with the space resolution in a few nanometers at least are needed.

(3) *In-situ* condition

For investigation of the interfacial phenomena, the measurements under battery operating (*in-situ*) condition are imperative. In lithium-ion batteries, the electrolyte consists of inorganic solute and an organic solvent. Therefore, the analytical techniques available under vacuum condition cannot be used. For example, transmission electron microscopy (TEM) or X-ray photoelectron spectroscopy (XPS) is not basically available.

These restrictions make it difficult for developing analytical techniques for investigating interfacial phenomena. Recently, several *in-situ* techniques have been developed.

Inaba *et al.* observed that the surface morphology of LiMn₂O₄ thin

film changed after potential cycling by using electrochemical scanning tunneling microscopy.[51]

Hirayama *et al.* has developed *in-situ* synchrotron X-ray reflectometry (*in-situ* XRR) for the lithium-ion battery system and applied the technique to an epitaxial film of LiCoO_2 . [52] They reported that a SEI layer formed on the surface of LiCoO_2 after soaking into the electrolyte, and that the surface roughness of the intercalation (110) plane increased with applying voltage, while no significant changes in surface morphology were observed for the intercalation non-active (003) plane during the pristine stage of the charge/discharge process. The *in-situ* XRR technique has also been applied to other epitaxial films and observed that the similar surface structure changes as seen in the LiCoO_2 epitaxial film occurred.[53,54] Hirayama *et al.* have also developed *in-situ* neutron reflectometry (*in-situ* NR) for the lithium-ion battery system and reported that the surface of LiFePO_4 was stable during the first charge/discharge process by using *in-situ* NR and XRR.[55] *In-situ* XRR and NR have also been applied to investigation for the structure of the electrical double layer in an ionic liquid system, although the ionic liquid system is different from the lithium-ion battery system.[56-60]

Sakamoto *et al.* has developed *in-situ* surface X-ray diffraction (*in-situ* SXRD) and observed that structural changes at the surface of epitaxial films of $\text{LiNi}_{0.8}\text{CoO}_2$ were different from those in the bulk by using the technique.[61] They reported that contact with the electrolyte caused an abrupt

deformation of the surface crystal lattice, followed by restructuring upon applying a cell voltage. Surface structural changes of other epitaxial films have also been observed via the *in-situ* SXRD technique. [62,63]

Becker *et al.* investigated the interfacial structure between LiCoO₂ thin film and diethyl carbonate by employing low-temperature adsorption and synchrotron radiation XPS (SXPS).[64] In this report, LiCoO₂ behaves like a semiconducting electrode and exhibits band bending. The band bending is attributed to the transfer of lithium ions from the electrode to the adsorbed phase, driven by the difference in the lithium-ion chemical potential between the electrode and adsorbed layer.

Ensling *et al.* observed that the valence band of LiCoO₂ shifted to higher binding energy after electrolyte contact via synchrotron XPS and mentioned that the shift was associated with the formation of SEI layer at the surface of LiCoO₂. [65]

Liu *et al.* has developed *in-situ* sum frequency generation vibrational spectroscopy (*in-situ* SFG) and observed two adsorption modes of propylene carbonate molecules with opposite orientation geometries on the LiCoO₂ surface by using the technique.[66] The group observed that the preferential adsorption of ethylene carbonate (EC) molecules on the LiCoO₂ surface compared to the linear carbonates, such as diethyl carbonate (DEC) and dimethyl carbonate (DMC). Moreover, they proved that the molecular density of the adsorbed EC on the LiCoO₂ is almost 20 times higher than DMC in 0.5

M LiClO₄/EC:DEC (1:1 v/v%), which is far from that in the bulk solution.[67]

These techniques are powerful for the investigation of the electrode/electrolyte interfacial phenomena.

1.5.3. Control of Electrode/Electrolyte Interfacial Structure in Lithium-Ion Batteries

There has been a large number of reports about controlling the interfacial structure to enhance the battery performance such as cyclability or rate performance.

One potent method to control the interfacial structure is a surface coating of electrodes with metal oxides. The surface coating enhances the cyclability,[68-70] durability at high potential[71-73] or rate performance.[74,75] Several researchers have designed efficient coating materials and suggested various mechanisms underlying the surface coating effects.[76-84] For example, the surface coating protects the electrode from the attack of HF emanating from the electrolyte,[79,80] and stabilizes the surface structure of the electrode.[77,78] As another method to control the surface of electrodes without metal oxide, Park *et al.* reported that the rate performance of LiFePO₄ is enhanced by modification of its surface with nitrogen or sulfur.[85]

Not only controlling the interfacial structure from the electrode side, but also that from the electrolyte side has been attempted. Adding additional

electrolytes such as vinylene carbonate (VC) to conventional electrolytes are also known to be effective for enhancement of the battery performance.[86-91] It has been reported that the addition of VC to electrolyte improves cyclability of cathodes because VC decreases parasitic reaction rate between the electrode and electrolyte.[88-90] It has been reported that the nature of the SEI formed on the electrodes by decomposition of VC additives and the dependency of several electrodes to decomposition of VC.[86,87] However, when VC is used as an additive, the surface structure of the electrode has not been clarified.

It is well known that controlling the interfacial structure is effective to improve the battery performance as mentioned above. However, the mechanism underlying the control of the interfacial structure has not been clarified. This is because the techniques to investigate directly the interfacial structure are limited, resulting in that the information about the interfacial structure is a shortage.

1.6. Objective

As mentioned above, clarification and control of the electrode/electrolyte interfacial phenomena are necessary to improve the lithium-ion battery performance. In order to achieve these aims, it is necessary to clearly the electrolyte and electrode interaction from the analysis of electrode/electrolyte interface phenomena.

1.7. Outline of the Present Thesis

The present thesis consists of five chapters, we elucidate the formation mechanism of electrode/electrolyte interface under thermally stable solvent, characterize composition of formed solid electrolyte interface and its contribution to improve battery performance.

In chapter 1, lithium ion batteries and the phenomena occurring within the batteries are described. Mainly, the interfacial phenomena between electrode and electrolyte are focused on. Since the interfacial phenomena largely influence the battery performance such as cyclability, investigation of the phenomena is important for further improvement of the battery performance, especially under *in-situ* condition. The importance of controlling interfacial phenomena is also presented. On the basis of the general knowledge and previous reports, the importance of designing the interface is summarized (this chapter).

In chapter 2, Tri (ethylene glycol)-substituted trimethylsilane/ LiBOB electrolyte is prepared. Ion transportation in liquid electrolyte, optimize electrolyte formulation with various lithium salt, impact of lithium salt concentration and battery performance are discussed.

In chapter 3, Electrode surface film formed by the result of cycling with tri (ethylene glycol)-substituted trimethylsilane solvent is analyzed. We clearly pointed out that LiBOB salt act as major contributor to form electrode electrolyte interface film under this electrolyte system.

In chapter 4, It is investigated the formation steps of solid electrolyte interface with tri (ethylene glycol)-substituted trimethylsilane solvent. Changing of the solid electrolyte interface electrochemical behavior is discussed.

In chapter 5, Conclusion obtained from the present studies.

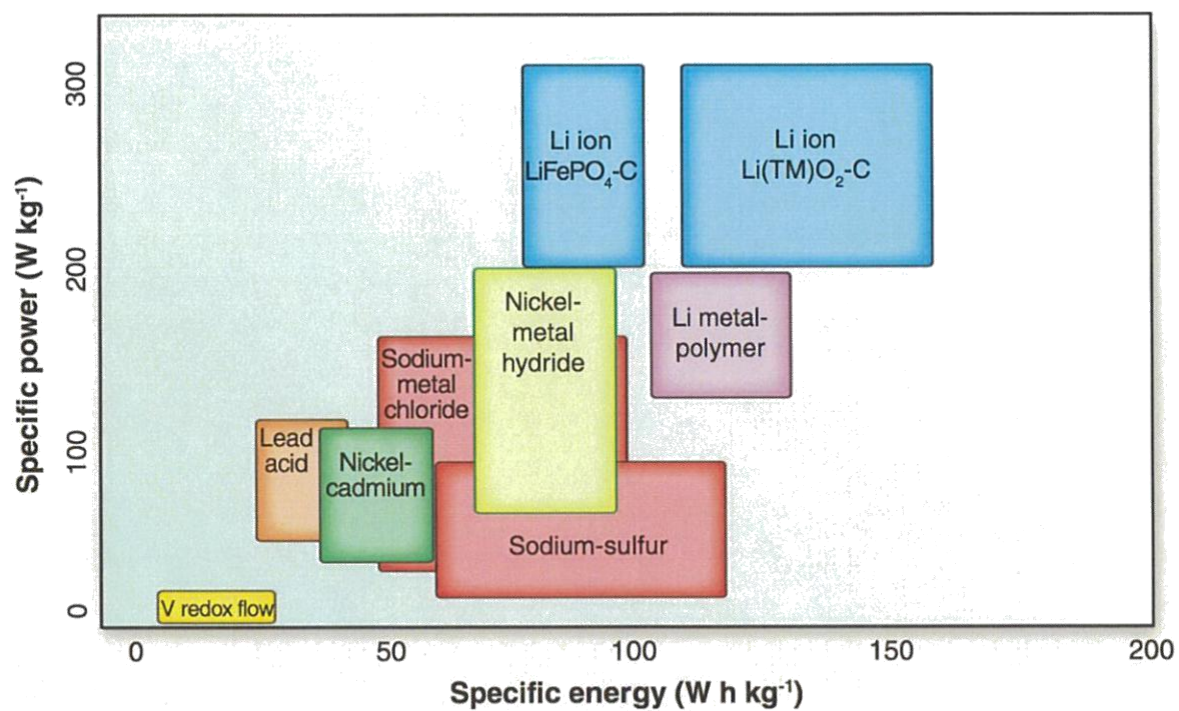


Figure 1. Gravimetric power and energy densities for different rechargeable battery chemistries.³

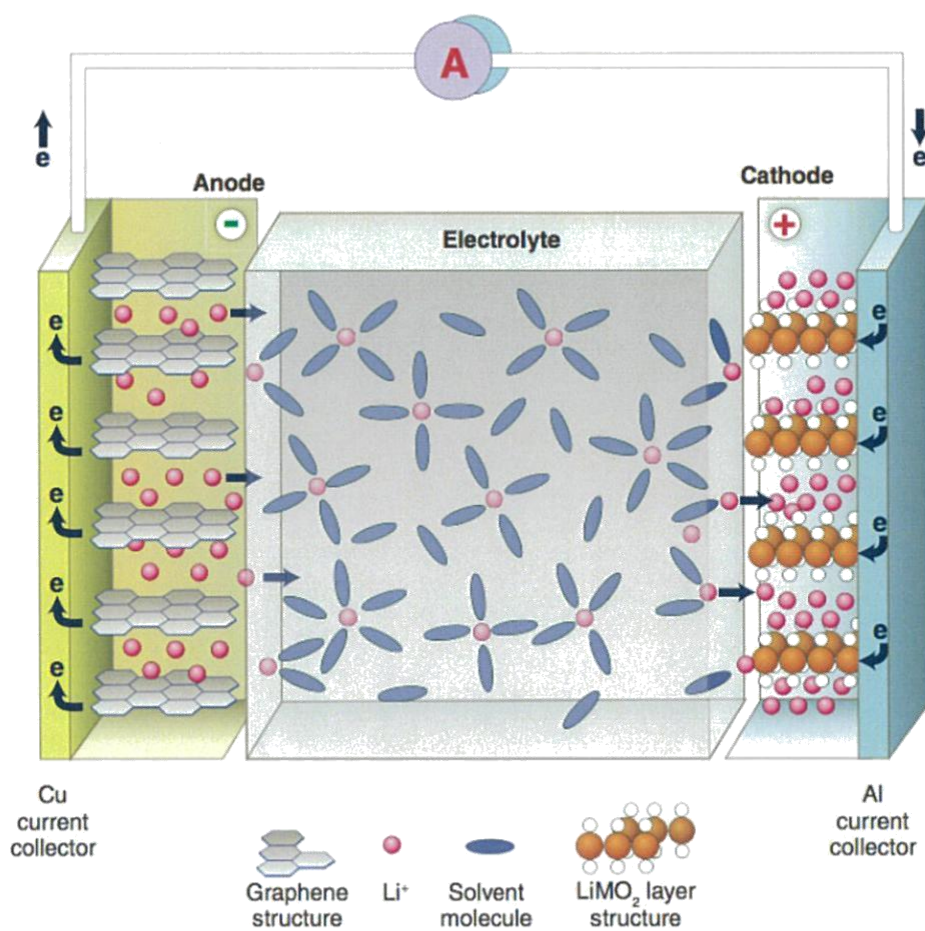


Figure 2. Schematic of a lithium ion battery.³

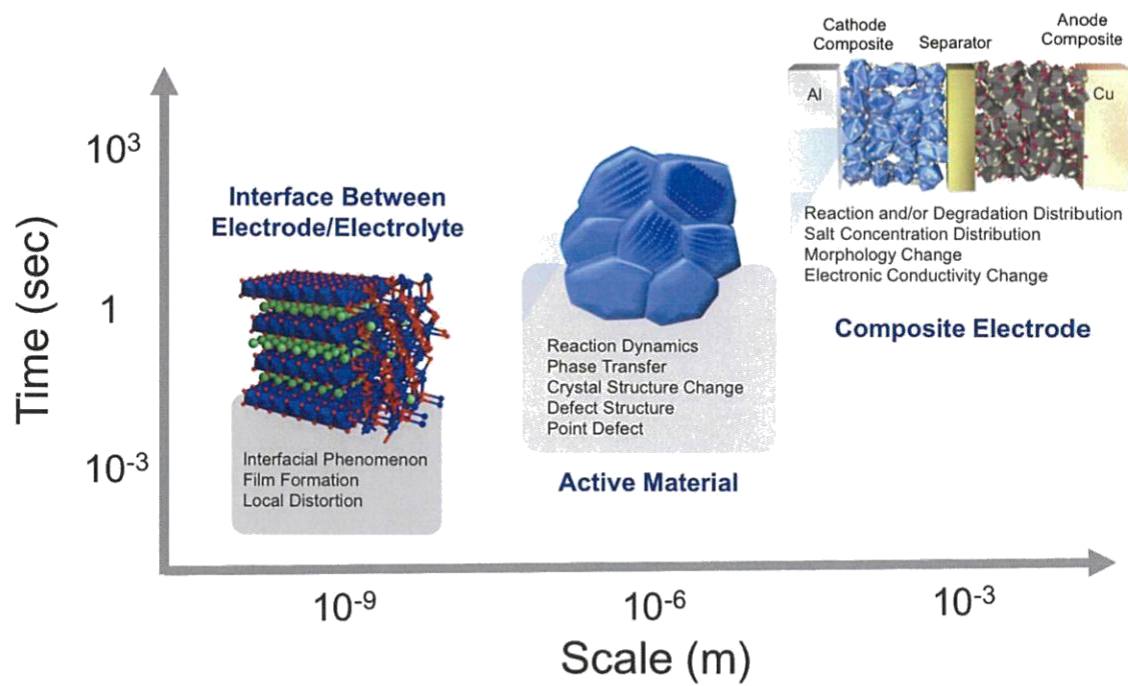


Figure 3. Elementary reactions in lithium ion battery in each time and space scale.

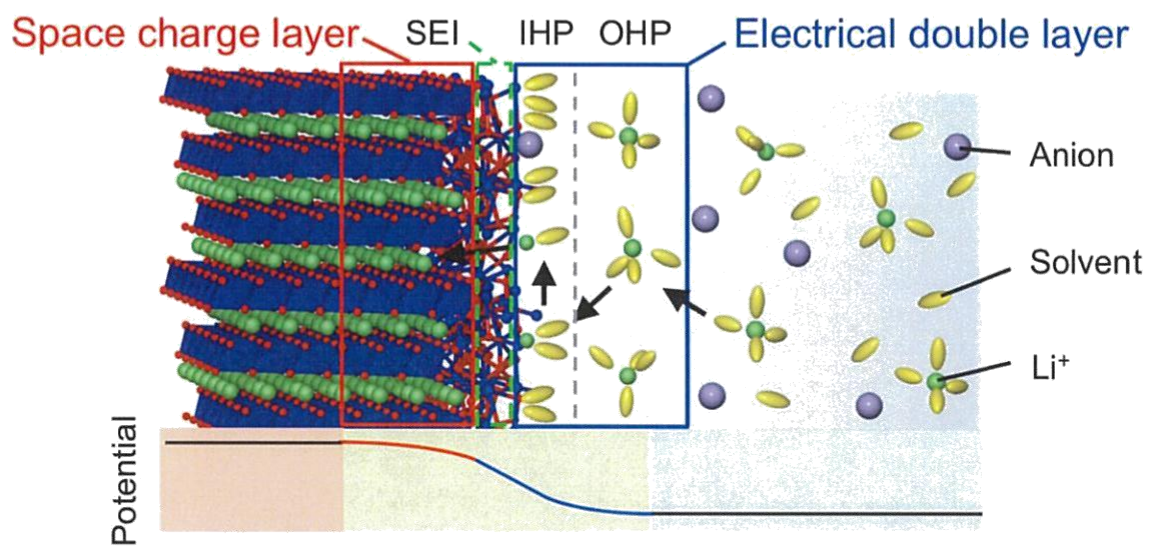


Figure 4. Schematic view of electrode/electrolyte interface. SEI, IHP and OHP mean solid electrolyte interface, the inner Helmholtz plane, the outer Helmholtz plane, respectively.

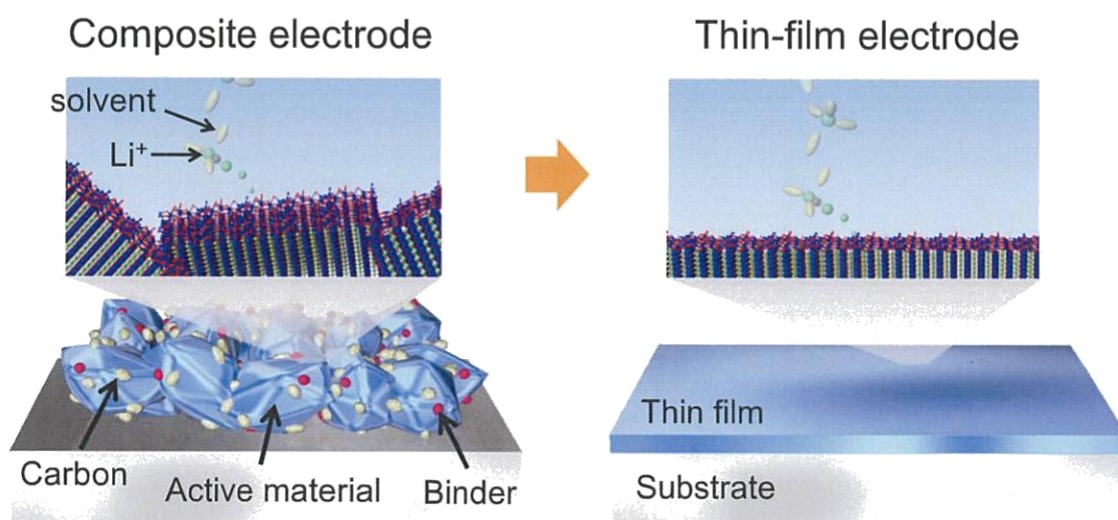


Figure 5. Modeling electrode/electrolyte interface by preparing thin-film electrode.

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2. A study of tri (ethylene glycol) – substituted trimethylsilane (1NM3) / LiBOB as lithium battery electrolyte

2.1. introduction

Numerous attempts have been made to improve the thermal stability and safety characteristics of the electrolytes in the lithium-ion battery in the last two decades. The silicon-based electrolyte has emerged as a primary candidate for the development of the rechargeable lithium-ion battery in an application such as implantable medical device, electric vehicles (EV), and hybrid electric vehicles (HEV) in which safety is a primary consideration.[1] Comparing to the electrolytes used in the conventional lithium-ion batteries, which are flammable, volatile, and highly reactive organic carbonate solvent, silicon-based electrolytes are thermally and electrochemical stable, less flammable and environmentally benign. By overcoming the disadvantages of poly(ethylene glycol) (PEG) as polymer electrolytes, such as electrochemically instability and crystallization at room temperature[2], polysiloxanes have been conjugated to PEG in order to improve its conductivity and physical properties, thus (ethylene glycol)-functionalized polysiloxane electrolytes have become one of the most popular majors in silicon-based electrolytes. These approaches were investigated by

Watanabe, Smid, Shriver, and others more than two decades ago.[3–6] However, their polymers, when doped with lithium salts, were only modest electrical conductors, with ambient conductivities $\sigma \approx 10^{-4} \text{ Scm}^{-1}$. [3,7] For commercial applications, conductivities of at least 10^{-3} Scm^{-1} are needed. Recently, the oligo(ethylene glycol)-functionalized silane electrolyte solvent was found to dissolve most lithium salts easily and showed a comparable ionic conductivity (10^{-3} Scm^{-1}) at room temperature to that of conventional organic carbonate-based electrolytes. Tri(ethylene glycol)-substituted trimethylsilane (1NM3) was identified as a focus of interest due to its well-balanced properties: high conductivity and low viscosity when it was used as a non-aqueous electrolyte.[8] Though the conductivity and solvation kinetics of lithium salts in oligo(ethylene glycol)-functionalized silane electrolyte was investigated[7], only scattered cell performance evaluations of the 1NM3 electrolyte are known. A half cell cycling performance test (Li/0.8M LiBOB-1NM3/LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA)) at room temperature was reported and the cell cycled well and showed no capacity fade up to 80 cycles [8]. At the same time, it was found that a full cell performance test with LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ as the positive electrode and MCMB graphite as the negative electrode had shown excellent cyclability at elevated temperature (40°C).[8] In both cases, no cell performance evaluation was made with Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM) cathode and graphite (MAG) anode when 1NM3 was used as the electrolyte. NCM and MAG are both commercial electrode materials and widely used in the state-of-the-art rechargeable lithium-ion battery

industry. We believe the studies of the cells using these electrodes are important towards the further understanding of the role of silane materials as electrolytes in the lithium-ion battery. A series of studies had been made in our group at Argonne National Laboratory to enable the silane-based electrolyte towards the next generation electrolyte in EV/HEV applications from the support and funding from the lithium-ion battery industry. LiBOB salt was found to be very suitable in the silane electrolyte because it doesn't contain labile fluorine and is thermally stable. It can also provide a passivation film on a graphite anode.[9,10] In this work, we have undertaken the evaluation of using LiBOB as well as other lithium salts in 1NM3 as the electrolyte in NCM/MAG cell system.

2.2. Experimental

2.2.1. Materials and apparatus

Tri(ethylene glycol) monomethyl ether (95%), chlorotrimethylsilane (99.0%), triethylamine (99.5%), and THF (99.9%, anhydrous) were purchased from Aldrich and dried over molecular sieves before use. Lithium hexafluorophosphate (LiPF_6) (99.9%) and lithium bis(oxalate)borate (LiBOB) (99.87%) were purchased from Novolyte. Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) (99.95%) was purchased from Sigma–Aldrich. Lithium difluoro(oxalato)borate

(LiDfOB) was supplied by Central Glass Co., Ltd. All lithium salts were used as received. $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM)cathode and MAG graphite anode electrodes were obtained from EnerDel Inc. The active materials loading were 13mg cm^{-2} for NCM cathode. The active loading of MAG graphite anode was paired with its corresponding cathode. The synthesized 1NM3 sample was analyzed by NMR and FTIR to identify the impurity. ^1H -NMR analysis of the sample was carried out on a Bruker 500 MHz FT-NMR spectrometer. FTIR measurement of the sample was obtained on a Perkin-Elmer Spectrum 100. Ionic conductivity was determined by YSI3200 Conductivity Instrument equipped with a YSI3253 conductivity cell. The conductivity was recorded over a temperature range from -20 to 80°C . The charge-discharge cycling performance was tested on a Maccor Electrochemical Analyzer using 2032 coin cells with NCM as the cathode, MAG graphite as the anode, and a microporous polyethylene/polypropylene/polyethylene separator. The effective electrode area was 1.6cm^2 and the cell capacity is determined by the cathode electrode. A two-cycle formation step was applied prior to the cycling test at the $C/5$ rate. Performance data were acquired and analyzed by the software associated with the instrument.

2.2.2. Synthesis

The silane solvent 1NM3 was synthesized according to ref. [11] with a modified scale-up procedure (Fig. 1). Chlorotrimethylsilane (329.2g, 3.03mol) was added dropwise to a solution of triethylene glycol monomethyl ether (451.6g, 2.75mol) and triethylamine (306.6g, 3.03mol) in THF (1.0L) with an ice-water bath. Mechanical stirring was used due to the high viscosity of the mixture and an inert atmosphere (Argon) was used to prevent moisture. The reaction mixture was kept on stirring at room temperature for 12 hours after complete addition. The reaction was followed with FT-IR by frequent sample measurements until no –OH absorbance ($\sim 3400\text{cm}^{-1}$) was detected. The solution was then filtered. THF and unreacted materials were removed by rotary evaporator prior to the vacuum distillation. A colorless liquid (yield 80%) was obtained for the fraction with a boiling point of 60–63°C/0.2mmHg.

2.3. Result and discussion

2.3.1. 1NM3-lithium salts: conductivities and cycling performance

The silane solvent 1NM3 has a high boiling point and a low viscosity.[8] It can

easily dissolve most of the lithium salts, such as LiBOB, LiDfOB, LiPF₆, LiBF₄, and LiTFSI to form liquid electrolytes. The ionic conductivities of the selected lithium salts-INM3 electrolytes as a function of temperature are shown in Fig. 2a. The nonlinear (curved) profile indicates that their conductivity–temperature relationships do not follow the Arrhenius equation. Instead, the Vogel–Tammann–Fulcher (VTF) can be applied to describe the temperature-dependent conductivity of the complex system

$$\sigma(T) = \sigma_0 T^{1/2} \exp[-E_a/R(T - T_0)]$$

Where σ_0 is the pre-exponential factor proportional to $T^{-1/2}$ and T_0 is the temperature at which the transport function ceases to exist or the solvent structural relaxation becomes zero and may be regarded as the glass transition temperature. It is interesting that the conductivity behavior of the oligomer compound (INM3) still falls into the empirical VTF equation[2,11], which is normally valid for polymer and glassy electrolytes, or concentrated electrolyte solutions.[12] According to the VTF equation, $\ln(\sigma T)$ should have a linear relationship with $(T-T_0)^{-1}$. Using the T_0 values in Table 1, the $\ln(\sigma T)$ versus $(T-T_0)^{-1}$ plot were established and fit well linearly (Fig.2b). As seen in Table1, the prefactor, σ_0 , might be related to the number of mobile charge carriers in the system [13], which lies in the order of LiPF₆ > LiBOB > LiTFSI. It seems to be in the same order as the average ion mobility of lithium salts.[1] The term B can

be thought of as the energy barrier for the rotational motion of oligomer or polymer segments[13], and the value of that is following the order of $\text{LiPF}_6 > \text{LiBOB} > \text{LiTFSI}$. The lower energy barrier when using LiTFSI as a salt may be due to the fact that LiTFSI favors solvents with a low dielectric constant ($\epsilon_{\text{1NM3}} = 5.13$), which makes it an interesting salt to be investigated for the polymer/oligomer based electrolytes.[14] The fitting parameter T_0 of each lithium salts follows an order of $\text{LiPF}_6 < \text{LiBOB} < \text{LiTFSI}$. The value of T_0 in 1NM3-LiTFSI electrolyte is also consistent with the reported value (206K with 1.25M concentration).[11] Since T_0 values are usually observed lie 50 K below the glass transition temperature T_g [15], we may be able to predict their T_g would have the same trend as the values of T_0 against the salt selections.

Fig. 3 shows the cycling performance of the above electrolytes in NCM/MAG cells cycled between 2.7 and 4.1V with a constant current of 0.4 mA at room temperature. The electrolytes used were LiPF_6 , LiTFSI, LiBOB, and LiDfOB in 1NM3 with the same concentration (0.8M). Despite an observable irreversible capacity occurred during the first cycle, the cell using LiBOB or LiDfOB in 1NM3 as the electrolyte shows good cycling performance due to the passivation film formed on the graphite anode surface by the reductive decomposition of the lithium salts. While the cell used 1NM3- LiPF_6 or 1NM3-LiTFSI as the electrolyte, significant capacity fading was observed with 80% loss even after first 3 cycles. The lack of solid electrolyte interface (SEI) film on the surface of the negative electrode (MAG) for the cell using LiPF_6 or LiTFSI in 1NM3 electrolyte might

be problematic. Given the fact that LiDfOB is not a commercially available salt, LiBOB seems to be the best lithium salt candidate for the silane electrolyte.

2.3.2. Optimization of 1NM3-LiBOB electrolyte

It is of great interest to carry out more detailed investigations to illustrate the optimization of 1NM3-LiBOB as the electrolyte for these state-of-the-art commercial electrode materials. Therefore, the ionic conductivity, cycling performance, upper voltage stability, and rate capability of the electrolyte with 1NM3-LiBOB were selected for the following study.

2.3.2.1. Ionic conductivities of 1NM3-LiBOB with various concentrations

The conductivities of the 1NM3-LiBOB with different concentrations were measured as a function of temperature (-20 to 80°C). Plots of conductivity against temperature ($\log \sigma$ versus $1000/T$) for the 1NM3 electrolyte are shown in Fig. 4. As expected, non-linear Arrhenius behavior of the conductivity of 1NM3-LiBOB complexes in the given temperature range was observed, suggesting that besides electrical transport by an ion hopping mechanism, oligomeric ethylene glycol

segmental motion also contributes to the conductivity.[2] Accordingly, VTF equation has been used to fit to the behavior the temperature-dependent conductivities of 1NM3, which couples cation mobility to oligomeric segmental motion. The activation energy (E_a) and the ideal glass transition temperature (T_0) could be determined using the VTF equation (Table 2). As the lithium concentration increased, the prefactor, σ_0 , should also increase since it might be related to the number of mobile charge carriers in the system.[13] The value of energy barrier B is also predicted to increase monotonously as the concentration of the lithium salt rises as is also the case for this system.[13,16] It can be seen in Fig. 4 that 0.8 M LiBOB in 1NM3 electrolyte has the highest conductivity ($\sim 1.7 \text{ mScm}^{-1}$) at room temperature (25°C). At low temperature, the slope versus the reciprocal of the temperature increases greatly, indicating the high activation energy for the ion transportation for 1NM3-LiBOB, which is attributed to the combined effect of salt dissociation and solution viscosity.[17]

2.3.2.2. Cycling performance of 1NM3-LiBOB

Fig. 5 shows the cycling performance of lithium-ion cells $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM)/MAG graphite with 0.8M, 1.0M, and 1.2M LiBOB in 1NM3. Cells were charged and discharged at a C/5 rate and cycled between 3.0 and 4.1V. All cells cycled extremely well with 100% efficiency and showed fairly

stable capacities. To our surprise, the cell with 0.8M LiBOB in 1NM3 electrolyte shows less capacity and stability than that of 1.2M LiBOB in 1NM3 electrolyte, which is inconsistent with their room temperature ionic conductivities since higher conductivity electrolyte facilitates ion transport during the charge/discharge cycle in a lithium-ion battery. An attempted explanation has been made based on the fact of a large amount of LiBOB was anticipated to provide an effective passivation film on the graphite anode surface during the first charging process.[18–20] Considering typically less than 0.4mL electrolyte was used in each 2032 coin cell, the consumption of LiBOB salt could be significant in the cell. The 1NM3-LiBOB electrolyte with lower concentration might not be able to maintain sufficient salt concentration after the formation of the passivation film during the first cycle. In the viewpoint of cell performance, the optimized concentration of LiBOB in 1NM3 is 1.2M.

2.3.2.3. Upper cutoff voltage of 0.8M 1NM3-LiBOB

Fig. 6 shows the capacity retention of the above NCM/MAG cells cycled at room temperature with a constant current of 0.4mA. The electrolyte used was 0.8 M LiBOB in 1NM3. When the cell was cycled between 2.7 and 3.9 V, the cell performed extremely well with 100 % efficiency and showed no capacity fade after 100 cycles. When the cell was cycled over 2.7–4.1 V or 2.7–4.2 V, the cell

showed slow capacity fading, which is acceptable under the lower concentration (0.8M) electrolyte condition. When the upper cut off voltage of the cell was increased to 4.3 V, the cell showed severe capacity fading, with almost 50% fading after only 10 cycles. The capacity fading is due to the upper voltage limit (4.5 V) of LiBOB salt as reported when an inert electrode (platinum) was used.[21] Nevertheless, the upper voltage limit of the 1NM3-LiBOB (4.2V) is higher than our previous results of disiloxane (2SM3)-LiBOB system (4.0V).[22]

2.3.2.4. Rate capability of 1NM3-LiBOB electrolyte

The rate capabilities of 1NM3-LiBOB electrolyte were evaluated by charging an NCM/MAG lithium-ion cell with a constant current equivalent to $C/10$ to 4.1 V, followed by a constant voltage charge until a cutoff current equivalent to $C/20$. The cell was then discharged to 2.7V at constant currents of $C/20$, $C/10$, $C/5$, $C/2$, C , and $2C$. As shown in Fig. 7, the NCM/MAG cell using LiBOB-1NM3 as the electrolyte demonstrated more than 80% capacity retention at the $C/20$, $C/10$, and $C/5$ rates. However, less than 40% capacity was retained at the $C/2$ rate. The severe capacity fading is attributed to the growing SEI formed by the continuous decomposition of LiBOB on the graphite anode surface at higher voltage.[19,20,22]

2.4. Conclusions

The tri(ethylene glycol)-substituted trimethylsilane (1NM3) was synthesized and evaluated as an electrolyte solvent with a variety of lithium salts. The ionic conduction behavior of the electrolyte system agrees well with the VTF equation. The ion transport in the electrolyte system is dominated by the mobility of the solvent molecule and the conductivity is correlated with the ion-hopping mechanism. Cycling results showed that the 1NM3-LiBOB exhibits great stability over the other lithium salts due to the SEI formation capability of the LiBOB salt. Additionally, we found that the rather lower ionic conductivity of 1.2 M 1NM3-LiBOB electrolyte is indicative of a much-improved cycling performance in an NCM/MAG cell. A possible explanation is that the 1NM3-LiBOB electrolyte with higher concentration would be able to maintain sufficient transport performance even after a significant consumption of the LiBOB salt during the first formation cycle. A critical full cell upper cutoff potential, 4.2V, was then identified for 1NM3-LiBOB as the electrolyte in NCM/MAG chemistry. Extensive investigations involving the state-of-the-art LiPF_6 salt in 1NM3 electrolyte system and the development of novel SEI additives tailored for 1NM3/ LiPF_6 electrolyte system are in progress and will be reported in a next chapter.

2.5. References

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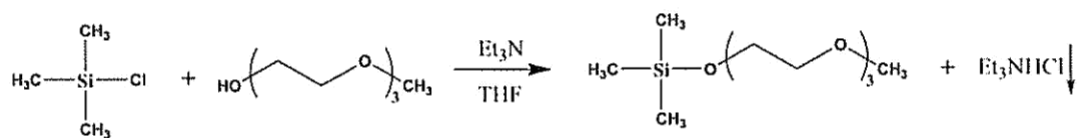


Figure 1. Schematic synthesis route for tri(ethyleneglycol)-substituted silane(1NM3).

Table 1. Fitting parameters of VTF equation to the temperature-dependent conductivities of 1NM3 electrolytes.

Electrolyte	Concentration	T_0/K	$E_a/\text{kJ mol}^{-1}$	$\sigma_0/\text{S cm}^{-1}$
1NM3-LiTFSI	0.8M	202	1.08	0.115
1NM3-LiBOB	0.8M	196	1.36	0.146
1NM3-LiPF ₆	0.8M	192	1.90	0.256

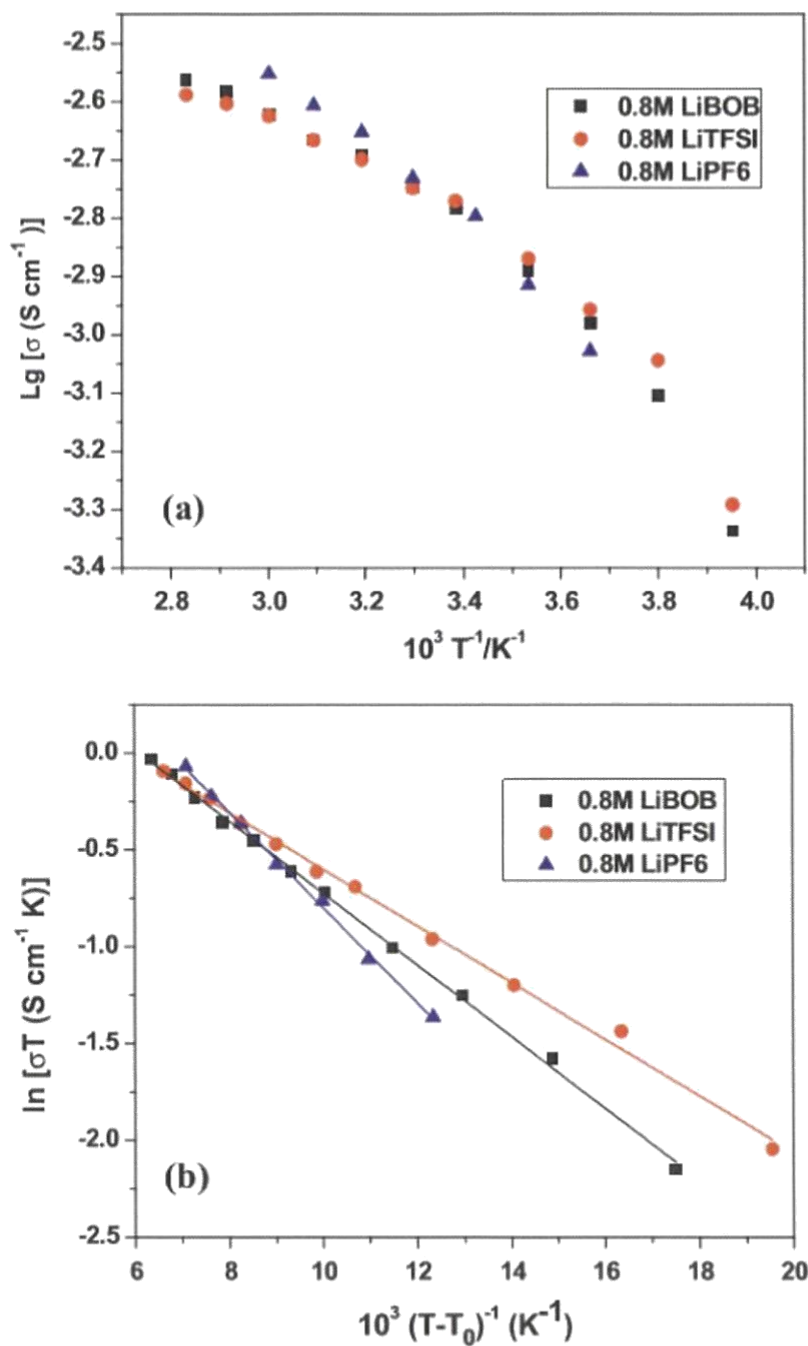


Figure 2. (a) Arrhenius plots of conductivity versus temperature for 1NM3 with various lithium salts at 0.8M concentration. (b) Vogel–Tammann–Fulcher (VTF) plots of conductivity versus temperature for 1NM3 with various lithium salts at 0.8M concentration.

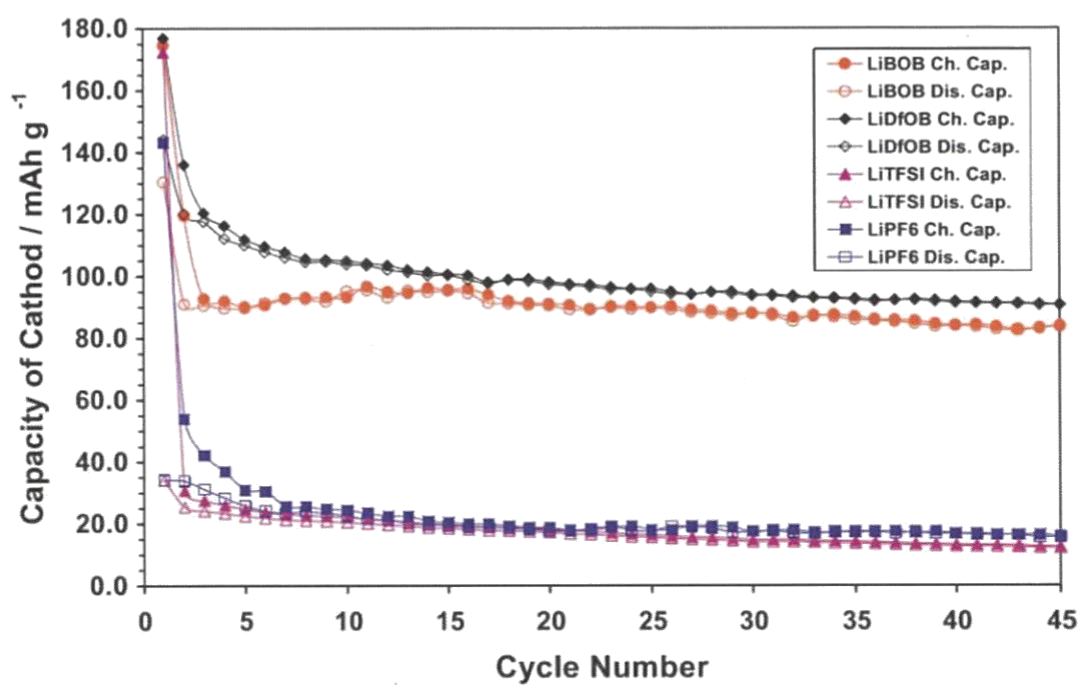


Figure 3. Cathode specific capacity versus cycle number for NCM/1NM3-LiSalts/MAG cells at 25°C.

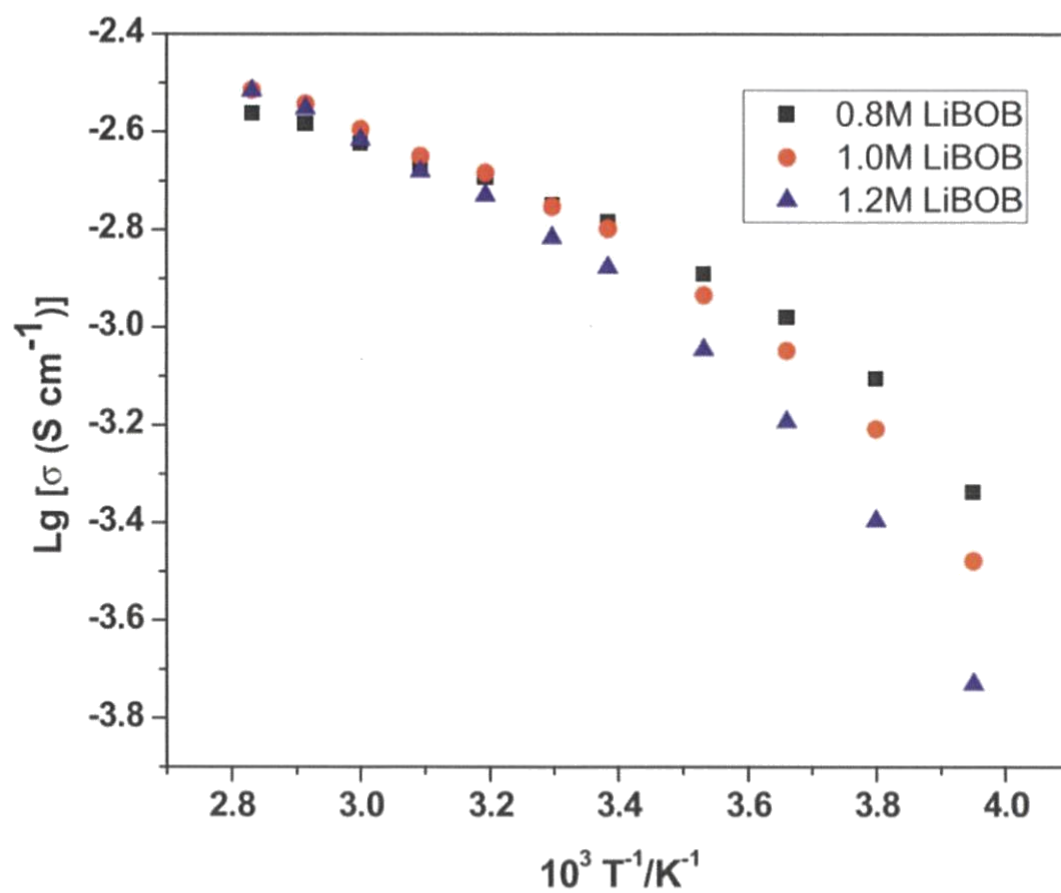


Figure 4. Arrhenius plots of ionic conductivity for 1NM3 electrolyte with various LiBOB concentrations.

Table 2. Fitting parameters of VTF equation to the temperature-dependent conductivities of 1NM3-LiBOBelectrolytes.

Electrolyte	Concentration	T_0/K	$E_a/\text{kJ mol}^{-1}$	$\sigma_0/\text{S cm}^{-1}$
1NM3-LiBOB	0.8M	196	1.36	0.146
	1.0M	193	1.82	0.224
	1.2M	193	2.25	0.311

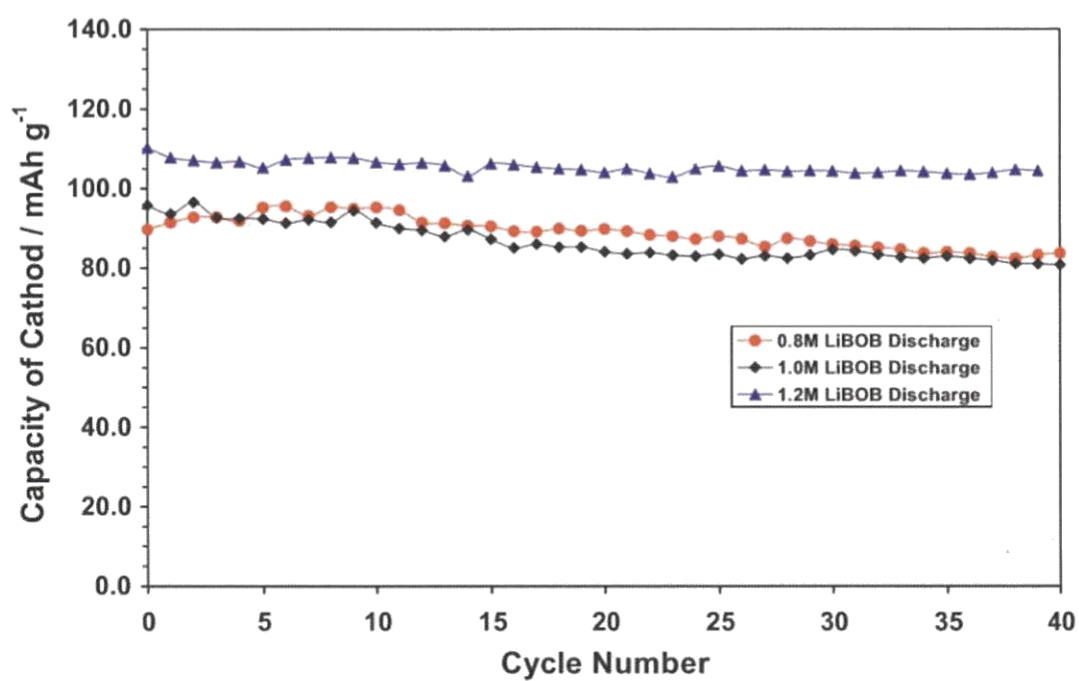


Figure 5. Cathode specific capacity versus cycle number for NCM/1NM3-LiBOB/MAG cells with various LiBOB concentration sat 25°C.

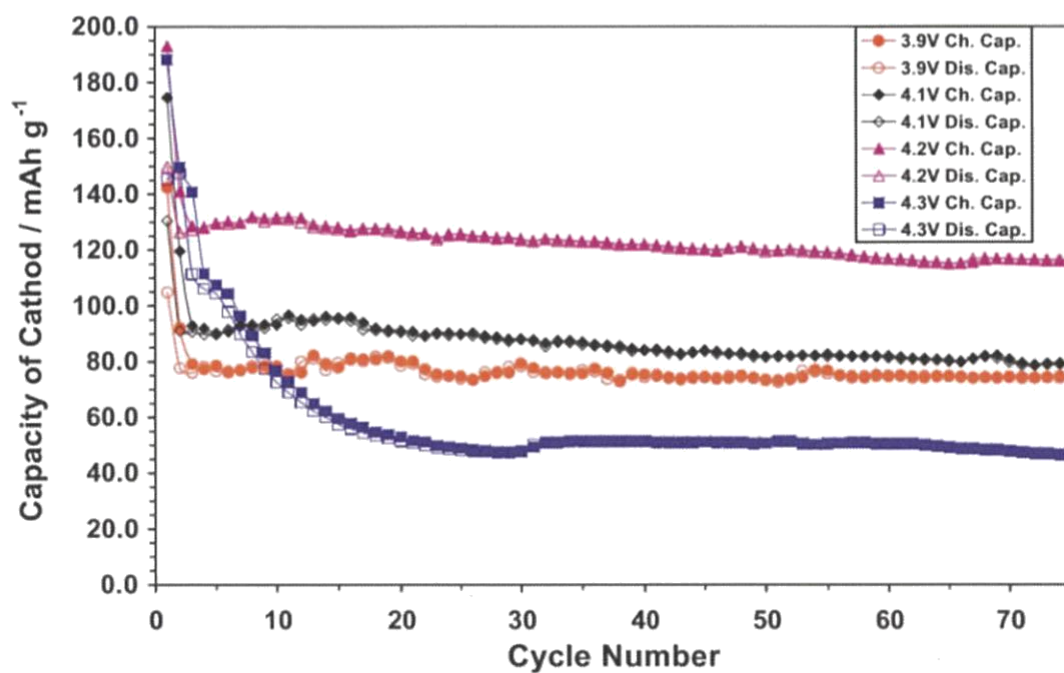


Figure 6. Cathode specific capacity versus cycle number for NCM/INM3-LiBOB/MAG cells with different upper cut off voltages.

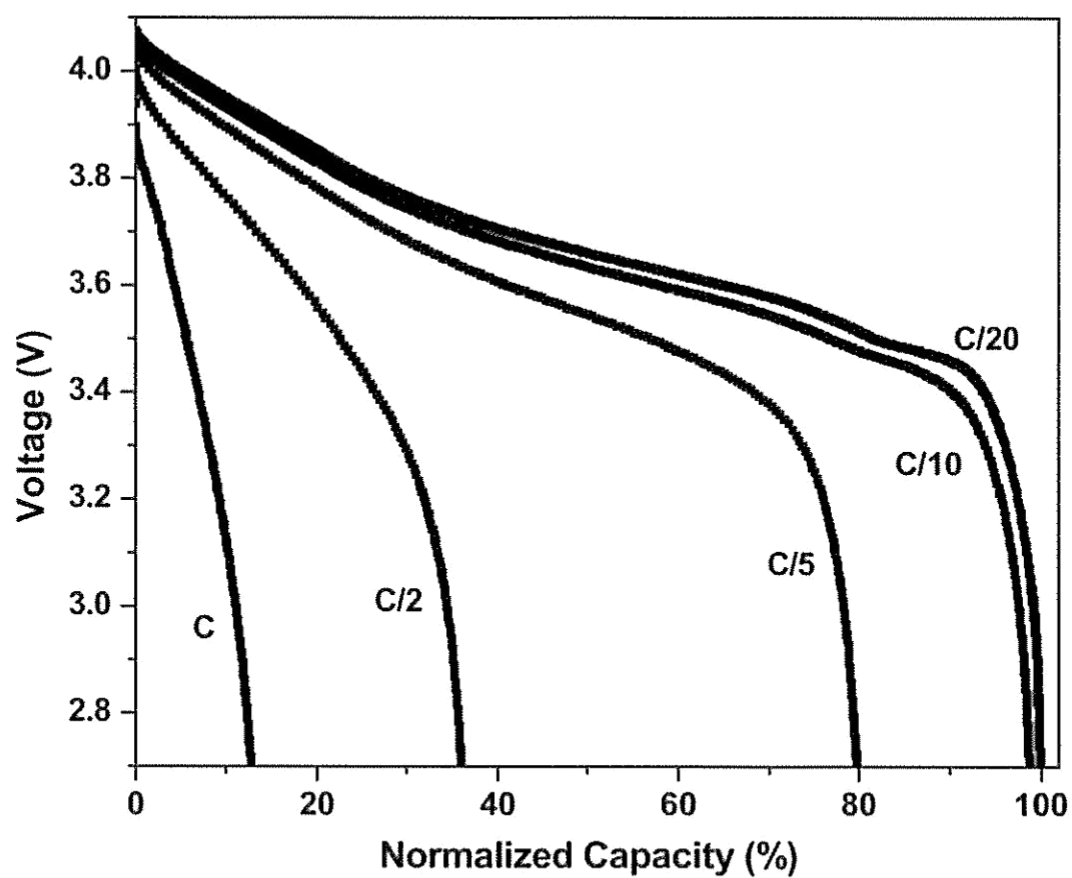


Figure 7. Discharge profiles of NCM/1NM3-LiBOB/MAG cells at different C-rates with cut off voltage of 2.7–4.1 V.

3. Electrode Surface Film Formation in Tri(ethylene glycol) - Substituted Trimethylsilane (1NM3) / LiBOB Electrolyte

3.1. Introduction

Lithium-ion batteries have been a major component of Plug-in hybrid electric vehicles (PHEV) and electric vehicles (EV) as power storage devices due to its characteristics of high energy, high power and long life. The module of lithium-ion battery pack in the vehicle is generally designed in huge size in order to achieve a satisfied driving range. Thus, high safety of lithium-ion battery cell is greatly desired compared with the consumer electronics applications, such as laptop and mobile phones. Selection of cathode materials for enhanced battery safety is limited due to the trade-off with cathode capacity. LiMn_2O_4 has been commercialized as a cathode active material to achieve safer lithium-ion batteries due to its thermally stable characteristics.[1,2] Although LiMn_2O_4 cell can satisfy the battery requirement for EV and PHEV applications, there is still an increasing demand for cell capacity and safety. Another important approach for battery safety is the selection of appropriate electrolytes which act as an ionic conductor between the positive and negative electrodes. The electrolyte is one of the most

important components in the lithium ion battery because it dictates the power, cycle and calendar life of lithium-ion cells. In addition, the electrolyte will affect the cell capacity through the selection of appropriate cathode and anode as well as cell safety. Typical electrolyte for high power application is based on non-aqueous organic carbonates as electrolyte solvents which are flammable and volatile. The commercialized electrolyte for lithium ion battery is generally composed of LiPF_6 as lithium salt and the mixture of linear/cyclic carbonate as a solvent. Ethylene carbonate (EC) is indispensable for graphite anode because of its miraculous enabling lithium ion intercalation process on the graphite anode. Previous studies[3-6] have revealed that surface film formation on the graphite by decomposition of EC acts as a passivation film or solid electrolyte interface (SEI), which prevents the side reactions between the lithiated graphite and the electrolyte thus ensure the regular lithium ion insertion into graphite layers. It is well accepted that SEI property is critical for lithium-ion battery performance.[7-11]

To achieve safer lithium-ion batteries for automotive application, the battery group at Argonne National Laboratory has been focusing on the silicon-based electrolytes. At the first stage of the research, LiBOB was found to be suitable lithium salt for the silicon-based electrolyte.[12-16] Additional to act as a lithium salt, it also can provide a passivation film on the surface of the graphite anode.[17-21] Recently, we published our results of tri(ethylene glycol)-

substituted trimethylsilane (1NM3)-LiBOB based electrolyte, one representative of the silicon-based electrolytes, in $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM)/graphite (MAG) lithium ion chemistry[22] and LiMn_2O_4 /graphite lithium ion chemistry.[23] Since the EC, the major SEI formation component for carbonate based electrolytes, is absent in the 1NM3/LiBOB silane electrolyte, we expect that SEI characteristics and components formed by silane electrolyte will be different from that formed by EC-based carbonate electrolytes. The purpose of this work is to investigate the new SEI and its characteristic formed by 1NM3-LiBOB electrolyte using LiMn_2O_4 as cathode and graphite as an anode.

3.2. Experimental

LiBOB (99.87%) and LiPF_6 (99.98%) were purchased from Novolyte. 1.2 M LiPF_6 in 3/7 ethylene carbonate (EC)/ethyl methyl carbonate (EMC) were purchased from Tomiyama Pure Chemical (Japan). These salts and electrolyte were used as received. LiMn_2O_4 cathode and MAG anode were provided by EnerDel Inc. The cathode active material loading is 11.5 mg cm^{-2} and balanced with the corresponding anode electrode. Polyvinylidene fluoride (PVdF) was used as a binder for both cathode and anode and acetylene black (AB) was used as a conductive additive for the cathode.

1NM3 solvent was synthesized and analyzed according to our previously reported procedure.[22] ^1H , ^{13}C NMR and FT-IR spectroscopy were employed to identify the structure of 1NM3 and its purity.

2032 coin cells were assembled with LiMn_2O_4 as the cathode, MAG graphite as the anode, and a microporous polyethylene/polypropylene/polyethylene as the separator. The effective electrode area was 1.6 cm^2 . Electrodes were dried in a vacuum oven at $80\text{ }^\circ\text{C}$ for an overnight before the cell assembling. A two-cycle formation step was applied at room temperature by C/10 rate by Maccor cycler. The formation was operated in constant current constant voltage charge and constant current discharge mode and voltage range were controlled between 4.2 and 3.0 V. Performance data were acquired and analyzed by the software associated with the instrument.

After the formation process, cells fully discharge state was carefully disassembled without any electrical shortage. Then, due to removing electrolyte solvent and salt, electrodes from disassembled cell were dipped in dimethyl carbonate (DMC) for 10 minutes. Dipping process was repeated twice with fresh DMC, and dried under vacuum. All disassemble operation was performed in an Argon filled glove box with O_2 level lower than 5ppm.

The morphology of electrodes and element distribution were visualized by Hitachi S-3400 scanning electron microscope (SEM) equipped with a PGT energy

dispersive X-ray analyzer. Samples were mounted on SEM stabs in Ar glove box and stored into the transfer container.

The Graphite layer structure of cycled anode electrode was determined on a Rigaku MiniFlex X-ray diffractometer using $\text{Cu K } \alpha$ radiation (30 kV, 15 mA) with a scanning speed of $1.2^\circ (2 \theta) \text{ min}^{-1}$.

To analyze chemical component on the surface of the electrode, X-ray photoelectron spectroscopy (XPS) analysis was performed. Samples were mounted on XPS stabs in Ar glove box and stored into transfer container. Sample transfer from transfer container to XPS chamber was carried out inside a glove bag attached to XPS loading chamber to prevent exposure to the air. XPS was performed with an Omicron ESCA probe equipped with EA 125 energy analyzer using $\text{Al K } \alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) with operation power of 300 W. For all analysis, the take-off angle of the photoelectron was 45° . The electron gun was applied to reduce the charging up effect. The depth profile was obtained by Argon ion beam etching with a rate of 0.5 nm min^{-1} on a Si wafer. Binding energies were referred to the graphite C 1s binding energy set at 284.3 eV. The peak fit was performed with Gaussian-Lorentzian sum functions using *XPSPeak 4.1*. [24]

3.3. Result and discussion

3.3.1. Electrochemical characteristics

1NM3 consists of trimethyl silane with oligo(ethylene glycol) chain and dissolves most of the lithium salts, such as LiBOB, LiPF₆, LiBF₄, and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI). In the previous papers,[13,22,23] we selected LiBOB as a lithium salt due to its solid electrolyte interface forming capability. Figure 1 shows the first charge and discharge profiles of LiMn₂O₄/MAG cell with three electrolyte systems 0.8M LiBOB 1NM3 (1NM3-LiBOB), 1.0M LiPF₆ 1NM3 (1NM3-LiPF₆) and 1.2M LiPF₆ EC/EMC (3/7) (EC/EMC-LiPF₆). The cell with EC/EMC-LiPF₆, the conventional electrolyte, showed a small shoulder around 3.3 V on the charging curve due to the EC reduction and SEI film formation.[3,4,25,26] Columbic efficiency of EC/EMC-LiPF₆ is 83.4 %. In contrast, the cell with 1NM3-LiBOB electrolyte showed a small plateau at early charge stage around 2.2 V and the columbic efficiency is much lower (70.2 %). This plateau was assigned to LiBOB decomposition and SEI film formation.[23,27] Nevertheless, the cell with 1NM3-LiPF₆ electrolyte showed larger charging capacity and less reversibility compared with other two electrolytes with a columbic efficiency of only 7.7 %. It indicates that 1NM3-LiPF₆ electrolyte lacks of SEI formation ability. We ever reported that

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode/MCMB graphite cell using LiPF_6 salt in oligo(ethylene glycol)-functionalized disiloxane electrolyte has large capacity fade due to the lack of SEI film formation in the component of electrolyte.[28]

3.3.2. Electrode surface morphology

The morphology of the electrode surface after formation was visualized by SEM. The microscale structure change and deposition of decomposed products on the electrode surface could be observed, as shown in Figure 2 and Figure 3. LiMn_2O_4 cathode morphology as illustrated in Figure 2, after cycling. Cycled LiMn_2O_4 samples were fully discharged and thoroughly rinsed by DMC prior to the SEM measurement. As seen in Figure 2, particles about few micrometers are LiMn_2O_4 and other smaller particles are probably complex of carbon black and PVdF binder. There is no significant difference from pristine and cycled cathode surface (Figure 2a, b, c). However, as shown in Figure 3, cycled MAG graphite electrode showed different surface morphology when different electrolytes were used. Graphite surface using 1NM3-LiBOB shows island-like spots with few micrometers in diameter (Figure 3a). EDS analysis data are shown in Figure 4 revealed that this spot is O rich and F poor surface. PVdF binder is the only fluorine source for 1NM3-LiBOB electrolyte; therefore, it was assumed that LiBOB is favorably reduced to form oxygen-rich film on PVdF-uncovered

graphite particle surface. In addition, graphite using 1NM3-LiPF₆ showed a significant difference from 1NM3-LiBOB and EC/EMC-LiPF₆ as shown in Figure 3b. Graphite morphology in Figure 3.b is similar to the exfoliated graphite particles with stacked sheets when propylene carbonate, tetrahydrofuran et al. electrolytes were used.[29-31] Due to the lack of SEI protection, the 1NM3-LiPF₆ electrolyte can co-intercalated into the graphite layer causing huge volume expansion and exfoliation of graphite layers.[32] This resulted in a large number of cracks on the surface of the cycled graphite electrode as observed in the macroscopic picture of Figure 3d.

3.3.3. Graphite microstructure

XRD technique can provide useful information for the microstructure change of graphite anode when different electrolytes are used.[3,33] Figure 5 shows the XRD patterns obtained from discharged MAG graphite electrode using 1NM3-LiPF₆, 1NM3-LiBOB and EC/EMC-LiPF₆ electrolyte. The graphite peak 0 0 2 (*h k l*) reflection was clearly shown in XRD profiles. However, it became broader for the graphite using 1NM3-LiPF₆ and an extra peak at 24° showed up, indicating the graphite structure is not well maintained after the cycling. These results support the SEI formation capability of 1NM3-LiBOB electrolyte and the lack of SEI formation of 1NM3-LiPF₆ electrolyte on the graphite electrode. The issue

associated with 1NM3-LiPF₆ electrolyte for graphite cell is being addressed and extensive investigations are discussed in next work.[32]

3.3.4. Electrode surface analysis by XPS.

To analyze the chemical component on the electrode surface, XPS analysis was performed on the cycled electrode samples through an analysis-chamber to avoid environmental contamination. For the binding energy, it was referred to the graphite C 1s binding energy set at 284.3 eV. Table 1 shows various element concentrations of the cathode surface obtained from the peak area of the narrow scan XPS spectrum. C, O, F and Mn element concentrations did not show a remarkable difference between 1NM3-LiBOB and EC/EMC-LiPF₆ electrolyte. It is worth to note that, the Si and B elements were not detected from the cathode XPS using 1NM3-LiBOB. Figure 6 shows C 1s and O 1s narrow XPS spectra of pristine and cycled LiMn₂O₄ cathode in 1NM3-LiBOB and EC/EMC-LiPF₆. C 1s spectra showed almost identical peaks (carbon black, 284.3 eV; PVdF, 286.0 eV and 290.5 eV[34-36]). However, O 1s spectra of LiMn₂O₄ cathode showed a large difference. The peak at 529.5 eV associated with the oxygen of LiMn₂O₄[37] didn't show up for EC/EMC-LiPF₆, indicating a SEI film formed and covered the surface of LiMn₂O₄. XPS spectrum of 1NM3-LiBOB is similar to that of pristine LiMn₂O₄ electrode, except broad peaks were observed between 530 eV to 534 eV,

which matched the peak assignment of C=O bonds and C-O bonds reported in the literature.[8,35,38-45] These XPS results indicate a unique SEI formation on the LiMn_2O_4 electrode surface using 1NM3-LiBOB as an electrolyte. More work needs to be done to fully understand the nature of this cathode SEI.

Table 1 is a summary of element concentrations of the graphite anode surface from the peak area of narrow scan XPS spectra. 1NM3-LiBOB showed higher atomic concentration of O, Li, and lower F and B. Nakahara[45,46] reported disiloxane and polysiloxane/LiBOB electrolytes form SEI composed of Si element on HOPG surface. However, our XPS results didn't show Si element on anode surface when 1NM3-LiBOB electrolyte was used. The difference of these results is probably due to the facile reduction of siloxane bond (Si-O-Si) which doesn't exist in the structure of 1NM3 molecule.

Figure 7 shows C 1s, O 1s, F 1s and B 1s narrow XPS spectra of anode electrode surface using 1NM3-LiBOB and EC-EMC-LiPF₆ electrolyte. In Figure 7 (1), C 1s spectra of both cycled anodes consist of graphite carbon peak (284.3 eV), hydrocarbon (285 eV), C-H of PVdF (286 eV), C-O (287 eV), C-O in lithium alkyl carbonate, lithium oxalate and alkyl oxalate (289.5 eV) and C-F of PVdF (291.2 eV).[8,35,38-49] The extra peak on XPS at 289.5eV is characteristic for 1NM3-LiBOB electrolyte, which is attributed from the decomposition of LiBOB forming the SEI on the anode surface. This is in good agreement with the previous

report of SEI formation consisting of semi-carbonate like the organic component from the reduction compounds of LiBOB salt.[19,36,42,50] Although the peak intensity of C-O-C ether for 1NM3-LiBOB anode is significant, it requires further studies to figure out the origination and its formation mechanism. In contrast to C 1s peaks, the O 1s XPS spectra (Figure 7 (2)) shows one broad and asymmetric peak consisting of compounds with C=O bonds at 532.5 eV and C-O bonds at 533 eV for both anodes. Figure 7 (3) shows F 1s XPS spectra. The peak at 685.8 eV and 688.6eV are attributed from LiF and PVdF,[8,35,35,38-42,45] respectively. It is surprising that LiF was detected on the anode surface using 1NM3-LiBOB electrolyte which doesn't contain any fluorine element. PVdF is the only source of fluorine in this cell system. As reported, LiF can be formed by PVdF reduction.[51] Figure 7 (4) shows B 1s XPS spectra. Only 1NM3-LiBOB anode showed a borate peak at 193.3 eV, indicating the decomposition of LiBOB forming the SEI, which is in good agreement with the previous report about LiBOB originated SEI.[36,42,52,53]

Since XPS is a surface sensitive technique, a depth profile of the anode surface in terms of XPS quantities was obtained by combining a sequence of ion gun sputtering cycles interleaved with XPS measurements starting from the surface. Figure 8 shows the typical in-depth profile analysis results of anode C 1s, F 1s and B 1s using 1NM3-LiBOB electrolyte. After 2 minutes sputtering, C 1s peaks at 287 eV and 289.5 eV in Figure 8(a) are dramatically decreased, which indicates

the semi carbonate-like species in the SEI are easily removed by Argon sputtering. Additionally, the peak intensity of graphite anode at 284.3eV as well as the hydrocarbon peak are gradually increased with increasing the sputtering time from 2 to 100 minutes. However, even after 100 minutes sputtering, lithium oxalate, alkyl oxalate compounds, and ether SEI compositions were still detectable, though the intensities are very low

F 1s in depth XPS analysis results were shown in Figure 8 (b). Many groups[38,40,41,54] reported the XPS analysis of graphite electrode using carbonate-LiPF₆ electrolytes and they assigned the peak of LiF around 686 eV to the decomposition products from LiPF₆ salt. However, our analysis for 1NM3-LiBOB electrolyte showed the same spectrum, but there is no LiPF₆ present. Before sputtering, the PVdF binder is the dominant peak with a minor peak of LiF at 685.8 eV. With the progress of sputtering, the PVdF peak is diminishing and the LiF became dominant for F 1s spectra. This confirms that the PVdF participates in the SEI formation process at the interphase with the graphite by reductive formation of LiF and the conjugated conductive polymers.[51]

The C-rate capacity of LiMn₂O₄/1NM3-LiBOB/MAG cell is not as good as that of the EC/EMC-LiPF₆ as reported by us.[23] Part of the reason is due to the resistive SEI formation on the graphite surface. In Figure 8 (c), B 1s peak is present in all the measurements at different sputtering times with limited

concentration change. For example, even after 100 minutes, the boron peak still presents on the anode surface. It implies that LiBOB participates in the SEI formation from the very beginning of the charging process. Considering the sputtering rate is 0.5nm min^{-1} of Si wafer, it is estimated that the B species containing SEI is more than 50 nm in thickness

Based on the above results from this study, a schematic diagram of the SEI composition on the graphite anode surface using 1NM3-LiBOB as electrolyte is conceived in Figure 8. The MAG graphite anode surface is not uniform, which comprises PVdF-covered and SEI -covered areas. On the surface of the anode, a small part is still covered by PVdF binder. However, with the increase of the depth of the surface, LiF is dominant which is produced from the PVdF reduction. The graphite exposed area is covered with oxalate and borate compounds produced from BOB^- decomposition as observed in the carbonate-LiBOB electrolyte. The moiety of LiBOB may form Li_xBO_y , lithium boro-oxalates and lithium oxalates in the SEI layer.

3.4. Conclusions

Electrode surface film formed by the tri(ethylene glycol)-substituted trimethylsilane (1NM3)-LiBOB electrolyte was investigated for LiMn_2O_4 as a cathode and MAG graphite as anode after formation cycles. It was found that SEI on the graphite anode is composed of lithium oxalates, lithium boro-oxalates, and Li_xBO_y . Additionally, PVdF binder also participates in the SEI formation process in the anode electrode by releasing fluorine to form LiF in 1NM3-LiBOB electrolyte. However, 1NM3 solvent reduction and participation of SEI film formation were not observed in this study. It is found that Si and B elements were not detected from the cathode XPS, indicating 1NM3-LiBOB electrolyte is relatively stable on the cathode side and does not participate the cathode SEI formation. We demonstrated that 1NM3- LiPF_6 electrolyte lacks SEI formation function and could not maintain graphite structure during electrochemical process. This study explains the 1NM3-LiBOB combination is an excellent electrolyte for graphite-based lithium ion battery.

3.5. References

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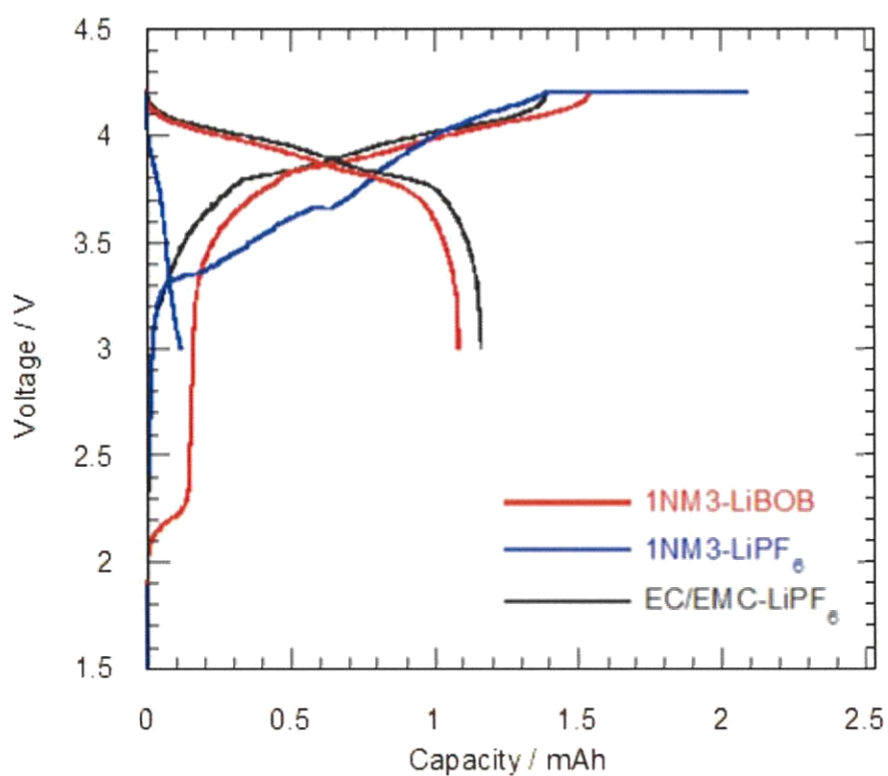


Figure 1. First charge-discharge profile of Graphite/LiMn₂O₄ cell using various electrolytes, (red) 0.8M LiBOB in 1NM3, (blue) 1.0 M LiPF₆ in 1NM3, (black) 1.2 M LiPF₆ in EC/EMC 3/7,

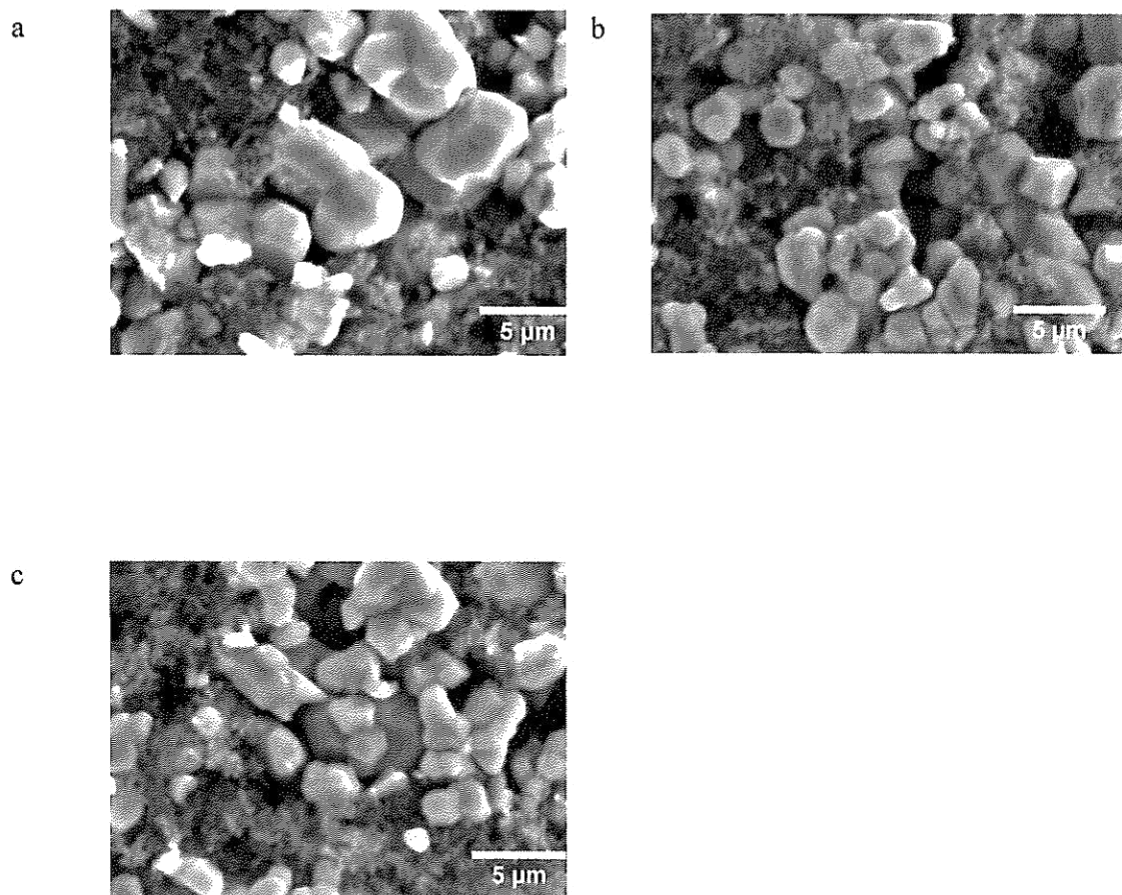


Figure 2. SEM images of LiMn_2O_4 cathode after two cycle formation using (a) 0.8M LiBOB in 1NM3, (b) 1.0 M LiPF_6 in 1NM3 and (c) 1.2 M LiPF_6 in EC/EMC

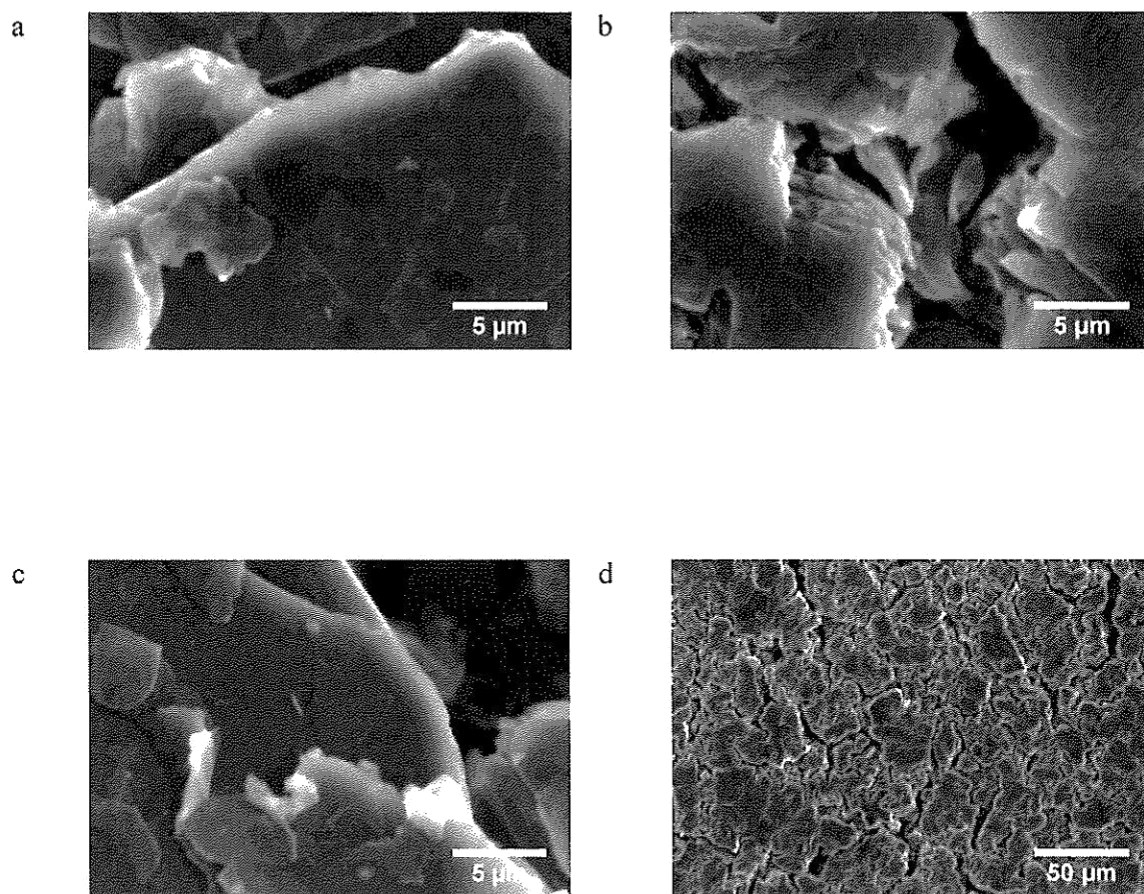


Figure 3. SEM images of MAG graphite anode after two cycle formation using (a) 0.8M LiBOB in 1NM3, (b) 1.0 M LiPF₆ in 1NM3, (c) 1.2 M LiPF₆ in EC/EMC, (d) 1.0 M LiPF₆ in 1NM3 lower magnitude picture.

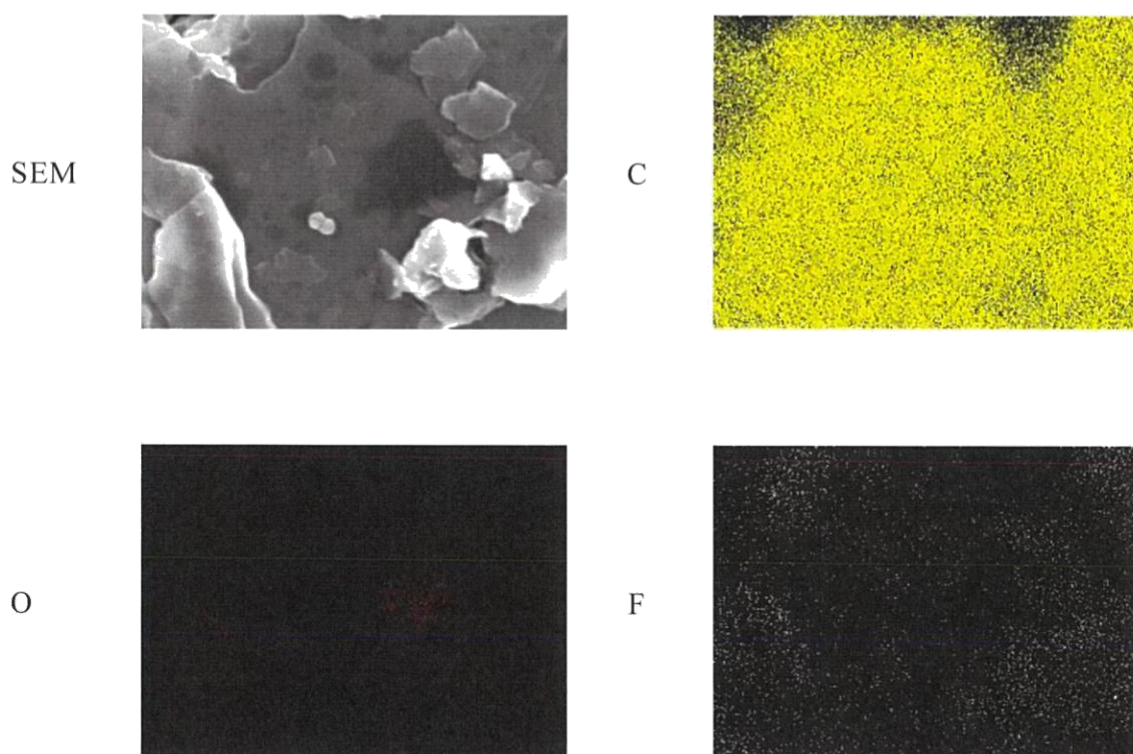


Figure 4. SEM micrographs and EDS mapping of C, O and F on cycled MAG graphite anode surface. EDS mapping data showed that island-like spots with few micrometers in diameter are O-rich and F-poor. PVdF binder is the only fluorine source for 1NM3-LiBOB electrolyte; therefore, the mapping of F element indicates the existence of PVdF. It suggests that LiBOB was favorably reduced to form oxygen-rich film on PVdF-uncovered graphite particle surface.

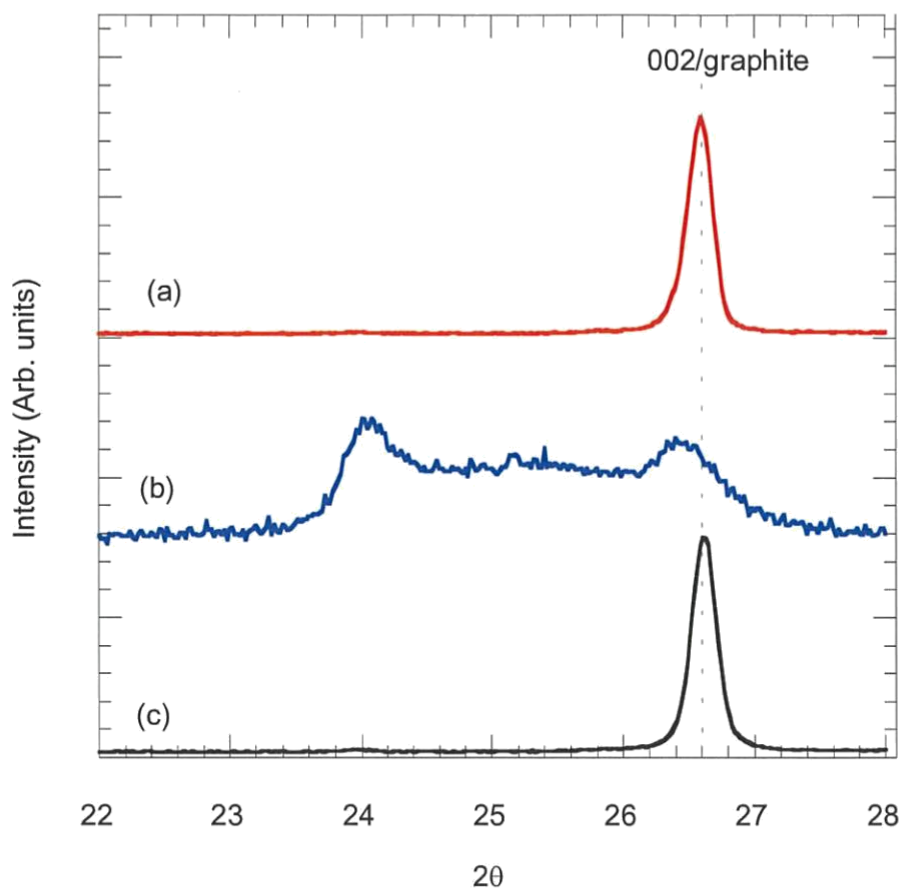


Figure 5. X-ray diffractograms of graphite electrode after two cycle formation using various electrolytes, (a, red) 0.8M LiBOB in 1NM3, (b, blue) 1.0 M LiPF_6 in 1NM3, (c, black) 1.2 M LiPF_6 in EC/EMC 3/7.

Table 1: Element concentrations, (ratio %) calculated from XPS spectra of LiMn_2O_4 electrode and MAG graphite electrode with various electrolyte systems.

Electrode	Electrolyte	C 1s	O 1s	F 1s	Li 1s	Mn2p	B 1s	Si2p	P 2p
LiMn_2O_4	1NM3- LiBOB	56	20	22	-	2	-	-	-
	Cathode EC/EMC- LiPF6	55	18	25	-	2	-	-	-
MAG	1NM3- LiBOB	41	31	11	15	-	2	-	-
	Anode EC/EMC- LiPF6	51	18	18	12	-	-	-	1

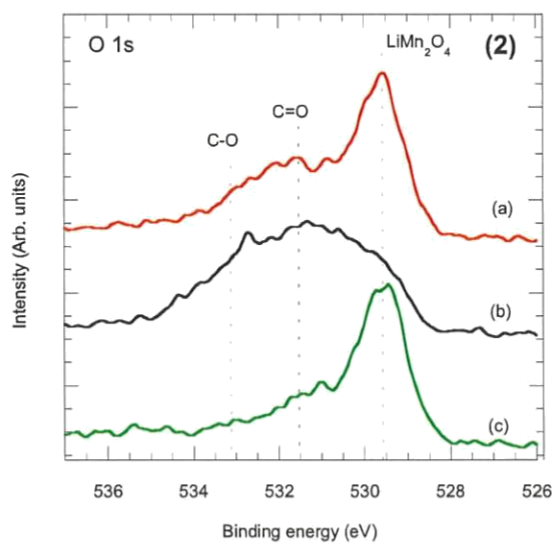
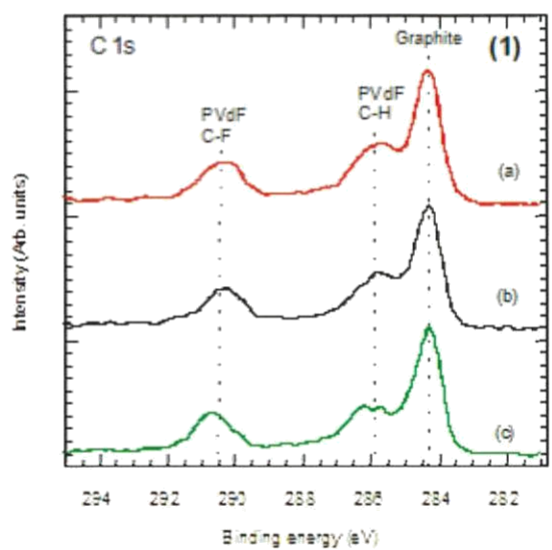


Figure 6. C 1s (1) and O 1s (2) XPS spectra of LiMn_2O_4 cathode electrodes after two cycle formation. (a) 0.8M LiBOB in 1NM3 electrolyte, (b) 1.2 M LiPF_6 in EC/EMC 3/7 electrolyte. (c) Pristine cathode.

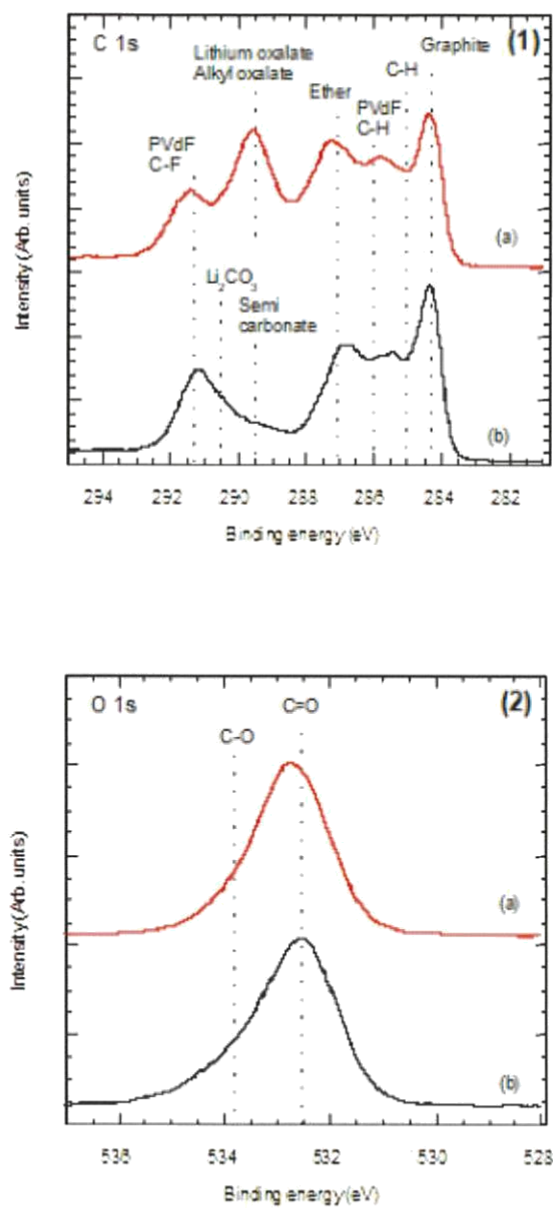


Figure 7.1. C 1s (1) and O 1s (2) XPS spectra of MAG graphite anode electrodes after two cycle formation. (a) 0.8M LiBOB in 1NM3 electrolyte, (b) 1.2 M LiPF₆ in EC/EMC 3/7 electrolyte.

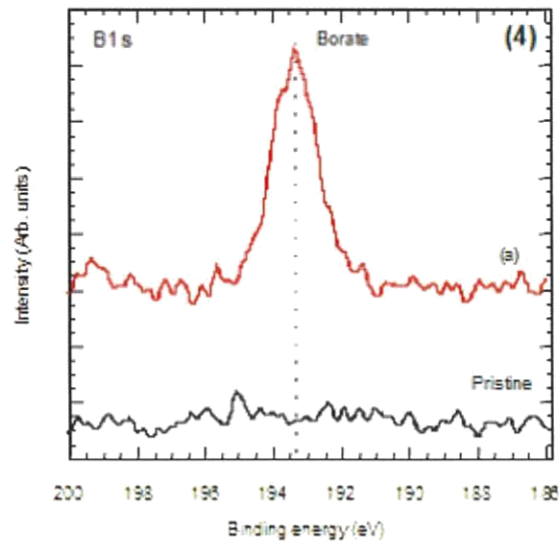
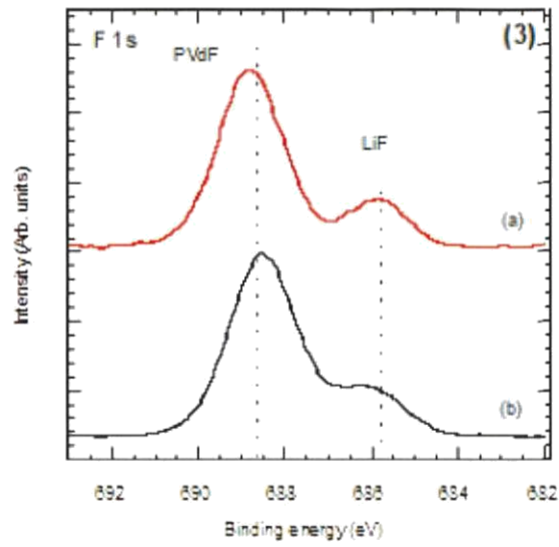


Figure 7.2. F 1s (3) and B 1s (4) XPS spectra of MAG graphite anode electrodes after two cycle formation. (a) 0.8M LiBOB in 1NM3 electrolyte, (b) 1.2 M LiPF₆ in EC/EMC 3/7 electrolyte.

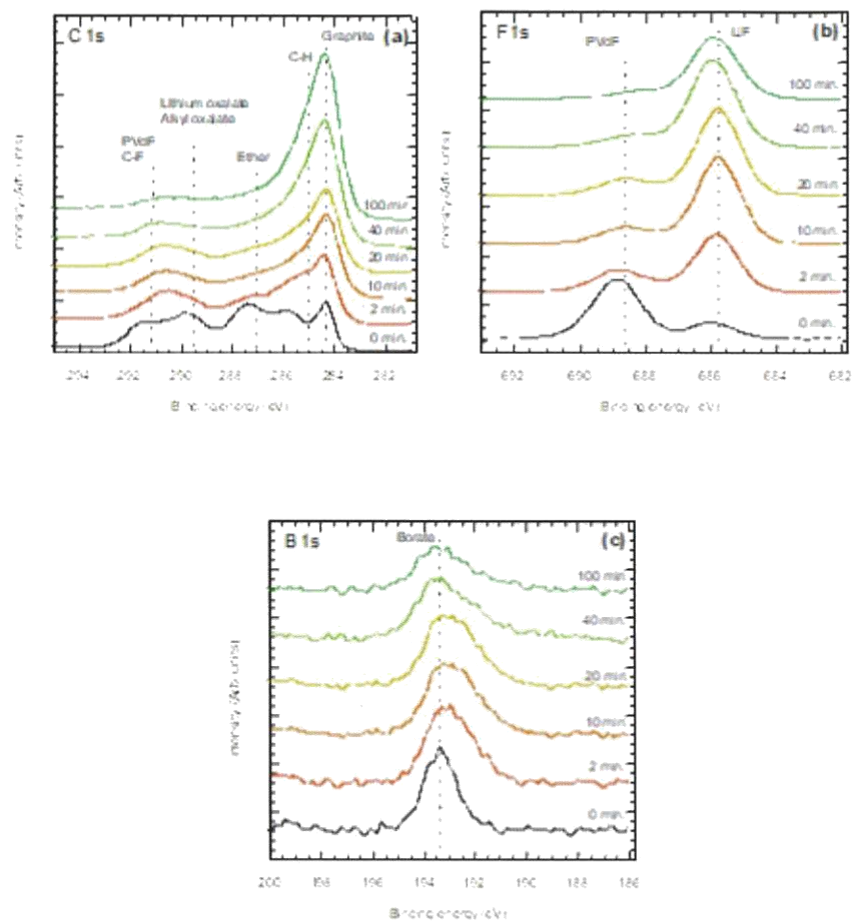


Figure 8. XPS spectra at different sputtering time from 0 min. to 100 min. for graphite anode using 0.8M LiBOB in 1NM3 electrolyte. (a) C 1s, (b) F 1s and (c) B 1s.

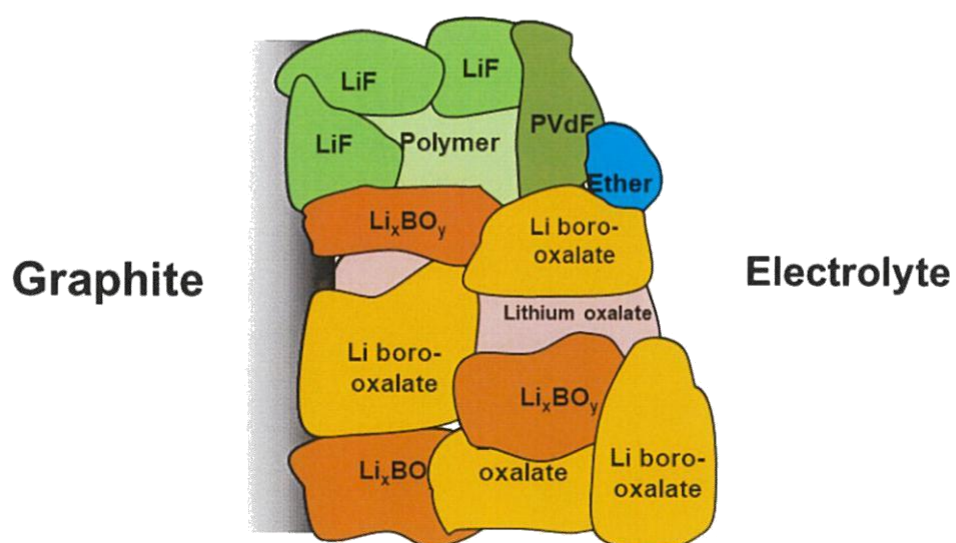


Figure 9. Schematic diagram of solid electrolyte interface on MAG graphite anode cycled with 0.8M LiBOB in 1NM3 electrolyte.

4. Tri(ethylene glycol) -substituted trimethylsilane / lithium bis(oxalate)borate electrolyte for LiMn_2O_4 / graphite system

4.1. introduction

Silane-based electrolyte is a promising candidate for safer electrochemical energy storage devices because it is thermally and electrochemically stable, less flammable and environmentally benign. In this paper, electrochemical properties of one of the silane-based electrolytes, tri(ethylene glycol)-substituted trimethylsilane (1NM3)–lithium bis(oxalate)borate (LiBOB) was studied using LiMn_2O_4 as a cathode and MAG graphite as an anode. When combined with LiBOB as lithium salt, the 1NM3–LiBOB electrolyte can provide solid electrolyte interface (SEI) formation due to the reductive decomposition of LiBOB at first charging cycle. Compared to the electrolyte used in the conventional lithium-ion batteries, 1NM3–LiBOB electrolyte showed compatible battery performance in LiMn_2O_4 /MAG chemistry. The AC impedance measurement indicates that the activation energy (E_a) obtained from the charge transfer impedance for 1NM3–LiBOB was higher than that of the state-of-the-art electrolyte. Due to its low conductivity, the rate capability of 1NM3–LiBOB electrolyte needs to be improved. The battery group at Argonne National Laboratory has undertaken tremendous efforts to enable the silane-based electrolyte towards the next

generation electrolyte for PHEV/EV applications. LiBOB was found to be suitable lithium salt for the silane electrolyte because it contains no labile fluorine and is thermally stable. It can also provide a passivation film on surface of the graphite anode.[12-16] We discussed our results of silane 1NM3/LiBOB-based electrolyte in Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM) cathode and graphite (MAG) anode lithium ion chemistry in chapter 2.[17] As a continuation of our silane electrolyte, here we report the performance of 1NM3–LiBOB electrolyte in LiMn₂O₄ cathode and graphite anode cell chemistry.

4.2. Experimental

LiBOB (99.87%) and ethylene carbonate (EC)/ethyl methyl carbonate (EMC) were purchased from Novolyte. 1.2 M LiPF₆ in 3/7 EC/EMC was purchased from Tomiyama Pure Chemical. All of purchased electrolyte chemicals were used as received. LiMn₂O₄ cathode and MAG anode electrodes were provided by EnerDel Inc. The cathode active material loading is 11.5 mg cm⁻² and balanced with the corresponding anode electrode. 1NM3 solvent was synthesized and analyzed according to our previously reported procedure.[17] ¹H, ¹³C NMR and FT-IR spectroscopy were employed to identify the structure of 1NM3 and its purity. Ionic conductivity measurement was performed using the YSI 3200 Conductivity Instrument equipped with a YSI 3253 conductivity cell.

The charge–discharge cycling performance was evaluated by an Arbin cycler

BT-2043. 2032 coin cells were assembled with LiMn_2O_4 as the cathode, MAG graphite as the anode, and a microporous polyethylene / polypropylene / polyethylene as the separator. The effective electrode area was 1.6 cm^2 . Electrodes were dried in a vacuum oven at 120°C for overnight before the cell assembling. A two-cycle formation step was applied prior to the cycling test at room temperature by C/5 rate. Performance data were acquired and analyzed by the software associated with the instrument.

AC impedance measurements were performed by Auto Lab electrochemical system. The impedance of full cell was measured by applying a sine wave of 10 mV rms over the frequency region of 1 MHz to 10 mHz in an environmental chamber. The impedance measurements were carried out at a fully charged state after four-cycle formation process at temperatures from -20 to 60°C in an environmental chamber. The impedance measurements at different initial charge state were carried out in the environmental chamber at 25°C . The cell was charged from an initial open circuit voltage (OCV) at a rate of C/20 for 15 min. After 20 min relaxation, OCV, and the impedance were measured, then the cell was charged for another 15 min and measured the OCV and impedance again. This process is repeated until cell voltage reaches 4.2 V. After that, the fully charged cell was stored at room temperature for 2 days, then discharge process was carried out, in the same manner, using constant current rate C/20 for 30 min. This discharge process was repeated until the cell voltage reaches 3.0 V. The lithium ion transference number was obtained using the combination of ac

impedance and dc polarization method described in Ref. [18] with lithium / electrolyte/lithium symmetry cells.

4.3. Result and discussion

4.3.1. Conductivity and transference number (t_{Li^+})

Silane solvent 1NM3 has a high boiling point and a low viscosity.[8] It can easily dissolve most of the lithium salts, such as LiBOB, lithium difluoro(oxalate)borate (LiDFOB), LiPF₆, LiBF₄, and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) to form the electrolytes. Among these, LiBOB was selected as a lithium salt due to its capability of forming a passivation film on the electrode. In this study, 0.8 M LiBOB in 1NM3 (1NM3–LiBOB) was investigated and its performance was compared with 1.2 M LiPF₆ EC/EMC (3/7) (EC/EMC–LiPF₆) as the reference electrolyte.

The ionic conductivities of the 1NM3–LiBOB and EC/EMC–LiPF₆ electrolytes as a function of temperature are shown in Table 1. The conductivity of 1NM3–LiBOB is higher than 1 mS cm⁻¹ at room temperature, and it is sufficient for the practical application for lithium-ion battery. The Li⁺ transference number was determined by the method proposed by Evans [19] and refined by Abraham [18], which is combining AC impedance test and DC polarization test on the same Li/Li symmetrical cell. In this test, following equation was used to calculate the lithium

transference number:

$$t_{\text{Li}^+} = \frac{I_s R_{es} (\Delta V - I_o R_l^o)}{I_o R_{eo} (\Delta V - I_s R_l^s)}$$

(1)

DC polarization voltage (ΔV) was applied 10 mV for 1 hour to obtain the initial current I_o and stable current I_s . The measurement of initial current I_o is well attuned to the switching noise, measurement time resolution and cell structure. After several tests, 100 ms after applying pulse was used as I_o and 2032 coin cell with 1.2 mm thick separator was used in this study. The bulk resistance, R_e and interfacial resistance, R_l were obtained from the AC impedance before and after dc polarization. A lithium ion transference number (t_{Li^+}) of 0.49 was obtained using this technique for 1NM3–LiBOB electrolyte, which is larger than that for EC/EMC–LiPF₆ electrolyte ($t_{\text{Li}^+} = 0.20$) and that for EC/EMC–LiBOB electrolyte ($t_{\text{Li}^+} = 0.30$). Higher lithium transference number of 1NM3–LiBOB is probably due to the smaller size of the solvated lithium cation–silane solvent complex.

4.3.2. First charge and discharge characteristics

Fig. 2 shows the first charge and discharge profiles of LiMn₂O₄/MAG cell charged from OCV to 4.2 V then discharged to 3.0 V with a constant current of C/10 at room temperature. In Fig. 2, 1NM3–LiBOB showed a small plateau at

early charge stage at around 2.2 V. The cell with 1NM3–LiBOB electrolyte delivered a discharge capacity of 0.85 mAh, which is lower than that for EC/EMC–LiPF₆. These characteristics are similar to the electrolyte comprising of carbonates and LiBOB.[12] In LiMn₂O₄/MAG cell, the voltage at 2.2 V corresponds to the anode potential at 1.7 V (Li/Li⁺) and it is consistent with the reduction potential of LiBOB at anode using carbonate solvents. Therefore even in the silane system, LiBOB decomposed at first charge process at 1.7 V (Li/Li⁺) forming solid electrolyte interphase on the graphite anode. The detailed characterization of this SEI layer formed by LiBOB in 1NM3–LiBOB electrolyte system will be described in chapter 3.

4.3.3. Cycling performance of 1NM3–LiBOB

Fig. 3 shows the cycling performance of LiMn₂O₄/MAG with 1NM3–LiBOB electrolyte. After the formation cycles, the cells were repeatedly charged and discharged with a current of C/5 rate between 3.0 and 4.2 V. Discharge capacity was normalized by the 2nd cycle discharge capacity. Fig. 3(a) is the room temperature cycling performance. It clearly shows that 1NM3–LiBOB electrolyte has a comparable property with the conventional EC/EMC–LiPF₆ electrolyte.

It was reported that LiMn₂O₄ suffers from the serious capacity fading in the lithium-ion cells due to Mn²⁺ dissolution in LiPF₆ based conventional electrolyte especially at high temperature.[20] To overcome this issue, LiBOB as a lithium

salt was investigated in carbonate electrolytes.[3] Silane electrolyte using LiBOB as salt may provide advantages over the conventional electrolyte due to its low polarity. Fig. 3(b) illustrates the cycling performance at 55 °C of the cell with EC/EMC–LiPF₆ showed significant capacity decay (54% capacity loss) at 60 cycles, while the cell using 1NM3–LiBOB still maintained high capacity retention (60% of the initial discharge capacity) at the same cycle number. The improved cell performance using 1NM3–LiBOB electrolyte is considered to be the lower solubility of the high oxidation state of Mn ions in 1NM3–LiBOB and absence of the HF generated by LiPF₆ with trace moisture in the conventional LiPF₆ based electrolyte. From this test, it is demonstrated that 1NM3 solvent is acceptable in LiMn₂O₄/MAG cell with LiBOB as a salt even at elevated temperature. However, the cell with 1NM3–LiBOB electrolyte showed fast capacity fade after 60 cycles at 55 °C. This phenomenon is not yet well understood.

4.3.4. Rate capability

The rate capabilities of 1NM3–LiBOB electrolyte were evaluated by charging a LiMn₂O₄/MAG cell with a constant current equivalent to C/10 to 4.2 V, followed by a constant voltage charge until the cutoff current equivalent to C/20. The cell was then discharged to 3.0 V at constant currents of C/5, C/2, 1C, 2C, and 3C. As shown in Fig. 4(a), the LiMn₂O₄/MAG cell using EC/EMC–LiPF₆ as the electrolyte can deliver more than 90% capacity retention at the C/2, 1C, 2C, and

3C rates. The $\text{LiMn}_2\text{O}_4/\text{MAG}$ cell using 1NM3–LiBOB as the electrolyte (Fig. 4(b)) showed more than 90% and 70% capacity retention at the C/2 and 1C rates, respectively. However, when discharged at the 2C rate, the 1NM3–LiBOB electrolyte cell only showed less than 40% capacity. The resistance calculated from the voltage drop within 1 s after the discharge showed 21 Ω and 149 Ω for EC/EMC–LiPF₆ and 1NM3–LiBOB, respectively. The severe capacity fading of 1NM3–LiBOB at a high rate should be attributed to the lower conductivity of electrolyte and the resistive SEI formed by the decomposition of LiBOB on the graphite anode surface.[21-23]

4.3.5. Electrochemical impedance spectroscopy of 1NM3–LiBOB

The ac impedance measurements of $\text{LiMn}_2\text{O}_4/\text{MAG}$ cell using EC/EMC–LiPF₆ electrolyte and 1NM3–LiBOB electrolyte was measured at 4.2 V fully charge state (Fig. 5). Two cells using different electrolytes showed two semicircles on Nyquist plots. The semicircle in the middle frequency (1 kHz to 1 Hz) showed a significant difference where the cell using 1NM3–LiBOB electrolyte showed larger impedance. It has been widely accepted that middle-frequency region is assigned to interfacial film on the electrode, and low-frequency region is assigned to charge transfer and solvation–desolvation process.[24-26] However, these data need to be assigned carefully due to the complex of impedances with cathode–

electrolyte interface and anode-electrolyte interface, impedance data were fitted to a common equivalent circuit model as shown in Fig. 6. The middle frequency region semicircle resistance was assigned to R1 and low-frequency region semicircle resistance was assigned to R2. Fig. 7 summarizes the extracted parameters from the ac impedance results measured at temperatures from -20 to 60 °C. For simplicity, if one R value is 10 times larger than another R, the smaller R was neglected due to the large fitting error. At middle-frequency semicircle, resistance R1 using EC/EMC-LiPF6 was independent with temperature. In contrast, R1 using 1NM3-LiBOB showed large temperature dependence and it follows Arrhenius relation with activation energy E_a of 32.4 kJ mol⁻¹. At low-frequency semicircle, R2 for 1NM3-LiBOB cell showed 25–50 times larger than that using EC/EMC-LiPF6 in the measurement temperature range. This huge resistance of R2 for 1NM3-LiBOB electrolyte may be due to the thick SEI formed by LiBOB decomposition. Activation energies of 63.9 kJ mol⁻¹ and 77.9 kJ mol⁻¹ were obtained for EC/EMC-LiPF6 and 1NM3-LiBOB, respectively. A typical activation energy of charge transfer resistance was reported in the range of 50–70 kJ mol⁻¹. [24-26] The activation energy value achieved for EC/EMC-LiPF6 in our test falls in this range. Therefore, it is rational to assign R2 as charge transfer impedance. However, for 1NM3-LiBOB system, it showed much larger E_a than the typical value. This large E_a could be related to the strong coordination of Li⁺ with oligo(ethylene glycol) group in 1NM3 molecular structure.

4.3.6. Impedance analysis of 1NM3–LiBOB during first cycle

As described above, $\text{LiMn}_2\text{O}_4/\text{MAG}$ cell using 1NM3–LiBOB electrolyte showed larger charging capacity, irreversible capacity, and impedance. To further understand the property of 1NM3–LiBOB electrolyte, ac impedances were measured during the first charge-discharge cycle. The cell was charged from an initial open circuit voltage (OCV) at a rate of C/20 for 15 min. After 20 min relaxation, the impedance was measured, then the cell was charged for another 15 min and measured the impedance again. This process is repeated until cell voltage reaches 4.2 V. After that, the fully charged cell was stored at room temperature for 2 days, then discharge process was carried out, in the same manner, using constant current rate C/20 for every 30 min until the cell voltage reaches 3.0 V. As shown in Fig. 8(a), large overpotential was observed during the charging plateau starting at 2 V due to LiBOB decomposition reaction. In order to extract the resistance parameter, AC impedance data during the first cycle was adapted to the model circuit shown in Fig. 6. The ohmic resistance, R_e was extracted from x-axis intercept on Nyquist plot. Then other parameters were extracted from the curve fitting. Fig. 8(b)–(d) shows resistance variation during the first cycle. It is clear that the ohmic resistance R_e was linearly increased with LiBOB decomposition extent at 2.2 V. R_e reached the maximum value of $13.1\ \Omega$ which is 50% larger than the initial resistance (Fig. 8(b)). In our previous paper [17],

we have reported the cell with 0.8 M LiBOB in 1NM3 electrolyte shows less capacity and cycling stability than that of 1.2 M LiBOB in 1NM3 electrolyte, which is inconsistent with their room temperature ionic conductivities since higher conductivity electrolyte facilitates ion transport during the charge-discharge cycle in lithium-ion battery. Both results indicate that LiBOB decomposition during the 1st charge process will lead to the reduction of LiBOB concentration. As a result, the 1NM3–LiBOB electrolyte was not able to maintain sufficient salt concentration after the formation of the passivation film during the first cycle. Compared with R_e at 2.2 V plateau, ohmic resistance R_e gradually became smaller. We ascribed this phenomenon to the excess electrolyte inside dead volume of coin cell. The excess electrolyte will diffuse to the active electrode pores, resulting to the ohmic resistance decrease. In contrast, after LiBOB decomposition, the middle frequency range resistance R_1 showed relatively stable and low-frequency range resistance R_2 decreased and stabilized gradually. This suggests the LiBOB decomposition at 2.2 V plays an important role for the interfacial impedance during the first charging. The subsequent electrochemical process does not affect too much on the electrode/electrolyte interfacial impedance. However, when stored at fully charged state for 2 days at room temperature, both R_1 and R_2 showed a significant increase as shown from Fig. 8 (c for R_1 , d for R_2), indicating that LiBOB continually decomposes forming a thick SEI at fully charged state after primary SEI formation during the first charge.

4.4. Conclusions

The tri(ethylene glycol)-substituted trimethylsilane (1NM3)–LiBOB was evaluated as an electrolyte for LiMn_2O_4 cathode and MAG graphite anode system. This new electrolyte can enable the lithium-ion cell performance after the first formation cycle due to the SEI formation by LiBOB decomposition on the surface of the electrode. Excellent cycling performance was achieved both at room temperature and at 55 °C which is comparable with the state-of-the-art electrolyte. However, due to the less conductive 1NM3–LiBOB electrolyte and resistive SEI, the rate capability was not as good as that for conventional EC/EMC–LiPF₆ electrolyte. Electrochemical impedance studies were carried out to understand interfacial phenomena. It was found that activation energy obtained from charge transfer impedance was higher than that of EC/EMC–LiPF₆. It could be noted that 1NM3 solvent has slower kinetics due to the strong coordination with Li^+ . More impedance measurements during first charging process revealed SEI formation by LiBOB decomposition leading to the decrease of the electrolyte conductivity. Our results in this study suggest that 1NM3 is an appropriate solvent for lithium ion battery and other electrochemical systems.

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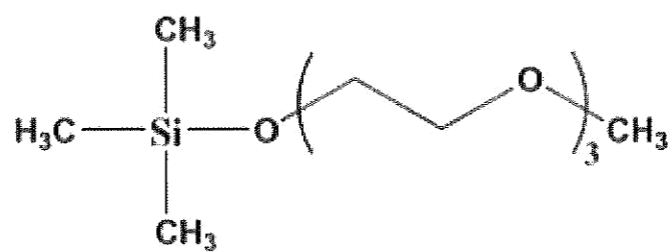


Figure 1. Molecular structure of tri(ethylene glycol)-substituted trimethylsilane (1NM3).

Table 1. Conductivities and lithium ion transference number for 1NM3 electrolyte and EC/EMC electrolyte.

Electrolyte	σ at $-20\text{ }^{\circ}\text{C}$ mS cm $^{-1}$	σ at $25\text{ }^{\circ}\text{C}$ mS cm $^{-1}$	σ at $50\text{ }^{\circ}\text{C}$ mS cm $^{-1}$	t_{Li^+}
0.8 M LiBOB-1NM3	0.46	1.7	2.2	0.49
1.2 M LiPF $_6$ -EC/EMC	2.2	8.1	12	0.20
0.8 M LiBOB-EC/EMC	–	–	–	0.30

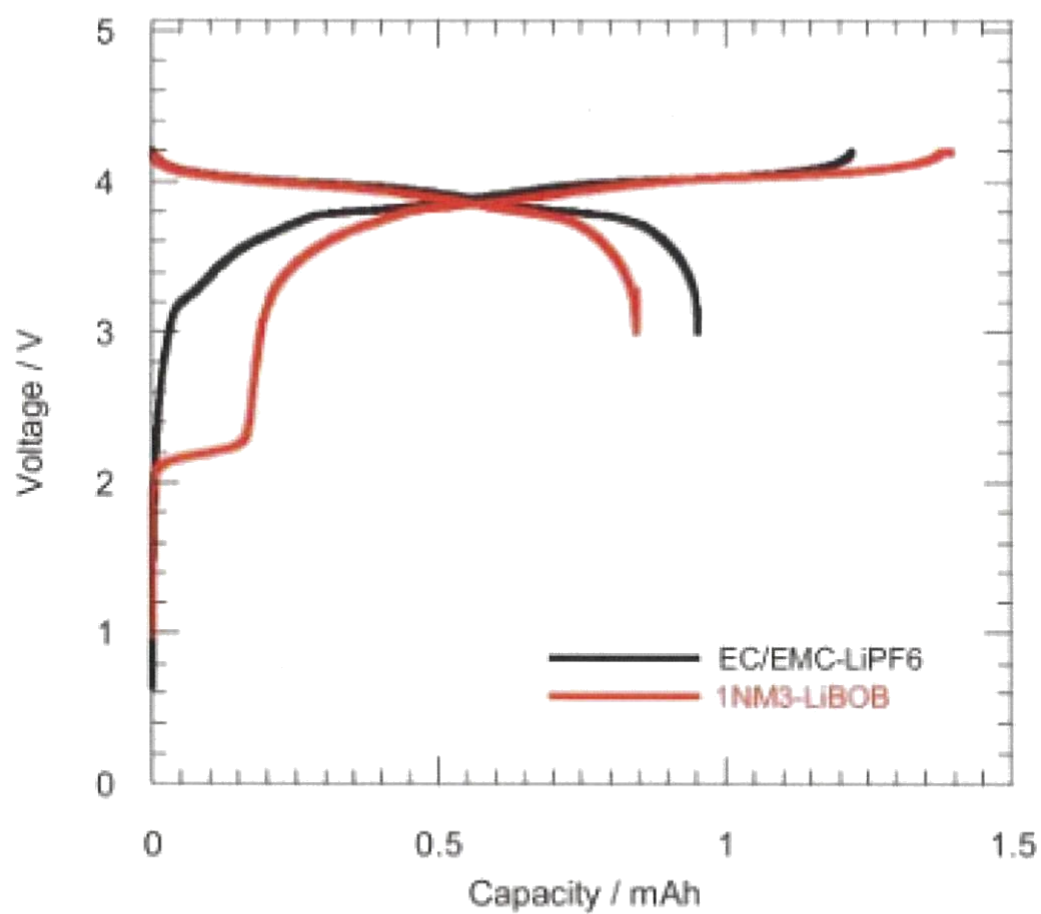


Figure 2. First charge–discharge profile of graphite/LiMn₂O₄ cell using 0.8 M LiBOB in 1NM3 and 1.2 M LiPF₆ in EC/EMC 3/7.

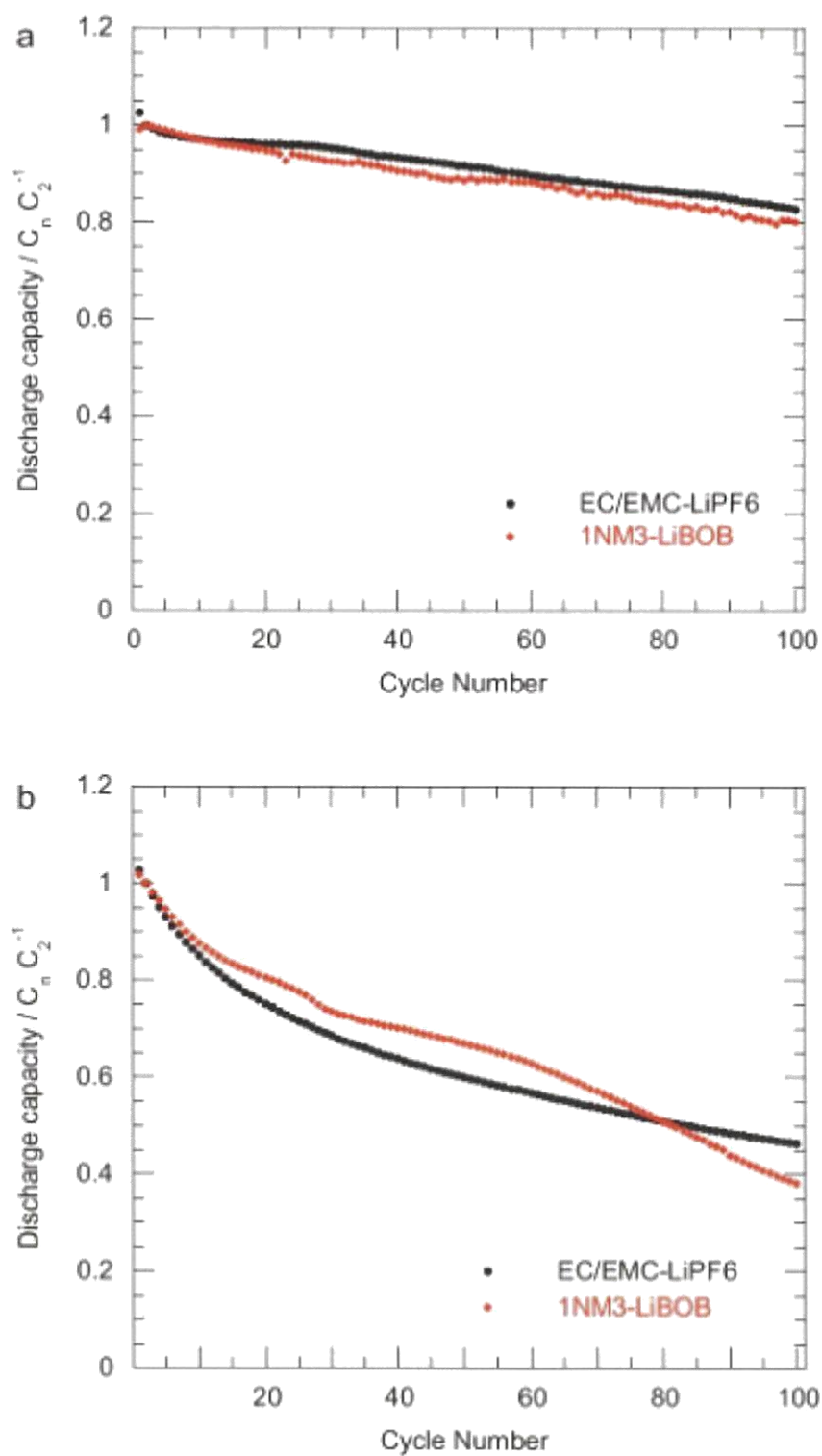


Figure 3. Cycling performance of graphite/LiMn₂O₄ cell using 0.8 M LiBOB in 1NM3 and 1.2 M LiPF₆ in EC/EMC 3/7: (a) 25 °C and (b) 55 °C.

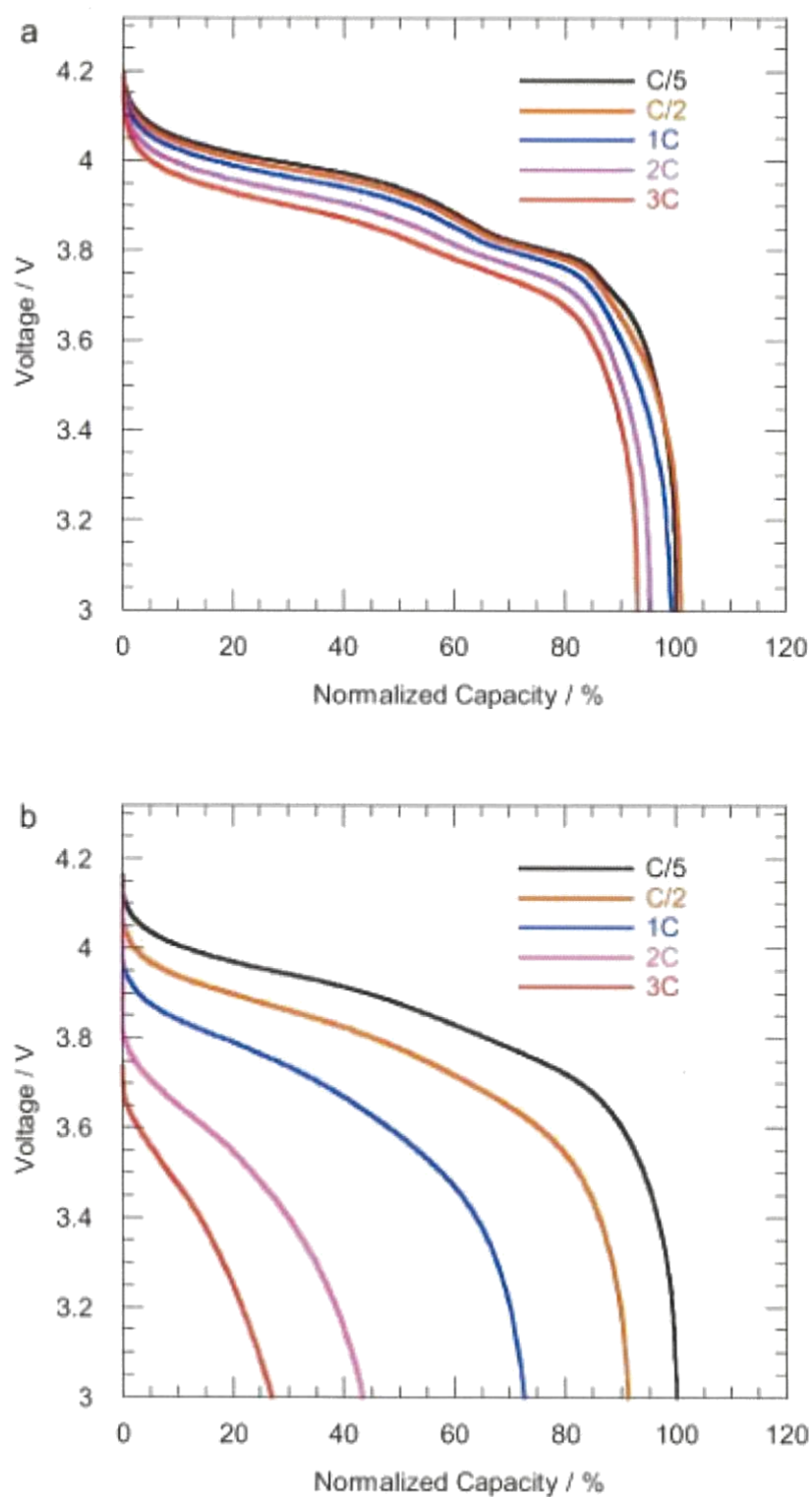


Figure 4. Discharge rate capability of graphite/LiMn₂O₄ cell with C/5, C/2, 1C, 2C and 3C rate: (a) 1.2 M LiPF₆ in EC/EMC 3/7 and (b) 0.8 M LiBOB in 1NM3.

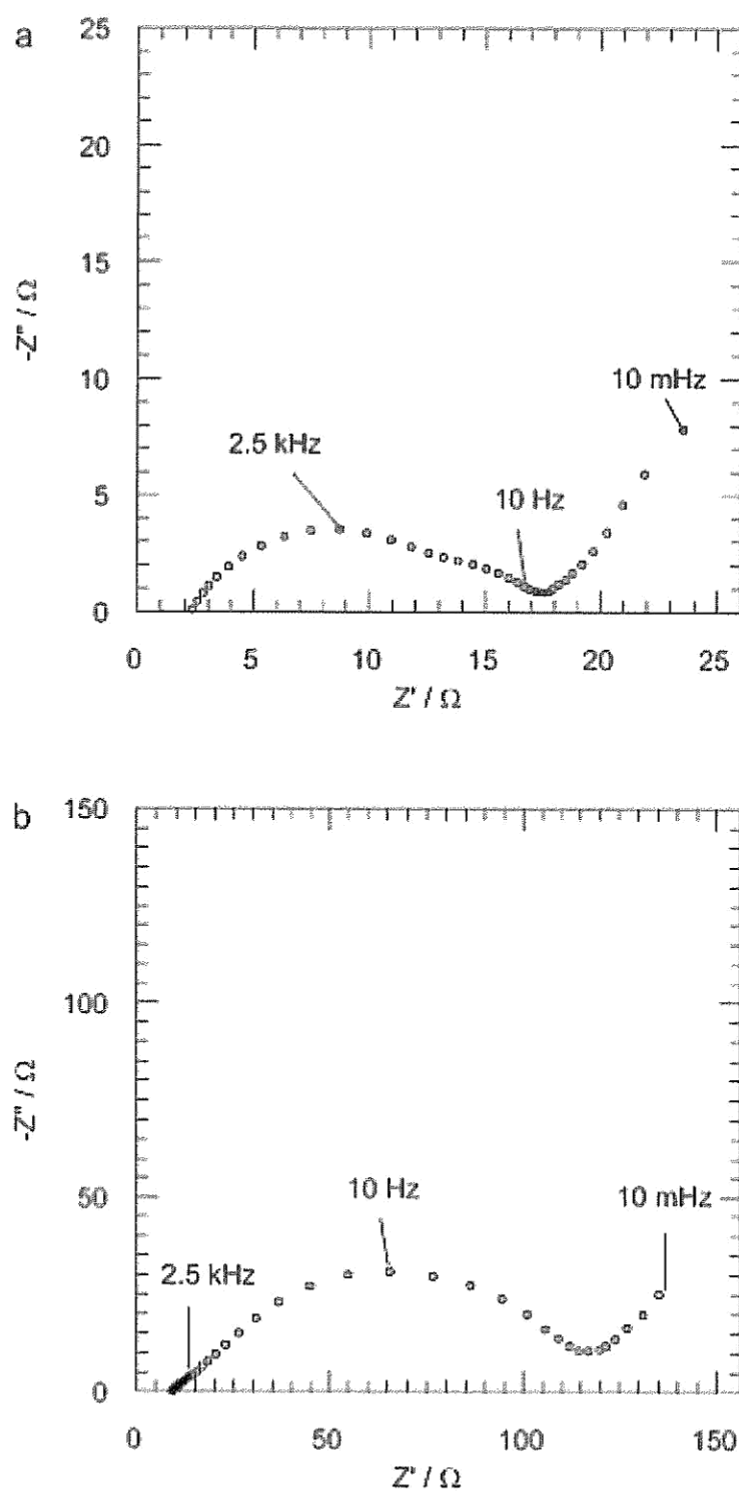


Figure 5. Nyquist plots of graphite/LiMn₂O₄ cells at 30 °C: (a) 1.2 M LiPF₆ in EC/EMC 3/7 and (b) 0.8 M LiBOB in 1NM3.

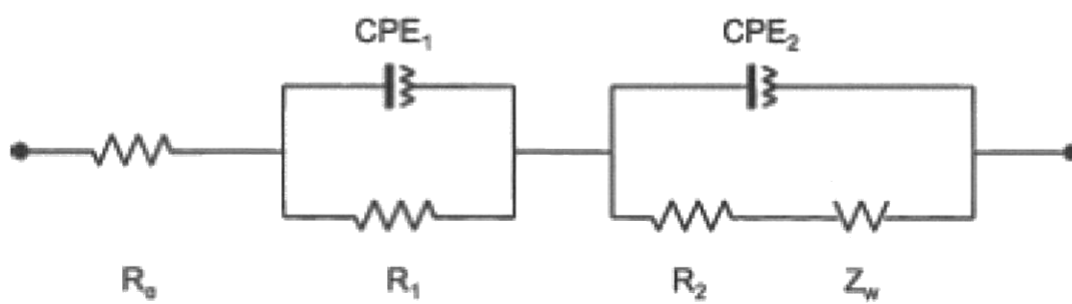


Figure 6. Circuit model of battery impedance adapted to parameter fitting.

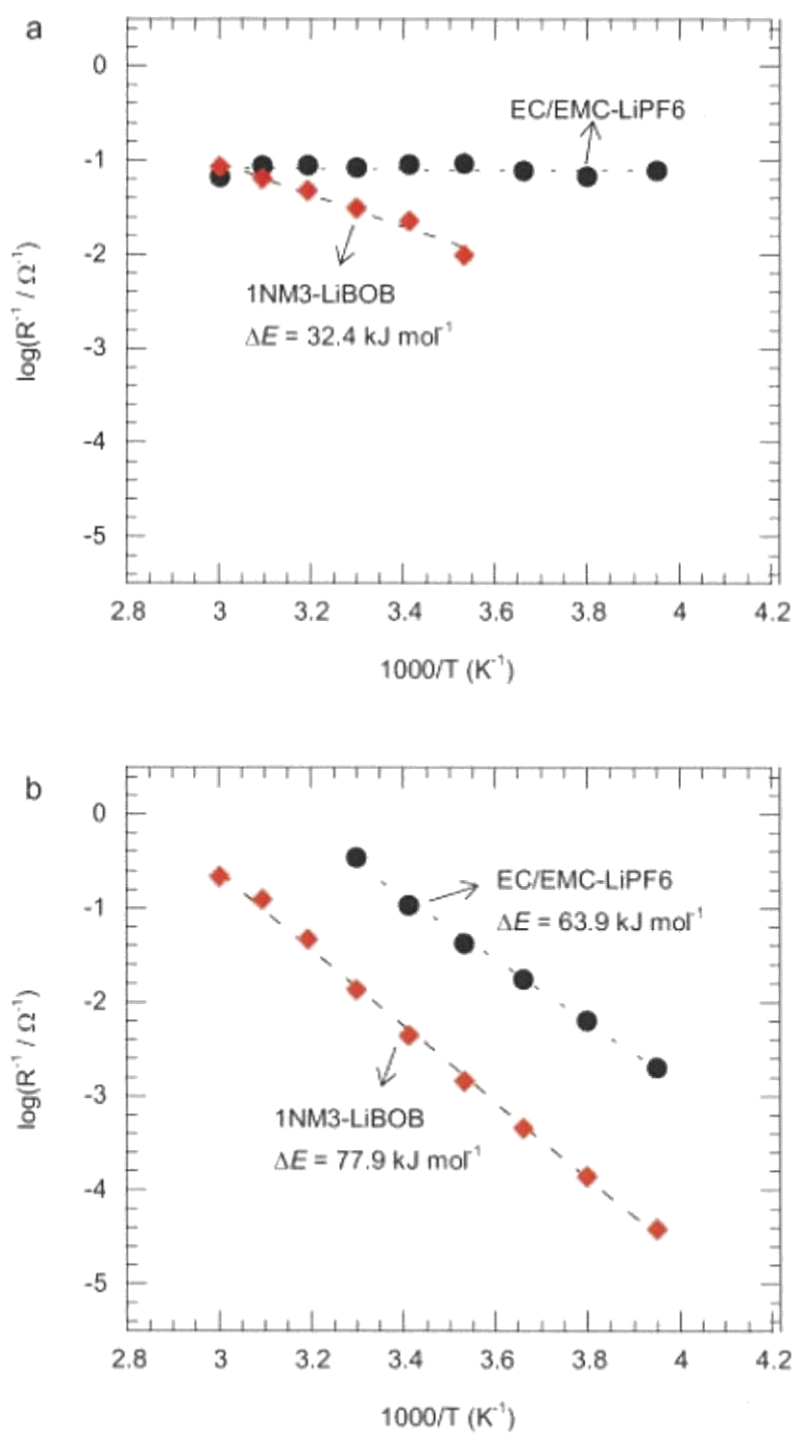


Figure 7. Cell ac impedance–temperature dependence at fully charged state: (a) R1 corresponding to middle-frequency range semicircle and (b) R2 corresponding to low-frequency range semicircle. The activation energy was obtained from the

slope.

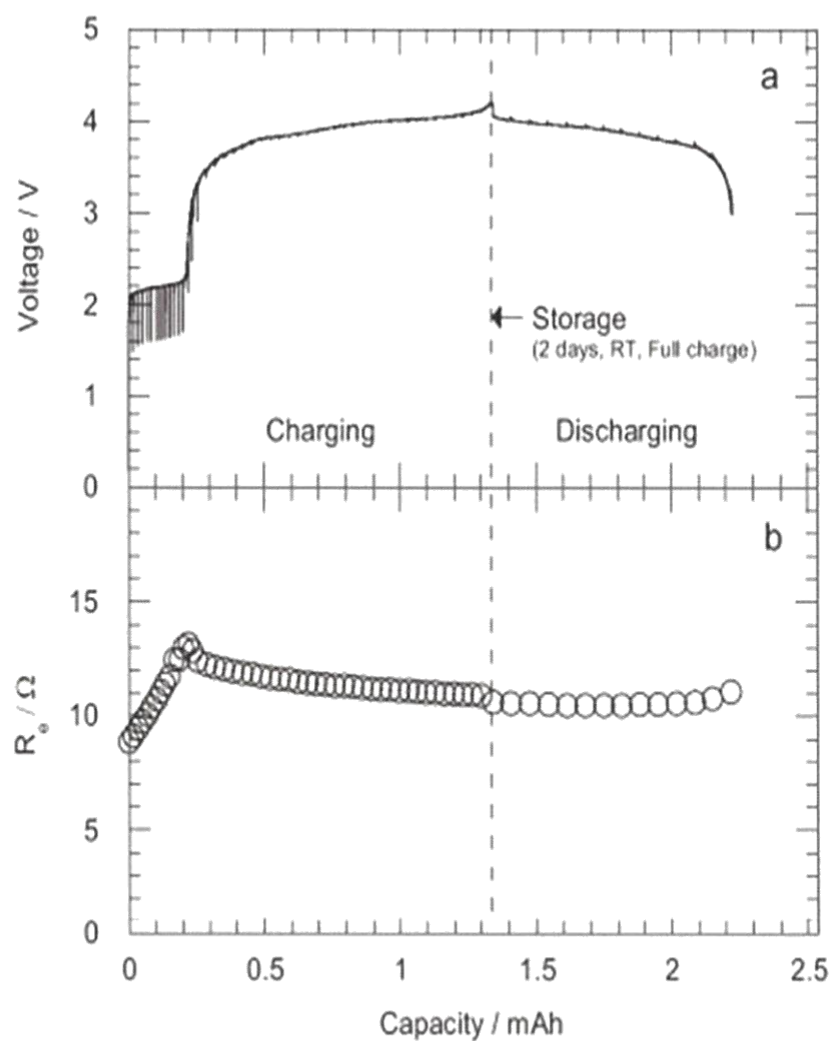


Figure 8.1. Cell impedance-charge state dependence of the graphite/0.8 M LiBOB in 1NM3/LiMn₂O₄ for the first cycle: (a) charge and discharge profiles of the cell with current interruptions, and (b) Ohmic resistance R_e .

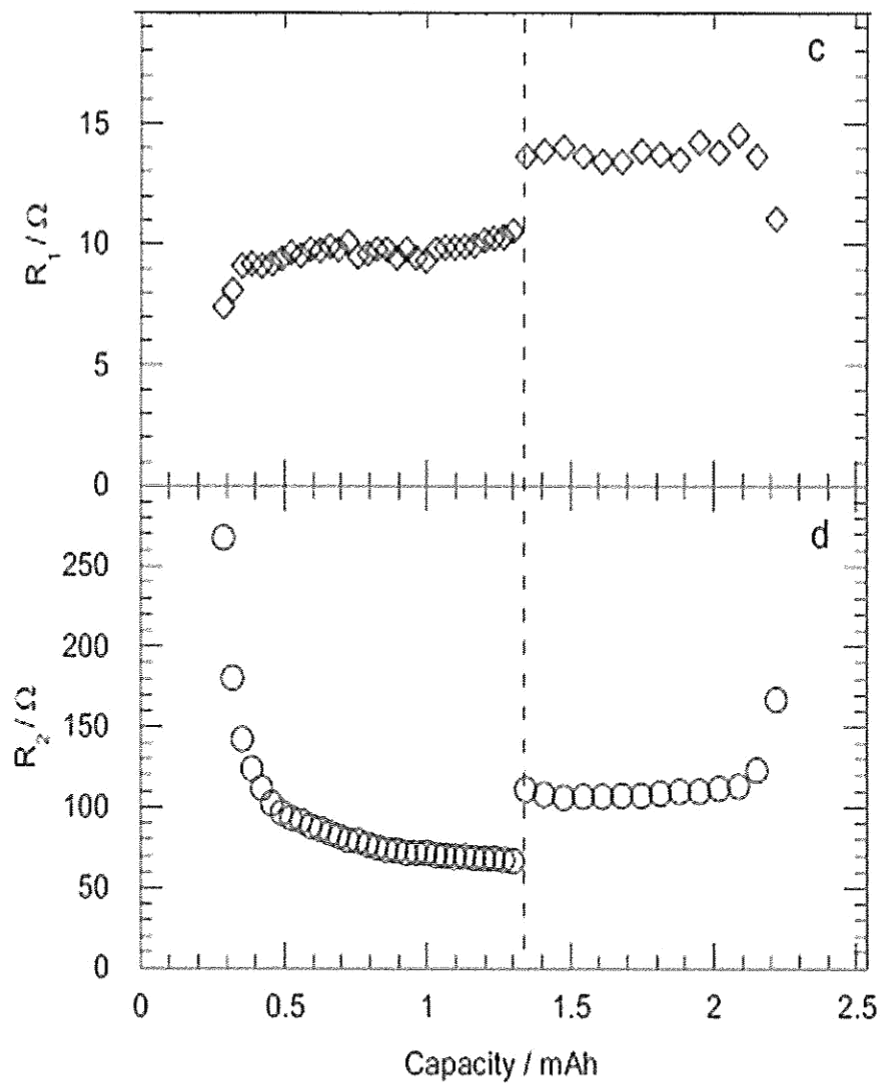


Figure 8.2. Cell impedance-charge state dependence of the graphite/0.8 M LiBOB in 1NM3/LiMn₂O₄ for the first cycle: (c) resistance corresponding to middle frequency range semicircle R_1 , and (d) resistance corresponding to low frequency range semicircle R_2 .

5. General Conclusion

As the world's energy demand increases, promoting the efficient use of energy has become an important and urgent issue on a global scale. In recent years, the cost of lithium ion secondary batteries having enough energy density and power density has been lowered, so lithium ion secondary batteries are adopted as a drive train power source for mobility applications, and electric vehicles are spreading worldwide. On the other hand, calendar life of lithium ion secondary batteries are still shorter than other electronic devices, and there is a risk of fire under abuse condition. As a result, much safer and longer-life lithium ion secondary battery is required.

As mentioned above, clarification and control of the electrode/electrolyte interfacial phenomena are necessary to improve the lithium-ion battery performance. The present thesis consists of five chapters, we elucidate the formation mechanism of electrode/electrolyte interface under thermally stable solvent, characterize composition of formed solid electrolyte interface and its contribution to improve battery performance.

In chapter 1, lithium ion batteries and the phenomena occurring within the batteries are described. Mainly, the interfacial phenomena between electrode and electrolyte are focused on. Since the interfacial phenomena largely influence the battery performance such as cyclability, investigation of

the phenomena is important for further improvement of the battery performance, especially under *in-situ* condition. The importance of controlling interfacial phenomena is also presented. On the basis of the general knowledge and previous reports, the importance of designing the interface is summarized (this chapter).

In chapter 2, Tri (ethylene glycol)-substituted trimethylsilane/ LiBOB electrolyte is prepared. Ion transportation in liquid electrolyte, optimize electrolyte formulation with various lithium salt, impact of lithium salt concentration and battery performance are discussed.

In chapter 3, Electrode surface film formed by the result of cycling with tri (ethylene glycol)-substituted trimethylsilane solvent is analyzed. We clearly pointed out that LiBOB salt act as major contributor to form electrode electrolyte interface film under this electrolyte system.

In chapter 4, It is investigated the formation steps of solid electrolyte interface with tri (ethylene glycol)-substituted trimethylsilane solvent. Changing of the solid electrolyte interface electrochemical behavior is discussed.

In chapter 5, Conclusion obtained from the present studies.

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