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Functional Electrolytes for Advanced Lithium Ion Batteries

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Functional Electrolytes for Advanced Lithium Ion Batteries

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A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Energy Science & Engineering. The study was conducted in accordance with Code of Research Ethics.

05. 30. 2018

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Functional Electrolytes for Advanced Lithium Ion Batteries

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ABSTRACT

Despite two decades of commercial history, enhanced lithium-ion batteries (LIBs) performance is required to satisfy the evolving electric vehicles (EVs) and energy storage system (ESS) market requirements which is essential for thermal stability, long-term cycle, safety, and fast charging. Here, we resolve these challenges using a mussel-inspired polydopamine (PD)-coating, novel additives, and analysis of superconcentrated electrolyte systems.

(1) it remains very difficult to simultaneously achieve both high rate capability and thermal stability in the graphite anodes of Li-ion batteries because the stable solid electrolyte interphase (SEI) layer, which is essential for thermal stability, impedes facile Li⁺ ion transport at the interface. The nanometer-thick PD coating layer allows the formation of a SEI layer on the coating surface without perturbing the intrinsic properties of the SEI layer of the graphite anodes. PD-coated graphite exhibits far better performances in cycling test at 60 °C and storage test at 90 °C than bare graphite. The PD-coated graphite also displays superior rate capability during both lithiation and delithiation. The usefulness of the proposed PD coating can be expanded to various electrodes in rechargeable batteries that suffer from poor thermal stability and interfacial kinetics.

(2) Next study introduces 3-fluoro-1,3-propane sultone (FPS) as a novel SEI additive to replace VC and another popular SEI additive, 1,3-propane sultone (PS). Vinylene carbonate (VC) has been the best performing solid electrolyte interphase (SEI) additive for the current lithium-ion batteries (LIBs). However, it is also true that the current LIB technology is being stagnated by the limit set by VC. Electrochemical experiments confirm that the presence of an electron withdrawing fluorine group is favourable in terms of the anodic stability and the SEI forming ability. Considering the high anodic stability, the excellent cyclability, and the good thermal stability, FPS is an outstanding SEI additive that can expand the performance boundary of the current LIBs.

(3) The swelling issue by gas evolution at elevated temperatures (85-90 °C) is one of the major challenges related to current Li-ion batteries (LIBs). We herein demonstrate that iodine (I₂) as a redox shuttle additive, when its dose is properly determined, can suppress the swelling behavior of LiCoO₂/graphite Al-pouch cells during storage at 90 °C without sacrificing other cell performances.

(4) Among the numerous additives, it remains very difficult to simultaneously adapt both spinel and layered cathode materials of Li-ion batteries. This study introduces a highly versatile new additive, sodium phosphate (P₂), as a novel LIBs additive to improve the thermal stability in both spinel (LiMn₂O₄ and LiNi₀.₅Mn₁.₅O₄) and layered (LiNi₀.₃Co₀.₁Mn₀.₆O₂) cathode materials. Our investigation reveals that P₂ additive scavenges harmful hydrofluoric acid (HF), effectively eliminates HF promoting metal dissolution from the
cathodes, and forms a passivation layer on the cathode surface against electrolyte decomposition at high temperature. Considering the good thermal stability and the storage performance at high temperature, P2 additive is an outstanding additive that can be expand to regardless of the type of LIBs that suffer from poor thermal stability.

(5) Lastly, the superior rate capability of the superconcentrated LiFSI/AN electrolytes, claimed in recent reports, is scrutinized in relation to the active mass loading of the graphite electrodes. Compared to a conventional carbonate electrolyte, a superconcentrated (4.5 M) LiFSI/AN electrolyte exhibits enhanced rate capability in a low-loading (< 5 mg/cm²) graphite electrode. However, the superconcentrated electrolyte displays an inferior rate performance in a high-loading electrode (9 mg/cm²), which is commonly employed in commercial electrodes. The electrochemical impedance study reveals that the superconcentrated electrolyte enables the lower charge transfer resistance at the graphite/electrolyte interface (R_{ct}), which is possibly associated with an unique solution structure in the concentrated electrolyte. However, as the graphite loading increases, the ion transport in the electrode pore (R_{ion}) becomes dominant, which dilutes the merit of the low R_{ct} in a superconcentrated electrolyte. This study indicates that the superior rate capability in superconcentrated solutions claimed in previous studies should be appreciated in conjunction with the electrode loading.

Keywords: Li-ion batteries, stability, fast charging, polydopamine, additives, superconcentrated electrolytes
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I. INTRODUCTION

The development of information technology (IT) and the spread of various portable information and communication devices are developing into a ‘ubiquitous society’ that can provide high-quality information services regardless of time and place. Lithium-ion batteries (LIBs) commercialized in the early 1990s are very important for the development of this ubiquitous society. LIBs have a higher operating voltages and energy densities than other secondary batteries and have the advantage of being able to be used for a long time.

Conventional LIBs are mainly used in portable electronic IT devices such as small electronic devices, communication devices, computers, entertainment devices, toys and game machines. These high energy densities are common in battery performance in mobile applications because their usage time is the most important element in a mobile environment. However, in recent years, application to devices requiring performance of batteries different from high energy density has been expanded. An example of this is the application to the transportation sector, including electric vehicles (EVs). In addition, although market dominance is not as high as that of mobile and transportation applications, there are energy storage devices where LIBs are expected to grow. These applications require high energy density, safety, fast charging and long-term cycle life.

In this study, I introduce to solve the challenges for advanced LIBs mentioned above by researching novel additives, new electrode coating, and super-concentrated electrolyte.

(1) Current Li-ion batteries (LIBs) heavily depend on graphite for anodes because they provide conspicuous advantages, including high specific capacity, low-cost, and have been widely studied and understood.\(^{[1,2]}\) Nonetheless, further development of the graphite anodes is necessary, to improve their thermal stability and high-power capability.\(^{[1,4]}\) However, these two properties have been very challenging to achieve simultane-
ously due to their contradictory nature: while a highly resistive solid electrolyte interphase (SEI) layer is preferred to suppress unwanted thermal degradation at the anode/electrolyte interface, this surface layer can, in turn, increase the interfacial resistance, and thus impair rapid Li⁺ transport.[5,6]

We herein report PD-coating for graphite anodes (hereafter PD-graphite) in LIBs.[7] The PD coating layer allows facile charge transfer at the interface while ensuring the stability of the SEI layer at elevated temperatures, effectively snaring the two challenging rabbits of graphite anode operation: rate capability and thermal stability.

(2) Employing functional electrolyte additives is a very promising way to improve the long-term stability of LIBs. Among the functional additives, vinylene carbonate (VC) is the most successful one for the current LIBs.[8,9] VC forms a stable solid electrolyte interphase (SEI) layer on the anode surface to bring substantial benefits in overall LIB performances.[10-13] However, a drawback of VC, which is due to its insufficient oxidation stability, has recently been highlighted: the remaining VC in the electrolyte decomposes at the cathode during elevated temperature storage.[14-17]

Besides VC, sulfur-based additives such as sulfites[18-23] and sultones[16,24-29] have long been studied as suitable SEI additives. The sulfur-based additives are also known to participate in the SEI formation and improve the thermal stability of LIBs.[16,18,20-29] None of them, however, has been reported to show superior cycle performances to VC so far.

In this study, we prepared 3-fluoro-1,3-propane sultone (FPS), a fluorine-substituted derivative of 1,3-propane sultone (PS), and compared the FPS as an SEI additive with PS and VC.[30]

(3) The swelling of LIBs is mainly ascribed to the irreversible gas-evolving reactions at both the cathode and anode interfaces.[31-39] It was reported that the gas evolution of LiCoO₂/graphite cells is dominated by the oxidative decomposition of the electrolyte at the cathode in the high potential region (> 4.0 V), while being governed by the reduction reaction at the anode in a low potential range (< 3.8 V). It was also claimed that the swelling is not significant when the state of charge (SOC) is low; instead, it dramatically increases as the SOC exceeds 80.[33]

We herein demonstrate that I₂ can serve as a versatile electrolyte additive to suppress the high-temperature swelling of 4 V LiCoO₂/graphite LIBs.[39] We propose that when a fully charged cell (SOC 100) is exposed to
a temperature of 90 °C, the self-discharge by I₂ is activated to lower the SOC of the cell, thus suppressing swelling in the cell.

(4) Current Li-ion batteries (LIBs) heavily depend on layered and spinel materials for cathodes because they provide conspicuous advantages, including high power and energy densities, and have been widely studied. Although LIBs have been successfully commercialized, a remarkable improvement in the energy densities of LIBs will be necessary to satisfy society’s needs for high energy density, for application such as electric vehicles (EVs) and grid storage. High energy density in a LIBs can be attained by increasing the reversible capacity of the electrodes, or by increasing the operating potential of the cathode. For example, in the case of commercially available spinel type LiMn₂O₄ (LMO), due to its superior electrochemical performance, low cost, and environmental inertness, LMO is considered a promising cathode material for LIBs. However, lithium hexafluorophosphate (LiPF₆)-based electrolytes are inevitably contaminated by a detrimental byproduct, hydrogen fluoride (HF), which causes fatal metal dissolution of cathode materials and unwanted side reactions on the anode materials. It is generally known that Mn dissolution is associated with a disproportionation which liberates soluble Mn²⁺ into electrolyte: Mn³⁺ (electrode) → Mn⁴⁺ (electrode) + Mn²⁺ (electrolyte). Then, the dissolved Mn²⁺ moves to the anode and exacerbates degradation of the anode/electrolyte interface, which is revealed to be a key failure mechanism of LMO-based LIBs at elevated temperature. Similarly, the spinel type LiNi₀.₅Mn₁.₅O₄ (LNMO) with high operating voltages (4.7 V vs. Li/Li⁺) suffer from Mn dissolution and the severe oxidative decomposition of electrolyte solutions beyond the upper voltage limit of LiPF₆-carbonate electrolyte, around 4.3 V vs. Li/Li⁺. As a result, large irreversible capacities are observed for the LNMO. In addition, increasing the cut-off voltage of LiNiₓCoₓMnₓO₂ (NCM) would catalyze the decomposition reaction of the electrolyte due to its high oxidizing activity, resulting in severe capacity fading of the battery.

We herein report sodium phosphate (hereafter P₂) additive, to scavenge fatal HF from electrolytes, and to eliminate severe electrolyte decomposition at high temperature. Furthermore, from an investigation of the surface chemistry on the SEI on various cathodes and anodes via X-ray photoelectron spectroscopy (XPS), we propose the possible mechanisms of effect of the P₂ additive, improving the thermal stability of LMO, LNMO,
and NCM cathodes in full- and symmetric-cells. In addition to, the P2 additive is expected to be universally applicable to many other LIB electrodes that similarly suffer from limitations in thermal stability.

(5) Recently, Yamada group reported superconcentrated acetonitrile (AN) solutions (> 4 M) as a promising for Li-ion battery (LIB) electrolytes exhibiting ultrafast-charging character, contrary to the general belief that AN electrolytes fail to operate Li metal anodes due to their poor reductive stability.\textsuperscript{[48]}

In this study, the claimed effects of superconcentrated AN electrolytes were scrutinized. First, the ionic conductivity and reductive stability against Li metal are examined. Second, the fast-charge capability of the super-saturated AN electrolytes are investigated in relation to the charge protocol and the active mass loading of the graphite electrodes. Finally, the effects of salt concentration on the anodic corrosion of Al and SUS are re-investigated.

References


Π. THEORY

2.1 Electrochemistry

The electrochemistry theory is excellently presented in the book “ELECTROCHEMICAL METHODS, Fundamentals and Applications” by Allen J. Bard and Larry R. Faulkner [1] and the handouts of the “Electrochemistry” course by Hochun Lee in DGIST. Here is a summary of the most important aspects of this paper.

2.1.1 Electromotive Force

The term electromotive force (EMF), was introduced to describe the force that the current flows through a conductor in a closed loop in the early 1800s. This can come from many sources, but for the scope of this paper only describes in terms of galvanic cells. In the case of galvanic cells, Faraday assumed that the chemical reactions taking place at the electrodes are the ‘seat of the EMF’, i.e. these reactions induce currents. The term is used to describe the cell potential, E, of a battery system. This is measured in volts (V) where the SI unit is Joule/Coulomb (J/C=[kgm²/s³A]). When the total reaction occurs in an electrochemical cell with negative \( \Delta G \) (\( -\Delta G \)), it is termed a galvanic cell and the corresponding EMF of that reaction would be;

\[
E = \frac{-\Delta G}{nF}
\]

(2.1)

where \( n \) is the charge transfer in a reaction and \( nF \) is the total charge, in C (coulomb), produced per M (mol).

2.1.2 Electrode Potential

A total reaction can be divided to at least two reactions in an electrochemical cell, one happening at the positive electrode (the cathode), and the other happening at the negative electrode (the anode). By convention, these reactions are used as reduction reactions and the corresponding electrode potentials are associated with each of these reactions. The electrode potential cannot be measured in absolute quantity, but is
always measured relative to a reference electrode, such as SHE (standard hydrogen electrode), the reaction of
\[ \text{H}^+/\frac{1}{2}\text{H}_2. \]
For example, for the potential of lithium we have the reaction
\[ \text{Li}^+ + e^- \rightarrow \text{Li}(s) \quad (2.2) \]
where the electrode potential (\(E\)) at standard conditions is \(-3.00\) V vs. SHE. When \(\text{Li}^+/\text{Li}\) itself is used as a reference in a Li-ion battery system, \(E\) of this reaction is \(0.0\) V.
For most reactions, standard electrode potential (\(E^0\)) has been defined. The actual electrode potential of a reaction usually differs from \(E^0\), and several factors influences the actual electrode potential, such as; concentration, solvent and temperature. These factors are summarized in the literature as activity (\(a\)) and the corresponding electrode potential is
\[ E = E^0 + \left(\frac{RT}{nF}\right) \ln \frac{a_O}{a_R} \quad (2.3) \]
where \(a_O\) and \(a_R\) denotes the activity of the oxidation and reduction, respectively.

The total EMF at zero current, also called the open circuit voltage (OCV) of a galvanic cell would then be
\[ E = E_a - E_c \quad (2.4) \]
where \(E_a\) and \(E_c\) denotes the electrode potential of the anode and the cathode, respectively. In this paper, the activity of a given specie will not be discussed, since only electrode potentials of systems are being investigated.

### 2.1.3 Energy Storage

The energy of a galvanic cell is operated by having two reactants separated by a media with low voltage and high voltage. The energy will be released after an electronic pathway is created between the reactants completing the circuit. Figure 2.1 shows a general overview of a galvanic cells (\(\Delta G_c < \Delta G_a\) and \(E_c > E_a\)).
The total cell potential of this cell is \(E=E_c - E_a\). The electrons are released through the external circuit as the chemical reaction of electrical work.
The total amount of charge that can be stored depends directly on the amount of electrode material in the battery.

### 2.2 Battery Theory

A battery generally refers to one or more electrochemical cells capable of storing chemical energy and releasing it as electrical energy. They are divided into two types (primary and secondary batteries). Primary batteries are commonly known as disposable batteries. It is based on irreversible electrochemical reactions and should be replaced after one discharge. These types of batteries include very common alkaline batteries and more speculative zinc/air batteries. However, secondary batteries are composed of reversible cells and are also referred to as rechargeable batteries. Common types of secondary batteries include lithium-ion, lead-acid, and nickel-metal hydride batteries.
2.4 Lithium Batteries

The normal operation of a lithium-ion batteries will be a good basis for the understanding of rechargeable batteries. Figure 2.2 shows a typical lithium-ion cell which contains three basic elements: the anode, the cathode and the electrolyte. In most modern batteries, a porous membrane is also present between the anode and the cathode to eliminate the possibility of electronic short-circuit, minimize the electrolyte usage and increase the structural integrity of the batteries. The anode and cathode are the negative and positive electrodes, respectively, meaning that upon discharge, electrons and cations w from the anode to the cathode. Connecting the electrodes to the complete circuit is what is collectively called current collectors.

![Figure 2.3 Schematic of a general Li-ion battery cell with cathode (ex. LiCoO₂), anode (ex. C₆) and electrolyte. The electrons in the external circuit is driven by a voltage source on charge and performs work on discharge. Adapted from the handouts of the “Electrochemistry” class.](image)

Li-ion batteries are a so-called structural or ion-transfer batteries, meaning that they have a structure that allows ions to enter and exit the electrode material in the process called intercalation. When the Li-ion
battery is charged, Li-ions are de-intercalated from the cathode, through the electrolyte and onto, or into, the anode. When the Li-ions flow out of the cathode, the cathode material itself must be oxidized to supply the charge. For example, for a LiCoO₂ cathode, one Co ion should be oxidized from +III to +IV for all Li ions leaving the structure. This occurs at an electrode potential of about 3.8 V (vs. Li). At the other end, in the anode, Li ions are reduced to Li atoms. When the anode is pure Li metal, it happens at the electrode potential of Li⁺/Li, 0 V (vs. Li). If a more commonly used graphite anode is used, the reduction occurs at a slightly higher potential than Li metal, around 0.1~0.3 V (vs. Li). The overall applied voltage should be higher than the combined voltage required to reduce Li ions and oxidize cathode material due to the overpotential. So for example, a standard cell with a LiCoO₂ cathode and a graphite anode has an approximate voltage of 0 V − 3.8 V = 3.8 V using the Equation 2.4. This voltage is influenced by various factors such as the electrolyte, the state of charge (SOC) and etc.

The last ion removed from the cathode requires much more energy than the initial ion and the oxidation voltage increases. Furthermore, as the graphite is more intercalated, the reduction potential of Li-ions in graphite drops towards the electrode potential of Li⁺/Li and further increases the total voltage.

2.4.1 Anode Materials

Anode material is the material that stores the reduced lithium atom. The performance of the electrode is affected by several factors: (1) the voltage to store lithium, (2) the kinetics of electron transfer, (3) the ability to store lithium, (4) the available surface area, and (5) the structural integrity of the material.

2.4.1.1 Metal

The most obvious choice for an anode of LIB system is pure Li metal. This is the densest material of the Li atoms and the reduction potential for Li⁺/Li is zero (0) V. There was a limit to the use of pure Li metal in consumer products. Li re-deposition is inherently difficult because the best electrolytes for a LIB create an SEI-layer on the electrodes. The redeposited Li has been shown to grow dendritic structures, which ultimately pose a risk of short-circuit and explosion.[3] This dendrite is created by the uneven re-deposition of the metal. During cycling, the elevated structure of the metal will have a higher current density than the lower...
part, so more metal will be deposited on the elevated structure. This is a self-reinforcing mechanism, that promotes the growth of the dendrites. The reactivity of dendrites in water and air is also very high and dangerous for use in consumer products.

2.4.1.2 Graphite

The most common anode material is carbon in the form of graphite. The average reduction potential for Li⁺ in graphite is 50–250 mV versus Li⁺/Li. This reduces the energy and power output by slightly reducing the overall battery voltage, but the cyclability and stability of graphite is much greater than the Li metal anodes that overcome the drawback of the voltage reduction. The charging of these materials is based on intercalation, which means that the material does not alloy with Li and stores only Li atoms between the graphene sheets. The fully lithiated graphite generally represented by the formula LiC₆, which stores one Li atom per six C atoms \((\text{Li}^+ + \text{C}_6 \rightarrow \text{LiC}_6)\), and the theoretical gravimetric capacity is 372 mAh/g.

2.4.2 Electrolytes

The electrolyte consists of two parts, a solvent and a Li-containing salt.

2.4.2.1 Salt

There are three main factors that determine the choice of salt; 1) the conductivity, 2) the chemical and thermal stability and, 3) the toxicity. To achieve high conductivity, it is important that the salt completely dissociates and dissolves, and that the solvated ions, especially the Li cations, have high mobility. Multiple electrolyte salts can be used in LIBs, among others, LiBF₄, LiClO₄, LiAsF₆, LiFSI, LiPF₆, and etc.

2.4.2.2 Solvent

Since Li and the Li salts have high reactivity to water, organic solvents should be used and several factors, such as salt, determines the choice of solvent. The primary selecting factor is that it needs to be polar to dissolve sufficient amounts of lithium salts, such as organic compounds with either carbonyl groups, nitrile groups, sulfonil groups or ether-linkages. In addition, it should exhibit high stability, both thermally and electrochemically, and as LIBs often operate at voltage differences of up to 4.5 V it requires a wide operating voltage. Finally, the composition of the solvent also determines the composition of the SEI layer.
Ethylene carbonate (EC) was used for the first time as a battery co-solvent by Elliot (1964) due to its low viscosity and high dielectric constant. Until the early 1970s, it was considered unusable for the purpose due to its high melting point (ca. 36 °C) when it was found that a co-solvent would lower the melting point and after Sony's initial launch of LIBs (1993), it was found that mixing EC with a linear carbonate would provide the required electrochemical and temperature window. Linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) have proved a good match and most batteries use a 1:1 or a 3:7 mixture of EC:linear carbonate as the solvent.

Table 2.1: Properties of commonly used solvents in LIBs. All data from the handouts of the “Electrochemistry” class.

<table>
<thead>
<tr>
<th></th>
<th>EC</th>
<th>DMC</th>
<th>EMC</th>
<th>DEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>88.07</td>
<td>90.08</td>
<td>104.11</td>
<td>118.13</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>244</td>
<td>90</td>
<td>107</td>
<td>126</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>39</td>
<td>0.5</td>
<td>-55</td>
<td>-74</td>
</tr>
<tr>
<td>Density</td>
<td>1.32</td>
<td>1.07</td>
<td>1.007</td>
<td>0.975</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>90</td>
<td>3.1</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>1.92 (40°C)</td>
<td>0.625 (20°C)</td>
<td>0.665 (25°C)</td>
<td>0.736 (25°C)</td>
</tr>
</tbody>
</table>

2.4.3 Solid Electrolyte Interphase (SEI)

Li metal anodes are known to react with both liquid and polymer electrolytes and are covered with a passive film that delays Li corrosion and decomposition of the electrolyte. This film is called solid electrolyte interphase (SEI) because it acts as an interface between the anode and the electrolyte. The SEI thickness is limited by the electron tunneling range because this film is electronically non-conductive and electrons are required for the decomposition and deposition of the SEI. The film is conductive for Li ions, but has a certain resistivity, so a very thick SEI layer can increase cell resistance. In a normal LIBs, the SEI layer is formed on the anode (Li or graphite) electrodes when Li ions is first applied to the anode during the first charge. The
chemistry of SEI layer formation is inherently complex and not well understood. The SEI composition is not fully understood but it generally consists of decomposed electrolyte, solvent and salt. Generally, the SEI layer contains LiPF₆, LiF, Li₂O, Li₂CO₃, (CH₂OCO₂Li)₂, and ROCO₂Li.[6]

2.4.4 Additives

Use of electrolyte additive is one of the most effective and economic methods for the improvement of Li-ion battery performance. Usually, the amount of an additive in the electrolyte is no more than 5% either by weight or by volume while its presence significantly improves the cycle life and rate performance of Li-ion batteries. For better LIBs performance the additives are able to: (1) facilitate formation of solid electrolyte interphase (SEI) on the surface of graphite. (2) reduce irreversible capacity and gas generation for the SEI formation and long-term cycling, (3) enhance thermal stability of LiPF₆ against the organic electrolyte solvents, (4) protect cathode material from dissolution, and (5) improve physical properties of the electrolyte such as ionic conductivity, viscosity, wettability to the polyolefin separator, and so forth. For better battery safety, the additives are able to: (1) lower flammability of organic electrolytes, (2) provide overcharge protection or increase overcharge tolerance, and (3) terminate battery operation in abuse conditions.

2.4.5 Cathode Materials

Cathodes in a secondary LIBs are so-called intercalation cathodes. The cathode material is a crystal structure containing lithium, which is one of the main components. The key factors for cathode materials are high ionic conductivity of Li, high electronic conductivity, favorable volume expansion at discharge, high energy density, and excess tension remaining in the structure when Li ions are removed from the structure. As you can see, the high ionic conductivity and electronic conductivity of the cathode are very important for the charging rate. For each Li ion de-intercalated in the structure, electrons must move from the cathode material to the current collector to complete the charge balance. This is significant because many of the best cathode materials are very poor electronic conductors. The electronic conductivity is increased by adding small amounts of electrical conductors, such as carbon black, to the cathode in most commercial LIBs. When Li ions are de-intercalated from the cathode material, the internal stress of the structure increases for two reasons. First, the residual ions must be oxidized to balance the charge and change the extent of the electron
orbitals of these ions. Second, the space previously occupied by a Li ion is now a defect, for which the structure itself must compensate for this.

**Figure 2.4** Voltage versus capacity for cathode- and anode-electrode materials presently used or under serious considerations for the next generation of rechargeable Li-based cells.[2]

### 2.6 References


Ⅲ. Mussel-Inspired Polydopamine-Coating for Enhanced Thermal Stability and Rate Performance of Graphite Anodes in Li-Ion Batteries

3.1 Introduction

Current Li-ion batteries (LIBs) heavily depend on crystalline graphitic carbon materials for anodes because they provide conspicuous advantages, including high specific capacity, low-cost, and have been widely studied and understood.[1,2] Nonetheless, to power emerging large-scale applications such as electric vehicles (EVs) and grid storage, further development of the graphite anodes is necessary, to improve their thermal stability and high-power capability.[3,4] However, these two properties have been very challenging to achieve simultaneously due to their contradictory nature: while a highly resistive solid electrolyte interphase (SEI) layer is preferred to suppress unwanted thermal degradation at the anode/electrolyte interface, this surface layer can, in turn, increase the interfacial resistance, and thus impair rapid Li+ transport.[5,6]

A common practice to enhance the thermal stability of graphite anodes is to employ functional electrolyte additives that give rise to robust SEI formation on the graphite surface.[7,8] For example, vinylene carbonate and succinic anhydride have been reported to greatly improve the long-term cycling and storage performances of graphite anodes at elevated temperatures.[7-9] However, the robust SEI layers derived from electrolyte additives inevitably hamper facile Li+ transport. Another well-known strategy to enhance thermal stability is to modify the graphite surface by coating with metal/metal oxides, polymers, or amorphous carbon.[10-12] Once uniformly coated over the graphite particles, the surface coating film (often referred to as an artificial SEI layer) can enhance thermal stability without sacrificing rate performance to a great extent.[13-15] In practice, however, fabricating a uniform coating is nontrivial for most solution-processes, making it very difficult to achieve both properties. Atomic layer deposition (ALD) has recently been introduced for surface coating of graphite anodes, taking advantage of its unique ability to control film thickness at the atomic scale.[16-18] Despite this delicate control over film thickness and homogeneity, however, the ALD process is generally slow and requires high cost. Hence, in general, solution-processes are more preferred for practical applications.
It is apparent that, to achieve high-power LIBs, the internal resistance involved in the electrochemical reactions needs to be minimized. Among several elementary processes related to Li$^+$ transport kinetics at the electrode/electrolyte interface, the desolvation process of the Li$^+$ ion has been identified as the rate determining step (RDS)\cite{7,19-23}. In detail, the desolvation process is comprised of the following serial steps: (i) partial desolvation, (ii) adion (partially desolvated Li$^+$ ion) formation on the electrode surface, (iii) surface diffusion of the adion, and (iv) loss of the remaining solvents. The last step is known as the actual RDS that accounts for the activation energy (Ea). Thus, a thorough understanding of the interactions among Li$^+$ ions, solvent molecules and the electrode surface would be useful in developing surface modifications to enhance the interfacial charge transport.

Recently, it has been reported that dopamine, a mussel-inspired wet-adhesion moiety bearing a catechol functional group, can be polymerized at mild basic pH to form an adhesive polymer film on a wide range of substrates\cite{24,25}. It is particularly notable that a polydopamine (PD)-coating layer can be controlled at the nanometer-scale using a simple dip-coating process. In fact, the unique wet adhesion and stability of PD and catechol group have been adopted for LIBs because their wet adhesion can be utilized in similar liquid environments. PD has been coated on polyolefin separators for enhanced power density and uniform Li$^+$ ion flux, and catechol groups were conjugated to alginate and polyacrylic acid binders to address the volume expansion issue of silicon anodes\cite{26-28}. However, to the best of our knowledge, a PD coating has never been applied to active materials of LIBs.

We herein report PD-coating for graphite anodes (hereafter PD-graphite) in LIBs. A series of spectroscopic and microscope characterizations indicate that the SEI layer formed on the PD coating layer is consistent in composition and properties with that on the bare graphite case. The PD coating layer allows facile charge transfer at the interface while ensuring the stability of the SEI layer at elevated temperatures, effectively snaring the two challenging rabbits of graphite anode operation: rate capability and thermal stability. The origin of the beneficial effects of the PD-coating can be explained by the Lewis basic character of PD, based on a surface free energy (SFE) analysis. In addition to graphite anodes, the PD coating is expected to be universally applicable to many other LIB electrodes that similarly suffer from limitations in rate performance and thermal stability.
3.2 Experimental

3.2.1 Chemicals and electrode preparation

Dopamine and tris-HCl buffer were purchased from Aldrich. Battery grade 1 M LiPF₆ ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1/2, v/v) was provided by LG Chem. The graphite electrode was fabricated on Cu foil (10 μm thick) using natural graphite (DAG, Sodiff) with polyvinylidene fluoride (PVdF) binder (3 wt%) and conductive carbon (2 wt%). The electrode density was adjusted to ca. 1.6 g cm⁻³ with two different loadings of graphite: 5.3±0.2 mg cm⁻² and 11.6±0.5 mg cm⁻² for medium- and high-loading electrodes, respectively. The one-step dipping process of polydopamine (PD)-coating was carried out following the previously reported method,[26] dopamine (2 mg/mL) was dissolved in tris buffer (10 mM, pH 8.5), and the graphite electrodes were dipped into the solution. The immersion time was 20 min unless otherwise mentioned. The PD-coated graphite electrodes were rinsed with deionized (DI)-water and dried in a vacuum oven (110 °C) for 24 h.

3.2.2 Surface analysis

The surface morphologies of the graphite anodes were examined using field emission scanning electron microscope (FE-SEM, NB 5000, Hitachi) equipped with cross sectional energy-dispersive spectrometer (EDS), and transmission electron microscopy (TEM, HF-3300, Hitachi). The surface compositions of the graphite anodes were examined using X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Scientific). For the depth profile analysis, fully delithiated graphite electrodes were collected from graphite/Li cells, and were rinsed in dimethyl carbonate (DMC) and dried inside a glove box (H₂O ≤ 5 ppm, O₂ ≤ 5 ppm, and temperature 25±1 °C). The sputtering rate was 7 nm min⁻¹ calibrated for SiO₂. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS 5-100, ION-TOF GmbH) was used to characterize the atomic composition of the PD layer.

3.2.3 Electrochemical measurements

For the battery tests, 2032-size coin cells were employed by integrating the same graphite electrode mentioned above and Li metal with a polyethylene separator (20 μm, Tonen). The SEI formation behavior was examined by differential capacity curve (dQ/dV vs. V) during the first lithiation process of the graphite/Li
coin cells at 0.1 C current. The cycle tests were carried out for graphite/graphite symmetric cells at 60 °C at 0.5 C between −0.5 V and +0.5 V. The graphite/graphite symmetric cells were fabricated by employing graphite electrodes with a state-of-charge (SOC) of 50 collected from graphite/Li cells that had been cycled three times over 1.5–0.005 V range at 0.5 C constant current (CC) charge (lithiation) followed by 0.005 V constant voltage (CV) charge, and 0.5 C CC discharge (delithiation). For the storage tests, fully charged graphite/Li cells were stored at 90 °C for 40 h. After storage, the cells were re-assembled using a new pair of Li counter electrode and separator to avoid any interference due to their thermal degradation. To assess thermal damage, the charge and discharge behaviors of the re-assembled cells were compared with those of the cells before storage. The discharge rate performance of the graphite/Li cells were examined at 0.2 C CC/CV charge and at various discharge rates from 0.2 C to 5 C. The charge rate capability was examined at 0.2 C CC discharge and at various charge rates from 0.2 C to 3 C. To quantify the charging performances, the ratio of CC charge capacity to total charge capacity was calculated. The battery charge/discharge tests were carried out using a battery cycler (Toscat-3000, Toyo System) equipped with temperature chambers. Electrochemical impedance spectroscopy (EIS) measurements were carried out for graphite/graphite symmetric cells over 15–35 °C with a VSP potentiostat (BioLogic) over a frequency range from 300 kHz to 10 mHz with an amplitude of 5 mV.

3.2.4 HF and H₂O contents measurements

The HF and water contents in the electrolytes were analyzed by acid-base titration methods (848 Titrino plus, Metrohm) and Karl Fisher (831 KF coulometer, Metrohm), respectively. Before the measurements, ten pieces of the graphite electrode (14 mm diameter) were stored at 60 °C for 4 days in a polytetrafluoroethylene (PTFE) bottle containing electrolyte (2 ml). To avoid possible interferences due to leakage during storage, the subsequent analysis was performed only when the weight change before and after the storage was negligible.

3.2.5 Surface free energy measurements

The contact angles of graphite electrodes were measured by the sessile drop method using a goniometer (DSA100, Krüss) at room temperature. All the graphite electrodes were dried in a vacuum oven (110 °C) for 24 h before measurements. The contact angles were measured using three probe liquids (diiodomethane,
formamide and deionized water), and three SFE components (Lifshitz-van der Waals, Lewis acid, and Lewis base) were determined based on the van Oss-Chaudhury-Good (vOCG) model.\(^{(29)}\)

### 3.3 Results and discussion

#### 3.3.1 PD-treatment of graphite electrodes

Polydopamine (PD)-coated graphite electrodes were prepared by a simple one-step immersion process of dipping the graphite electrodes into a dopamine solution (Figure 3.1). The self-polymerization of dopamine by alkaline pH-induced oxidation is known to generate a dihydroxyindole-type polymer, as displayed in Figure 3.1.

![Figure 3.1 Schematic illustration of polydopamine (PD)-coating onto composite graphite electrodes, together with a suggested PD structure resulting from alkaline pH-induced oxidation.](image)

The PD-coated graphite is hereafter denoted as PD-graphite. The formation of the PD layer is very difficult to visualize because of the dark color of the graphite host. Also, there is no discernible morphology change between SEM images of the pristine and PD-graphite electrodes (Figure 3.2), which is possibly due to the nanometer-scale thickness of the PD layer. Thus, energy-dispersive X-ray spectroscopy (EDS) was employed to detect the presence of the PD layer (Figure 3.3). The cross-sectional view clearly displays nitrogen (Figure 3.3b) and oxygen (Figure 3.3c) elements, which are a clear signature of the PD on the surface of graphite particles. It is noted that the distribution of fluorine (Figure 3.3d) arising from the PVDF binder is partly overlapped with the N and O regions, implying that a PD layer was formed on the binder surface as well.
Figure 3.2 SEM images of the medium-loading (a) pristine and (b) PD-graphite electrodes. No discernable difference is notable between the two electrodes.

Figure 3.3 Cross-sectional views of (a) SEM, and EDS images of the medium-loading PD-graphite with respect to (b) nitrogen (red), (c) oxygen (yellow), and (d) fluorine (green) elements. TEM images of PD-graphite for (e) the thinnest and (f) the thickest regions.

To estimate the thickness of the PD layer, the graphite surface was further analyzed by transmission electron microscopy (TEM). A previous study reported that the PD layer is uniform and its thickness increases
linearly with immersion time (ca. 7 nm h\(^{-1}\)).\(^{[24]}\) In our case, however, the PD layer thickness was varied at different spots, ranging from 1–8 nm (Figure 3.3e and 3f), although the polymerization conditions were the same as that in the literature.\(^{[24]}\) This disparity likely stems from the complex structure of the graphite electrodes: in contrast to the previous report, which used flat and homogenous substrates, our graphite composite electrodes have a porous and inhomogeneous morphology, which can cause variations in the local polymerization conditions (e.g., dopamine and O\(_2\) concentrations).

Figure 3.4 N1s, O1s and C1s XPS spectra of the uncycled medium-loading (a) pristine and (b) PD-graphite electrodes.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine graphite</td>
<td>77.9</td>
<td>1.4</td>
<td>0.0</td>
<td>20.7</td>
</tr>
<tr>
<td>PD-graphite</td>
<td>68.7</td>
<td>14.9</td>
<td>2.2</td>
<td>14.2</td>
</tr>
</tbody>
</table>
X-ray photoelectron spectroscopy (XPS) results further verify the presence of the PD layer on the graphite surface (Figure 3.4). Pristine-graphite showed the C1s peaks corresponding to bare graphite (284.5 eV), hydrocarbon (285.5 eV), alkyl carbonate (286.5 eV), and PVDF binder (291.8 eV), while N1s and O1s peaks were negligible. In contrast, PD-graphite exhibited distinct N1s and O1s peaks assigned to PD moieties; the C1s peak related to C-N (288.5 eV) newly appeared in the PD-graphite, and the C1s peaks originating from bare graphite and PVDF binder were significantly suppressed. This trend was also quantitatively revealed in the atomic composition analysis (Table 3.1). Overall, the series of EDX, TEM, and XPS results confirmed that the surface of the graphite electrode was coated with a nanometer-thick (1–8 nm) PD layer by a simple dip-coating method.

### 3.3.2 Effects of PD-coating on the formation and composition of the SEI layer

The effect of the PD layer on SEI formation was examined during the first charge (lithiation) and discharge (delithiation). The differential capacity curves (dQ/dV vs. V) of the pristine and PD-graphite are presented in Figure 3.5a. During the first lithiation of graphite anodes, the reduction peaks appearing above 0.4 V are known to be associated with electrolyte/additive reduction, which leads to SEI formation.28,30 In our measurements, the pristine graphite showed a distinct reduction peak at ca. 0.57 V, which is attributed to the reduction of EC.[28,30] The PD-graphite also exhibited a quite similar profile, except that the peak position was shifted upward by ca. 0.05 V, indicating that the reduction of EC was facilitated by the PD layer. An easier EC reduction was also observed in VC-containing electrolytes, in which a VC-reduction intermediate promotes EC ring-opening reaction.31 In our case, it may be that the electron-rich amine group in the PD layer facilitates the reduction of EC. The pristine and PD-graphite anodes both exhibited similar charge/discharge capacities and coulombic efficiencies during the first cycle without any signature of PD decomposition, suggesting that the PD layer is electrochemically stable in the given voltage window.

The chemical compositions of the SEI layers formed on the pristine and PD-graphite electrodes were examined using XPS analysis along the depth of each sample. In the case of pristine graphite (Figure 3.5b), the C atom ratio increased notably during the etching for the first 3 min, but saturated thereafter. After 3 min, the ratios of other elements (Li, F, O, and P) became negligible, indicating the end of SEI (or the start of bare
graphite). By contrast, the PD-graphite showed a rapidly rising N atomic ratio from 0.2% to 0.9% for the first 1 min of etching (Figure 3.5c), and its value remained constant until 3 min. After that, the N ratio as well as the other element ratios dropped, while the C element became dominant. This indicates that the PD layer was located between the SEI-layer and the graphite surface. This result was also supported by time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analysis. For PD-graphite, the characteristic signal of dihydroxy-indole-trimer, a possible fragment of PD,[24,25] became more prominent with sputtering time (Figure 3.6), supporting that the PD layer is preserved even after the SEI formation.

Figure 3.5 (a) Differential capacity (dQ/dV) curves of the medium-loading pristine and PD-graphite/Li cells with 1 M LiPF₆ EC/EMC (1/2, v/v) electrolyte. Elemental XPS depth-profiles of (b) pristine and (c) PD-graphite anodes at the fully delithiated state after 3 cycles.
3.3.3 Cycling and storage performance of PD-graphite at elevated temperatures

The cycling performances of the high-loading pristine and PD-graphite electrodes at 60 °C are presented in Figure 3.7a. In this test, graphite/graphite symmetric cells were employed to exclude any interference from Li counter electrodes. Note that the loading level of the high-loading electrode nears the highest values of commercial grade electrodes. While both electrodes showed similarly decent cyclability at 25 °C, their performance at 60 °C was quite distinct: after 100 cycles, the PD-graphite cell retained 56.9% of its original capacity, whereas the pristine-graphite cell preserved only 27.4% of its initial capacity.

Figure 3.7 (a) Cycle performances of the high-loading pristine and PD-graphite symmetric cells at 60 °C. (b) Potential profiles of the high-loading pristine and PD-graphite/Li cells before (dash line) and after (solid line) storage at 90 °C for 40 h.
The effects of PD-coating on high-temperature storage were also investigated. The charge and discharge profiles of the high-loading pristine and PD-graphite/Li cells were compared before and after storage at 90 °C for 40 h (Figure 3.7b). After storage, the pristine graphite cell exhibited huge overpotentials in the voltage profiles, and drastic capacity loss in both lithiation (84.7%) and delithiation (79.5%). In sharp contrast, the PD-graphite cell showed no significant changes in the voltage profiles, with only marginal capacity fading (8.8% and 8.4% during lithiation and delithiation, respectively), reconfirming the critical role of the PD layer for thermal stability.

Considering that the current study used state-of-the-art commercial graphite, the substantially enhanced high temperature performance provided by the PD coating is quite striking. Our previous reports revealed that the thermal stability of a SEI layer over 100–150 °C correlates closely with long-term cyclability and stability at high temperatures.\cite{9,32,33} However, this view does not explain the present result, because the DSC curves of the pristine and PD-graphite electrodes did not exhibit considerable difference in terms of the onset temperature and the amount of liberated exothermic heat (Figure 3.8). To investigate this further, the acid scavenging ability of the PD layer was examined to elucidate the superior thermal stability of the PD-graphite cell. To this end, the pristine and PD-graphite electrodes were stored in the electrolyte at 60 °C for 4 days and the changes in the H2O and HF contents of the electrolytes were compared (Table 3.2). The presence of the PD layer did not largely affect the H2O content during storage; starting at 5.6 ppm, the value increased to 68.3 ppm and 65.4 ppm for pristine graphite, and PD-graphite, respectively. Intriguingly, however, the increase of HF content was quite distinct between both electrodes; starting at 46.2 ppm, the amount changed to 81.5 ppm for PD-graphite and 138.4 ppm for pristine graphite, respectively, a dramatic difference in HF increase (35.3 ppm vs. 92.2 ppm). It is likely that the water trapped inside the composite electrode was dissolved into the electrolyte during storage, some of which generated HF through the hydrolysis of LiPF6 salt.\cite{34,35} The far smaller HF amount in the PD-graphite is attributed to the acid-neutralizing capability of the PD layer.
Figure 3.8 DSC curves of the fully delithiated graphite electrodes collected from the medium-loading pristine and PD-graphite/Li cells cycled in 1 M LiPF$_6$ EC/EMC (1/2, v/v).

Table 3.2 H$_2$O and HF contents in the electrolyte before and after storage for 4 days with the medium-loading pristine and PD-graphite at 60 °C. The numbers in the parenthesis denote the increases after the storage.

<table>
<thead>
<tr>
<th></th>
<th>Electrolyte before storage</th>
<th>Electrolyte stored with pristine graphite</th>
<th>Electrolyte stored with PD-graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O [ppm]</td>
<td>5.6</td>
<td>68.3 (+62.7)</td>
<td>65.4 (+59.8)</td>
</tr>
<tr>
<td>HF [ppm]</td>
<td>46.2</td>
<td>138.4 (+92.2)</td>
<td>81.5 (+35.3)</td>
</tr>
</tbody>
</table>
3.3.4 Rate capability of PD-graphite

The rate capabilities of the pristine and PD-graphite anodes were assessed by measuring discharge (delithiation) capacities at a series of current densities up to 5 C. Figure 3.9a compares the discharge profiles of the medium-loading pristine and PD-graphite/Li cells at 4 C. Notably, the higher discharge capacity of the PD-graphite is due to the smaller concentration overpotential near the end of discharge, and was not due to the IR drop (I and R denote the current and ohmic resistance, respectively) and charge transfer overpotential that are typically reflected at the beginning of discharge. Since the concentration overpotential is determined largely by the depletion (during lithiation) or accumulation (during delithiation) of Li$^+$ ions, its effect on the kinetics becomes profound near the end of each redox process, especially at high current densities.\[36-39\] Our observation that the PD-graphite cell exhibited superior rate capability to the pristine-graphite cell only at higher current densities above 1 C (Figure 3.9b) reconfirms that concentration overpotential was the main factor determining the rate performance of both graphite electrodes. It is also obviously expected that the thickness of the PD layer affects the rate capability of PD-graphite. To examine this aspect, the immersion time was varied from 20 min to 10 min or 30 min. As displayed in Figure 3.10, 20 min-coated PD-graphite exhibited the best rate capability, because immersion duration longer than this increases interfacial resistance too much, whereas at a duration shorter than this, PD formation on the surfaces of the graphite is insufficient to attain facile Li$^+$ transport.

The effect of the PD layer on the enhanced kinetics was also observed during the charge (lithiation) process (Figure 3.9c and 9d). It is well known that the lithiation of graphite is much slower than the delithiation.\[40\] For this reason, current LIBs adopt a charge protocol consisting of two steps to ensure the full storage of Li ions: a constant current (CC) charge followed by constant voltage (CV) charge, the so-called CCCV mode. In this protocol, the ratio of the CC charge capacity to the overall charge capacity (hereafter, the CC charge ratio) can serve as a measure of fast-charging capability. Because the switching to the CV mode is triggered when the active species (Li$^+$ ions and vacant graphite sites) are depleted at the graphite/electrolyte interface, the CC charge ratio can be regarded as inversely proportional to the concentration overpotential. During the initial stage of 1 C charge, both cells showed almost the same potential profiles (Figure 3.9c) implying again a similar IR drop and charge transfer overpotential. However, the PD-graphite cell showed a greater CC capacity (140
m Ah g$^{-1}$ than the pristine graphite (110 m Ah g$^{-1}$) at 1 C (inset in Figure 3.9c). This trend was maintained up to 3 C (Figure 3.9d).

Figure 3.9 (a) Discharging (delithiation) profiles of the medium-loading pristine and PD-graphite/Li cells at 4 C. (b) Discharge rate capability of the pristine and PD-treated graphite/Li cells. (c) Charging (lithiation) profiles of the pristine and PD-graphite/Li cells measured at 1 C followed by constant voltage step. (d) The CC charge ratio as a function of charge current rate. (e) Nyquist plots of the graphite/graphite symmetric cells at 25 °C. Inset: the equivalent circuit employed to retrieve component values. (f) Temperature dependence of R$\text{ct}$ in the graphite symmetric cells.
Figure 3.10 Discharge rate capability of the pristine and PD-graphite/Li cells. The immersion times were 10 min (blue), 20 min (red), and 30 min (green).

To better understand the enhanced kinetics of the PD-graphite, electrochemical impedance spectroscopy (EIS) measurements were performed for graphite/graphite symmetric cells at 15–35 °C. The EIS spectra of the graphite symmetric cells exhibited two semi-circles in the high and middle frequency regions, followed by an inclined line at the low frequency end (Figure 3.9e). It was found that the EIS spectra of the pristine and PD-graphite symmetric cells are quite similar to each other in terms of the size of the two semi-circles and their characteristic frequencies. The EIS spectra were fitted to an equivalent circuit (inset in Figure 3.9e), where $R_s$ is the ohmic resistance, $R_{SEI}$ is the resistance related to the migration of the Li$^+$ ion through the surface film, and $R_{ct}$ is the interfacial charge transfer resistance. The capacitances associated with $R_{SEI}$ and $R_{ct}$ are represented by the constant phase elements (CPEs), $Q_{SEI}$ and $Q_{ct}$, respectively. The finite diffusion by a CPE, $Q_D$, was used to replace a Warburg element to fit the inclined line at the lowest frequency region. All the fitted resistance values ($R_s$, $R_{SEI}$, and $R_{ct}$) of both graphite cells turned out to be quite similar. This is consistent with the similar IR drop and charge transfer overpotential observed at the early stages of the charge/discharge profiles of both graphite anodes (Figure 3.9a and 9c). To obtain more insight into the Li$^+$ transfer mechanism of the pristine and PD-graphite anodes, activation energy ($E_a$) values were obtained from Arrhenius plots of
The Ea value of the pristine graphite was calculated to be 66.0 kJ mol$^{-1}$, which is quite consistent with prior studies. In sharp contrast, the PD-graphite exhibited a much lower Ea value (51 kJ mol$^{-1}$), which is even comparable to that of Li$_4$Ti$_5$O$_{12}$, known as an SEI-free anode. This result indicates that the superior rate performance of the PD-graphite originates from the reduced activation barrier for Li$^+$ transfer at the interface.

### 3.3.5 Surface free energy analysis of PD-graphite

A surface free energy (SFE) analysis was carried out to determine the origin of the superior thermal stability and rate performance of the PD-graphite anode. Three SFE components, Lifshitz-van der Waals ($\gamma^{LVW}$), Lewis acidity ($\gamma^+$), and Lewis basicity ($\gamma^-$) were obtained based on the van Oss-Chaudhury-Good (vOCG) model (Table 3.3). The Lewis acid-base ($\gamma^{AB} = 2(\gamma^+ \gamma^-)^{0.5}$) and total ($\gamma^{Total} = \gamma^{LVW} + \gamma^{AB}$) values are also presented. To the best of our knowledge, this is the first vOCG-based SFE analysis for graphite electrodes. There was a prior work that reported two-component SFE results based on the Owens-Wendt (OW) model for graphite electrodes. However, the OW model gives only dispersive ($\gamma^d$) and polar ($\gamma^p$) SFE components, which correspond to the $\gamma^{LVW}$ and $\gamma^{AB}$ values of the vOCG model, respectively. The SFE values of the pristine graphite electrode obtained in this study ($\gamma^{Total} = 46.7$, $\gamma^{LVW} = 46.4$, and $\gamma^{AB} = 0.3$ mJ m$^{-2}$) are comparable to those reported in the previous work based on the OW model ($\gamma^{Total} = 50.2$, $\gamma^d = 43.3$, and $\gamma^p = 6.9$ mJ m$^{-2}$).

It is noted that the PD-treatment greatly increased the Lewis basicity ($\gamma^-$) and decreased the Lewis acidity ($\gamma^+$), while slightly lowering $\gamma^{Total}$. After the addition of PD, in fact, the ratio of Lewis basicity to acidity ($\gamma^-/\gamma^+$) increased by 2 orders of the magnitude. The increased basicity of the PD-graphite is ascribed to the secondary amine groups of the indole moieties in PD, and enables it to scavenge HF, a major culprit in thermal degradation of the SEI layer and graphite anodes. Although most of the PD layer would be covered by an SEI layer after cycling, it is likely that H$^+$ can penetrate through the porous SEI layer just as Li$^+$ does, and the PD layer can capture this H$^+$ before it reaches the graphite surface. In addition, TOF-SIMS results verified the presence of indole in the SEI layer of the PD-graphite (Figure 3.6). Also, as shown in the SEM images of the as-prepared PD-graphite electrode (Figure 3.2), the PD layer was formed over the PVDF binder exposed to the electrolyte, which is also beneficial for HF scavenging.
Table 3.3 Surface free energy (SFE) components of the high-loading pristine and PD-graphite electrodes based on the vOCG model. Lewis acid ($\gamma^+$) and Lewis base ($\gamma^-$) components refer to the electron-accepting and electron-donating parameters, respectively. Total ($\gamma^{\text{Total}} = \gamma^{\text{LW}} + \gamma^{\text{AB}}$), Lifshitz-van der Waals ($\gamma^{\text{LW}}$), and Lewis acid-base ($\gamma^{\text{AB}} = 2(\gamma^+ \gamma^-)^{0.5}$) values are also displayed. All the SFE values are expressed in mJ m$^{-2}$.

<table>
<thead>
<tr>
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<th>$\gamma^{\text{Total}}$</th>
<th>$\gamma^{\text{LW}}$</th>
<th>$\gamma^{\text{AB}}$</th>
<th>$\gamma^+$</th>
<th>$\gamma^-$</th>
<th>$\gamma^- / \gamma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine graphite</td>
<td>46.7</td>
<td>46.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>PD-graphite</td>
<td>43.0</td>
<td>42.6</td>
<td>0.4</td>
<td>0.02</td>
<td>0.8</td>
<td>40</td>
</tr>
</tbody>
</table>

As for the enhanced rate capability of PD-graphite, we consider that the attractive interaction between the Lewis basic PD layer and the partially-desolvated Li$^+$ ion (adion) leads to the stabilization of a transient complex consisting of three bodies: a Li$^+$ ion, solvent molecules (EC in our case) and the Lewis basic site of the PD. Although understanding of the detailed mechanism requires further investigation, the influence of the electrode component on the interfacial charge transport kinetics has been studied in a few recent reports; some studies found that the cathode materials doped with a hetero-atom or modified with Li$^+$-conducting polymer display lower $E_a$ values than the pristine ones.[23,45] In a previous study, PD was also coated onto a polyethylene (PE) separator to improve the rate performance of LIBs via enhanced electrolyte wetting.[25] In general, the $\gamma^{\text{Total}}$ values of un-modified polyolefin separators (30−35 mJ m$^{-2}$) are lower than those of conventional EC-based LIB electrolytes (35−40 mJ m$^{-2}$),[44,46,47] which means that most separators are bound to suffer from poor electrolyte wetting. Therefore, PD-coating that increases the $\gamma^{\text{Total}}$ of separators can contribute to the electrolyte wetting. In contrast, the $\gamma^{\text{Total}}$ of graphite (46.7 and 43.0 mJ m$^{-2}$ for pristine and PD-graphite electrodes, respectively, Table 3.3) is already higher than those of the electrolytes, so that the PD-coating would not improve the wetting of graphite electrodes to a large extent. Combining all the aspects considered, the enhanced thermal stability and rate performance in the present investigation can be explained mainly by the basicity of the PD, which can scavenge deleterious HF and form an intermediate triple-body complex, as depicted in Figure 3.11.
The Lewis basic sites of the PD layer can scavenge HF, which otherwise exacerbates the thermal degradation of the SEI layer and the graphite anode, leading to superior thermal stability. Also, the interaction between the Lewis basic sites and partially-desolvated Li⁺ ions (adions) stabilizes a transient complex, which lowers the activation energy (Eₐ) for the interfacial Li⁺ transport, leading to enhanced high-power capability of the graphite anodes.

3.4 Conclusions

We report PD-coating to be an unprecedented method for improving the thermal stability and rate capability of graphite anodes, which has been challenging to achieve simultaneously due to the contradictory nature of the two factors. A nanometer-thick PD layer was formed on the graphite surface using a simple dip-coating process. The PD-coating improved the 60 oC cycle and 90 oC storage performances, and the rate performance dramatically, largely as a result of the Lewis basicity of the PD, which scavenges fatal HF and facilitates interfacial Li⁺ transport. Along with the formidable benefits in electrochemical properties, the PD-treatment has advantages for commercial application: the overall polymerization procedure is environmentally friendly (ambient temperature process) and scalable, along with low materials cost. We thus expect that PD-coating can be expanded to a variety of active materials for current and next-generation LIBs where high rate performance and thermal stability have become very critical. At the same time, pursuing similar interfacial properties, other dopamine derivatives are also good candidates to investigate in the future.
3.5 References


IV. Fluoropropane sultone as an SEI-forming additive that outperforms vinylene carbonate

4.1 Introduction

Although lithium-ion batteries (LIBs) have dominated the market of the secondary batteries for mobile IT devices, there is still an urgent need for highly reliable LIBs as new application fields are being explored.\textsuperscript{[1-4]} In particular, electric vehicles and large-scale storage systems for renewable energies require a cycle life of more than ten years for their power sources, which is posing a serious challenge for the current LIB technology.

Employing functional electrolyte additives is a very promising way to improve the long-term stability of LIBs. Among the functional additives, vinylene carbonate (VC) is the most successful one for the current LIBs.\textsuperscript{[5,6]} VC forms a stable solid electrolyte interphase (SEI) layer on the anode surface to bring substantial benefits in overall LIB performances.\textsuperscript{[7-10]} However, a drawback of VC, which is due to its insufficient oxidation stability, has recently been highlighted: the remaining VC in the electrolyte decomposes at the cathode during elevated temperature storage.\textsuperscript{[11-14]} The adverse effects of VC may be worsened in high voltage or Ni-based cathode materials,\textsuperscript{[13,14]} which are expected to replace LiCoO$_2$ in the near future.

Besides VC, sulfur-based additives such as sulfites\textsuperscript{[15-20]} and sultones\textsuperscript{[13,21-26]} have long been studied as suitable SEI additives. The sulfur-based additives are also known to participate in the SEI formation and improve the thermal stability of LIBs.\textsuperscript{[13,15,17-26]} None of them, however, has been reported to show superior cycle performances to VC so far.

It is widely known that the formation and the properties of the SEI layer are greatly affected by even a subtle difference in the molecular structure of the electrolyte component.\textsuperscript{[5,6]} The most representative example of this is the dramatic difference between propylene carbonate (PC) and 3-fluoroethylene carbonate (FEC): the electron donating methyl group in PC hampers operation of the graphite anode,\textsuperscript{[27-32]} whereas the electron
withdrawing fluorine substitution in FEC is beneficial in SEI formation, and thereby in the graphite performance.\cite{29,32,33} Indeed, FEC is being widely employed as an SEI additive for graphite and Li-alloying anodes.\cite{33-41}

In this study, we prepared 3-fluoro-1,3-propane sultone (FPS), a fluorine-substituted derivative of 1,3-propane sultone (PS) (Figure 4.1), and compared the FPS as an SEI additive with PS and VC. First, we examined the impact of fluorine substitution on the anodic stability and the cathodic reaction of the additive itself through and electrochemical experiments. Then, the performances of the additives were investigated for commercial grade LiCoO$_2$/graphite cells. Our results clearly indicate that fluorine substitution into PS remarkably improves the LIB cyclability over a wide temperature range (25−60 °C). More importantly, FPS exhibits superior cyclability and thermal stability over VC, the currently most successful SEI additive. To the best of our knowledge, FPS is the first SEI additive demonstrated to outperform VC in commercial grade LiCoO$_2$/graphite cells.

![Figure 4.1 Chemical structures of ethylene carbonate (EC), vinylene carbonate (VC), 1,3-propane sultone (PS), and 3-fluoro-1,3-propane sultone (FPS).](image)

**4.2 Experimental**

**4.2.1 Chemicals**

Battery grade 1 M LiPF$_6$ in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) (1/2, v/v) from LG Chem were used as the base electrolyte solution. 3-Fluoro-1,3-propane sultone (FPS) was provided by patents.\cite{42}

**4.2.2 Electrochemical measurements**
To estimate the oxidation potential of the additives, linear sweep voltammetry (LSV) was employed with a three-electrode configuration. A Pt disk (area = 0.02 cm²) was used as the working electrode. Reference and counter electrodes were Li foil and Pt wire, respectively. Electrochemical experiments were carried out with an EG&G Princeton Applied Research model 273A. Preparation and LSV experiments for the electrolytes were performed in an Ar atmosphere glove box where H₂O and O₂ concentrations were kept below 5 ppm and temperature was held at 25±2 °C. The reduction behavior of the additive was examined using the differential capacity curve (dQ/dV vs. V) at the first lithiation process of graphite/Li coin cells.

For the battery-performance tests, commercial grade 503759-size Al-pouch cells (nominal capacity 1350 mAh) and 18650-size cylindrical cells (nominal capacity 2400 mAh) were employed. The cathode electrode was prepared by mixing LiCoO₂ (NCI, Japan) with 2.5 wt% PVdF binder and 2.5 wt% conductive carbon. The anode electrode of the Al-pouch cells was fabricated with mesocarbon microbeads graphite (Osaka gas, Japan) with 2.5 wt% PVdF binder and 2.5 wt% conductive carbon. The cylindrical cells employed artificial graphite (Hitachi, Japan) with 1.5 wt% SBR, 1wt% CMC binder, and 2.5 wt% conductive carbon as the anode electrode.

Both types of cells were cycled initially at 25 °C over a 3.0−4.2 V range with a 0.1 C current three times to complete the formation process. The pouch cells were degassed and resealed inside the vacuum chamber to eliminate the evolved gases during the formation process. The cycle test were performed with a 0.5 C constant current charging followed by 4.2 V constant voltage charging and a 0.5 C constant current discharging over a 3.0−4.2 V range.

4.2.3 High temperature storage test

Before the oven storage test, the pouch cells were fully charged after the degassing/reseal process. The oven temperature was raised from room temperature to 90 °C in 1 h, kept at 90 °C for 4 h, and then decreased back to room temperature in 1 h. The thickness of the pouch cells was measured by a thickness recording device.

4.2.4 Differential scanning calorimetry

Coin-type graphite/Li cells were cycled three times and disassembled in a glove box. The fully de-lithiated graphite samples were collected and put into the Al pans without a washing process or an additional
electrolyte. The differential scanning calorimetry (DSC) measurements were performed on a TA instruments Q100. The heating rate was 5 °C min^{-1}. The blank signal was obtained for the Al pan containing only the electrolyte, which was referred to the base line for the other measurements.

4.3 Results and discussion

4.3.1 Anodic stability

The anodic stabilities of the additives were assessed by means of the linear sweep voltammetry (LSV) on a Pt electrode (Figure 4.2). The anodic stability of the additives is in the following order: FPS > PS > VC. The oxidation current of VC starts to rise from 4.9 V and becomes huge above 5.0 V. PS has a much lower oxidation current than VC, but it is still higher than that of the base electrolyte (no additive). Note that FPS exhibits greatly improved anodic stability compared with PS. The LSV of FPS is quite similar to that of the base electrolyte, which reflects the absence of the FPS oxidation. The enhanced anodic stability of FPS is expected to secure superior long term cyclability and dimensional stability, especially at elevated temperature.

Figure 4.2 Linear sweep voltamograms of 1 M LiPF6 EC/EMC (1/2, v/v) solutions with no additive and 2 wt% of each additive. Pt (area = 0.02 cm2) working electrode. Scan rate was 20 mV s^{-1}. 

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4.3.2 Formation and property of the SEI layer on the graphite anode

The differential capacity curves (dQ/dV vs. V) were obtained to compare the reduction behavior of the additives during the SEI formation on the graphite anode (Figure 4.3). The reduction peaks appearing above 0.4 V can be attributed to electrolyte reductions, which lead to SEI formation on graphite.[7,8] The base electrolyte exhibits a main peak at around 0.57 V, which can be assigned to the reduction of EC.[7,8] With the addition of VC, the reduction tail starts at about 1.1 V and a reduction peak is observed at 0.69 V. Similar VC reduction behavior has also been reported elsewhere, where it was claimed that the reduction of VC starts above 1.0 V and that of EC is shifted to more positive potential in the presence of VC.[8] In the presence of FPS or PS, the reduction peak of EC is significantly suppressed, while new peaks that can be assigned to the FPS or the PS reduction appear at 1.02 V or 0.71 V, respectively. Note that the reduction peak potential of FPS is much more positive than that of PS.

Figure 4.3 Differential capacity (dQ/dV) curves of graphite/Li coin cells with 1 M LiPF₆ EC/EMC (1/2 v/v) solutions with no additive and 2 wt% of each additive.

- 44 -
Table 4.1 Charge capacity ($Q_{\text{ch}}$), discharge capacity ($Q_{\text{dis}}$), and the coulombic efficiency ($\eta_{1\text{st}}$) at the first cycle of graphite/Li coin half cells.

<table>
<thead>
<tr>
<th>Additive</th>
<th>$Q_{\text{ch}}$ [mAh g$^{-1}$]</th>
<th>$Q_{\text{dis}}$ [mAh g$^{-1}$]</th>
<th>$\eta_{1\text{st}}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>329.0</td>
<td>302.9</td>
<td>92.1</td>
</tr>
<tr>
<td>VC</td>
<td>326.1</td>
<td>293.1</td>
<td>89.9</td>
</tr>
<tr>
<td>PS</td>
<td>324.4</td>
<td>302.3</td>
<td>93.2</td>
</tr>
<tr>
<td>FPS</td>
<td>329.5</td>
<td>305.6</td>
<td>92.7</td>
</tr>
</tbody>
</table>

The charge (lithiation)/discharge (de-lithiation) capacities, and the coulombic efficiencies at the first cycle of the graphite/Li cells are summarized in Table 4.1. PS or FPS-added cells exhibit similar or slightly higher discharge capacity and coulombic efficiency than the cell with the base electrolyte, while the VC-added cell has a slightly decreased discharge capacity and coulombic efficiency compared with the cells with the base electrolyte. This implies that the SEI formation by FPS or PS is accompanied with less capacity loss than that by VC.

The thermal stability of the SEI derived from each additive was examined using differential scanning calorimetry (DSC). The DSC profiles of the fully-delithiated graphite anodes cycled in the corresponding electrolytes are compared (Figure 4.4). Since the reactions due to the intercalated Li are absent, the exothermic peaks around 120–140 ºC can be assigned to the breakdown or transformation of the SEI itself.$^{[8,43-45]}$ The SEI formed in the base electrolyte starts to decompose at around 120 ºC. The onset temperature of the SEI derived by VC is increased to 127 ºC, which implies that VC enhances the thermal stability of SEI formed on graphite.$^{[8,45]}$ The SEI formed by PS shows an onset temperature (126 ºC) similar to that by VC (127 ºC). Note that the SEI derived from FPS exhibits higher onset temperature (129 ºC) than the others. Thus, the thermal stability of the SEI derived from FPS is supposed to be higher than that from VC. Our previous reports confirmed that the thermal stability of the SEI is closely linked to the cyclability and the stability at elevated temperature storage of LIBs.$^{[12,13]}$ The effects of the additives on the LIB performances were evaluated in the next steps.
4.3.3 Cyclability of LiCoO$_2$/graphite cells at various temperatures

The cycle behavior of commercial grade LiCoO$_2$/graphite cells with an electrolyte containing 2 wt% additives are compared (Figure 4.5−7). The Al-pouch cells (nominal capacity 1350 mAh) were employed for 25 °C and 45 °C tests (Figure 4.5 and 6). The 60 °C cycle test (Figure 4.7) was performed on the cylindrical cells (nominal capacity 2400 mAh) since the pouch cell deteriorates too fast at the 60 °C cycle to reveal the impact of the additives. In order to check the reproducibility, two or three cells were tested for each electrolyte. The capacity ratio presented in Figures 4.5−7 and Table 4.2 was derived from the ratio of the discharge capacity at a specific cycle to the nominal cell capacity (1350 mAh or 2400 mAh). The capacity ratio serves as a versatile measure to compare the cyclability and the initial discharge capacity at the same time.

Note that the capacity ratios at 25 °C of the pouch cells are in the following order: FPS > VC > PS > base (no additive). The cells with the base electrolyte has the lowest initial discharge capacity and rapid capacity fading with only a 57.8% capacity ratio after 300 cycles at 25 °C (Table 4.3). VC addition increases the initial capacity close to the nominal capacity and improves cyclability with the capacity ratio of 73.9%. PS slightly improves cycle performances compared with the base electrolyte, but its beneficial effect is less than that by VC. Note that the FPS-added cell exhibits the highest capacity ratio of 81.2% with a fairly high initial capacity. The cycle behavior at 45 °C follows the same trend as that observed at 25 °C (Figure 4.6). Capacity
fading becomes more rapid at 45 °C for all the cells tested so that the capacity ratio at the 250th cycle was compared (Table 4.3).

At the 60 °C cycle test (Figure 4.7), the cells with the base electrolyte suffer from severe capacity fading from as early as the 25th cycle and the capacity ratio falls below 50% before the 100th cycle. The poor cycle behavior at 60 °C is hardly improved with PS addition. VC-added cells maintain decent cycle behavior at the initial stage compared to the cells with the base electrolyte. However, capacity fading is somewhat accelerated after around the 100th cycle, and the current interrupt devices (CIDs) of VC-added cells are activated before the 250th cycle. The CID activation points to the huge pressure buildup inside the VC-added cells. In contrast, the CID activation is significantly delayed in the FPS-added cells: one cell at the 282th cycle and the other cell not until the 300th cycle.

In summary, FPS exhibits superior cycle performances to PS, especially at an elevated temperature. It should also be noted that FPS is the first SEI additive that exceeds VC in the cyclability of commercial grade LiCoO2/graphite cells over a wide temperature range (25−60 °C).

![Figure 4.5 Cycle behavior of LiCoO2/graphite pouch cells (1350 mAh) at 25 °C with 1 M LiPF6 EC/EMC (1/2, v/v) solutions with no additive and 2 wt% of each additive.](image)
Figure 4.6 Cycle behavior of LiCoO$_2$/graphite pouch cells (1350 mAh) at 45 °C with 1 M LiPF$_6$ EC/EMC (1/2, v/v) solutions with no additive and 2 wt% of each additive.

Figure 4.7 Cycle behavior of LiCoO$_2$/graphite cylindrical cells (2400 mAh) at 60 °C with 1 M LiPF$_6$ EC/EMC (1/2, v/v) solutions with no additive and 2 wt% of each additive. x mark denotes the point where CID is activated.
Table 4.2 Charge capacity (\(Q_{\text{ch}}\)), discharge capacity (\(Q_{\text{dis}}\)), and the columbic efficiency (\(\eta_{\text{1st}}\)) at the first cycle of graphite/Li coin half cells.

<table>
<thead>
<tr>
<th>Additive</th>
<th>(Q_{\text{ch}}) [mAh g(^{-1})]</th>
<th>(Q_{\text{dis}}) [mAh g(^{-1})]</th>
<th>(\eta_{\text{1st}}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>329.0</td>
<td>302.9</td>
<td>92.1</td>
</tr>
<tr>
<td>VC</td>
<td>326.1</td>
<td>293.1</td>
<td>89.9</td>
</tr>
<tr>
<td>PS</td>
<td>324.4</td>
<td>302.3</td>
<td>93.2</td>
</tr>
<tr>
<td>FPS</td>
<td>329.5</td>
<td>305.6</td>
<td>92.7</td>
</tr>
</tbody>
</table>

Table 4.3 Discharge capacity (\(Q_{\text{1st}}\)) at the first cycle, capacity ratio (\(Q_R\)), and the maximum thickness change (\(\Delta T_{\text{max}}\)) at 90 °C storage of LiCoO\(_2\)/graphite Al-pouch cells (1350 mAh). \(Q_{\text{1st}}\) and \(Q_R\) (25 °C) are the average values of three cells, and \(Q_R\) (45 °C), and \(\Delta T_{\text{max}}\) the average value of two cells.

<table>
<thead>
<tr>
<th>Additive</th>
<th>(Q_{\text{1st}}) [mAh]</th>
<th>(Q_R(25 \degree C)^a) [%]</th>
<th>(Q_R(45 \degree C)^b) [%]</th>
<th>(\Delta T_{\text{max}}) [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>1296</td>
<td>57.8</td>
<td>45.9</td>
<td>1.08</td>
</tr>
<tr>
<td>VC</td>
<td>1347</td>
<td>73.9</td>
<td>66.4</td>
<td>2.68</td>
</tr>
<tr>
<td>PS</td>
<td>1318</td>
<td>65.2</td>
<td>66.4</td>
<td>1.41</td>
</tr>
<tr>
<td>FPS</td>
<td>1339</td>
<td>81.2</td>
<td>75.5</td>
<td>1.44</td>
</tr>
</tbody>
</table>

\(^a\) \(Q_R(25 \degree C) = Q_{300th}(25 \degree C) / 1350 \text{ mAh} \times 100. \)

\(^b\) \(Q_R(45 \degree C) = Q_{250th}(45 \degree C) / 1350 \text{ mAh} \times 100. \)
4.3.4 Swelling behavior on elevated temperature storage

The swelling behavior during 90 ºC storage for the pouch cells tested in Figure 4.5 was investigated (Figure 4.8). Duplicate tests were performed for each electrolyte to check the reproducibility. The order of the dimensional stability (the reverse order of thickness change) is in the following order: base ≥ PS ≈ FPS >> VC. The maximum thickness change (ΔT_max) of each cell is summarized in Table 4.3. VC-added cells suffer from huge swelling (ΔT_max = 2.68 mm) compared with the cell with the base electrolyte (ΔT_max = 1.08 mm). Such a severe swelling may lead to serious physical damage, cell rupture, and electrolyte leakage, which devastates the long-term stability of LIBs. In contrast, FPS or PS-added cells show only slightly increased ΔT_max values (1.44 or 1.41 mm, respectively) over the cell with the base electrolyte. This indicates that FPS or PS-added cells have much higher thermal stabilities than the cells with VC.

The thickness increase of the pouch cells during the elevated temperature storage is mainly ascribed to the irreversible gas-evolving reactions at both the cathode and anode interfaces.\(^{47-53}\) It has been reported that the oxidative decomposition of the electrolyte at the cathode interface is the main source for the evolved gas.
for the fully charged and overcharged 4 V LIBs.\cite{47-53} It has been also claimed that thermal decomposition of SEI on the anode results in gas generation.\cite{51-53} It seems that the swelling observed in VC-added cells stems mainly from the gas evolution at the cathode rather than the anode. This is based on the fact that VC exhibits insufficient anodic stability compared with the other additives (Figure 4.2), whereas VC significantly improves the thermal stability of the SEI formed at the anode (Figure 4.4).

When integrating all the results obtained in this study, the different behaviors of VC and FPS can be explained as follows:

- VC forms a stable SEI layer at the anode, which is beneficial in cyclability at 25 °C and 45 °C. However, the poor anodic stability of VC itself leads to oxidative decomposition of residual VC at the cathode, thereby leading to failure at 60 °C cycling and huge swelling at 90 °C storage.

- The anode SEI derived by FPS is more stable than that by VC, and the anodic stability of FPS is much higher than that of VC. Thus, FPS offers excellent cyclability over 25–60 °C and decent thermal stability during 90 °C storage.

Considering the high anodic stability, the excellent cyclability, and the good thermal stability, we see that FPS is a superior SEI additive that can possibly replace VC for the current LiCoO$_2$/graphite LIBs.

4.4 Conclusions

We investigated 3-fluoro-1,3-propane sultone (FPS) as a novel SEI-forming electrolyte additive for LIBs in comparison with 1,3-propane sultone (PS) and vinylene carbonate (VC). The electrochemical experiments confirmed that the fluorine substitution is beneficial in terms of the anodic stability and the cathodic reactivity. We demonstrated that FPS exhibits cycle performance superior to PS and VC for commercial grade LIBs over a wide temperature range (25–60 °C). In addition, FPS exhibited good thermal stability in stark contrast to VC. Based on the high anodic stability, the excellent cyclability, and good the thermal stability, FPS was proposed as an outstanding SEI additive that can expand the performance limit of the present LIBs set by VC. The impact of FPS would be more highlighted on Ni-rich cathode and 5V LIBs, for which the issues of long term cyclability and thermal stability at elevated temperature are critical.
4.5 References


V. Iodine as a temperature-responsive redox shuttle additive for the swelling suppression of Li-ion batteries at elevated temperatures

5.1 Introduction

Along with the rapid expansion of the Li-ion battery (LIB) applications, the needs for highly reliable LIBs are ever increasing. In particular, the swelling issue during cycling and storage at elevated temperatures (> 60 °C) has been one of the most critical challenges related to current LIBs, especially for Al-pouch or prismatic cells, which are vulnerable to mechanical deformation compared to cylindrical cells.[1,2]

The swelling of LIBs is mainly ascribed to the irreversible gas-evolving reactions at both the cathode and anode interfaces.[3−10] It was reported that the gas evolution of LiCoO2/graphite cells is dominated by the oxidative decomposition of the electrolyte at the cathode in the high potential region (> 4.0 V), while being governed by the reduction reaction at the anode in a low potential range (< 3.8 V).[1,5] It was also claimed that the swelling is not significant when the state of charge (SOC) is low; instead, it dramatically increases as the SOC exceeds 80.[1,5]

To address the swelling issue, surface modifications of cathode materials with various oxides and phosphates have long been examined.[11−13] The surface coating effects are assumed either to minimize direct contact between the cathode and the electrolyte or to deactivate the catalytic sites of cathode surfaces toward electrolyte oxidation. The surface coating process, however, generally introduces cost and homogeneity issues during mass production.

Functional electrolytes have also been investigated in an effort to suppress swelling. It was reported that an addition of Li imide salts (LiFSI and LiTFSI) to a LiPF6-based electrolyte mitigates gas generation in NCM/graphite cells.[14,15] It was also revealed that sulfur-based electrolyte additives such as 1,3-propane sulfone and prop-1-ene-1,3-sultone readily reduce gas evolution at high temperatures by forming a protective layer on the cathode surface.[16−17] However, imide salts are associated with the corrosion of aluminum current...
collectors.[18−21] Moreover, the surface film caused by sulfur additives usually impedes interfacial charge transport,[15] and the toxicity of these additives is still a subject of debate.[22] Among the various electrolyte additives, redox shuttle (RS) compounds have been widely studied for the purpose of overcharge protection in LIBs.[23,24] RS additives consume extra charging current by repetitive redox reactions between the cathode and the anode. The application of RS additives, however, has been limited because they cannot work with high levels of overcharge current.

Iodine (I2) as a representative redox shuttle compound had long been studied as a means of overcharge protection of 3 V LIBs,[25,26] mainly in relation to its high diffusion coefficient and facile charge transport kinetics. Moreover, I2 and iodide compounds exhibit good compatibility with graphite and lithium anodes. It has also been reported that natural graphite shows remarkably improved electrochemical performance after a heat-treatment with I2.[27] In addition, iodide additives such as LiI and NH4I are claimed greatly to suppress irreversible reactions at the graphite/deposited Mn/electrolyte interface via the specific adsorption of iodide on metallic Mn.[28] It was also demonstrated that AlI3 can improve the Li cycling efficiency because the formation of a Li-Al alloy layer on the Li surface suppresses the growth of Li dendrites.[29] However, I2 is not considered to be feasible for 4 V LIBs owing to its low redox potential (ca. 3.6 V vs. Li/Li+).

We herein demonstrate that I2 can serve as a versatile electrolyte additive to suppress the high-temperature swelling of 4 V LiCoO2/graphite LIBs. Importantly, we noted the two facts: (1) the swelling of LiCoO2/graphite cells during storage at 90 °C is severe only when the cell is fully charged (i.e., when the SOC is close to 100), and (2) the redox shuttling reaction of I2 can be tuned to be activated only when the temperature is as high as 90 °C if an appropriate amount of I2 additive is used. Based on these two findings, we propose that when a fully charged cell (SOC 100) is exposed to a temperature of 90 °C, the self-discharge by I2 is activated to lower the SOC of the cell, thus suppressing swelling in the cell. This temperature-responsive shuttling reaction of I2 can be explained by the adsorption of I2 mainly on the cathode surface. This novel strategy was confirmed for commercial-grade LiCoO2/graphite Al-pouch cells.
5.2 Experimental

5.2.1 Chemicals

Reagent-grade iodine (I$_2$, 99.8%) was purchased from Aldrich. Battery-grade 1 M LiPF$_6$ in ethylene carbonate/ethylmethyl carbonate (EC/EMC) (1/2, v/v) was provided by LG Chem. All of the electrolytes were prepared in an Ar-filled glove box (H$_2$O and O$_2$ levels < 5 ppm and 25 ± 1 ºC). The water content of the electrolytes was less than 25 ppm.

5.2.2 Electrochemical measurements

Cyclic voltammetry (CV) of I$_2$ was conducted using a three-electrode system in an Ar-filled glove box. A Pt disk (0.02 cm$^2$) was used as a working electrode. Li foil and Pt wire were used as a reference electrode and counter electrode, respectively. For the battery performance tests, 2032-type coin cells and commercial-grade 383562-size Al-pouch LiCoO$_2$/graphite cells (nominal capacity of 760 mAh) were employed. They used Li disk or mesocarbon microbeads graphite (Osaka Gas, Japan) as an anode material and LiCoO$_2$ (NCI, Japan) as a cathode material with a polyethylene separator (Tonen, Japan). The cathode or anode was prepared by mixing LiCoO$_2$ or graphite with 2.5 wt % PVdF binder and 2.5 wt % conductive carbon. The pouch cells were opened and degassed inside a vacuum chamber to eliminate the gases which evolved during the first charge (formation gases) after the first charge at a constant current of 0.1 C. The cells were resealed under a vacuum and discharged to 3 at a constant current of 0.1 C. In order to examine the cycle performance, the cells were cycled at 25 ºC over a range of 3–4.2 V with charging at a constant current of 0.5 C followed by charging at a constant voltage 4.2 V and discharging at a constant current of 0.5 C. Electrochemical impedance spectroscopy (EIS) was conducted for the fully discharged (SOC 0) Al-pouch cells with a frequency response analyzer (Solartron 1260) combined with a potentiostat (EG&G Princeton Applied Research 273A). The frequency range was 10 kHz to 0.1 Hz and the AC amplitude was 5 mV.

5.2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were taken using an ESCALAB 250Xi (Thermo Scientific). For the sample preparation, LiCoO$_2$/graphite coin cells were cycled three times over 3–4.2 V and the fully discharged cell was dismantled to retrieve the cathode and anode electrodes, which were rinsed with
dimethyl carbonate (DMC) and dried inside a glove box. Uncycled pristine cathode and anode electrodes that were merely immersed in an I₂-containing electrolyte and washed with pure DMC were also prepared for a comparison.

5.2.4 Swelling tests

Linear sweep voltammetry (LSV) of the Al-pouch cells was conducted at 25 °C or 90 °C over 3.4–4.8 V at a scan rate of 0.1 mV s⁻¹, and the cell thicknesses were recorded simultaneously using a thickness gauze. For the open-circuit voltage (OCV) measurements, the voltage changes of the fully charged (SOC 100) cells were monitored during storage at 60 °C or 90 °C. For the 90 °C storage tests, the thickness of a fully charged (SOC 100) cell was measured as the oven temperature was increased from room temperature to 90 °C in 1 h. It was then maintained at 90 °C for 4 h and subsequently decreased back to room temperature in 1 h. The recovery ratios of the 0.2 C discharge capacities before and after the 90 °C storage were then compared.

5.3 Results and discussion

5.3.1 Redox reaction of the I₂ additive in LiCoO₂/graphite cells

The cyclic voltammogram (CV) of 0.1 wt % I₂ in 1 M LiPF₆ EC/EMC (1/2, v/v) on a Pt working electrode is presented in Figure 5.1. The CV exhibits two pairs of reversible redox peaks corresponding to the following reactions:

\[ \text{3I}_2 + 2e^- \rightleftharpoons 2\text{I}_3^- \]  
\[ \text{I}_3^- + 2e^- \rightleftharpoons 3\text{I}^- \]

The formal potentials of the I₂/I₃⁻ and I₃⁻/I⁻ couples were determined to be 3.56 V and 3.02 V (vs. Li/Li⁺), respectively. Therefore, I₂ as an electrolyte additive is expected to hamper the normal charge process of 4 V LIB cathode materials. To this end, the effects of the I₂ concentration on the charge process of LiCoO₂/graphite coin cells were investigated (Figure 5.2). When the I₂ amount is as high as 0.5 wt %, the cell voltage increases only up to 2.9 V and then falls with a long tail. This abnormal charge behavior is clearly ascribed to severe
self-discharge by the $I_2$ shuttling reaction. In contrast, normal charge/discharge behavior was noted when the $I_2$ content was reduced to less than 0.1 wt %.

Figure 5.1 (a) Cyclic voltammograms in 1 M LiPF$_6$ EC/EMC (1/2, v/v) containing 0.1 wt % $I_2$. Pt (area = 0.02 cm$^2$) as a working electrode. Scan rate = 20 mV s$^{-1}$.

Figure 5.2 The 1st cycle charge/discharge profiles of LiCoO$_2$/graphite coin full cells with 1 M LiPF$_6$ EC/EMC (1/2, v/v) containing various amounts of $I_2$. 
The charge ($Q_{ch}$) and discharge ($Q_{dis}$) capacities and the coulombic efficiency (CE) values at the first three cycles of the cells containing various I$_2$ concentrations are presented in Table 5.1. When comparing the behavior during the first cycle, $Q_{ch}$ increases with an increase in the I$_2$ content, while $Q_{dis}$ varies only marginally, which results in lower CE at a higher I$_2$ content. Intriguingly, however, the effect of I$_2$ becomes negligible during the subsequent cycles; the charge/discharge behavior of the I$_2$-containing cells becomes similar to that of a pristine cell without I$_2$ at the third cycle. This point will be discussed further in section 5.3.3.

Table 5.1 Charge ($Q_{ch}$), discharge ($Q_{dis}$) capacities and the coulombic efficiency (CE) at the first three cycles of LiCoO$_2$/graphite coin cells.

<table>
<thead>
<tr>
<th>I$_2$ [wt %]</th>
<th>1$^{st}$ cycle</th>
<th>2$^{nd}$ cycle</th>
<th>3$^{rd}$ cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{ch}$ [mAh]</td>
<td>$Q_{dis}$ [mAh]</td>
<td>CE [%]</td>
</tr>
<tr>
<td>0</td>
<td>5.1</td>
<td>4.6</td>
<td>90.2</td>
</tr>
<tr>
<td>0.01</td>
<td>5.4</td>
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<tr>
<td>0.05</td>
<td>6.1</td>
<td>4.7</td>
<td>77.0</td>
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<tr>
<td>0.1</td>
<td>7.2</td>
<td>4.5</td>
<td>62.5</td>
</tr>
<tr>
<td>0.5</td>
<td>20.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

To reveal the effects of I$_2$ as an additive on the cathode and the anode independently, the initial cycle behaviors of LiCoO$_2$/Li and graphite/Li half cells were examined. It should be noted that LiCoO$_2$/Li cells show features identical to those of LiCoO$_2$/graphite cells (Figure 5.3 and Table 5.2): a notably increased $Q_{ch}$, slightly varying $Q_{dis}$, decreasing CE with an increase in the I$_2$ concentration at the first cycle, and vanishing I$_2$ effects with an increase in the cycle number. In contrast, graphite/Li cells are scarcely affected by the presence of the I$_2$ additive (Figure 5.4 and Table 5.3). These results indicate that the shuttle reaction of I$_2$ as described in Eqs. 1 and 2 works in LiCoO$_2$/graphite and LiCoO$_2$/Li cells: I$_2$ is reduced to I$_3^-$/I$^-$ at the graphite or Li anodes, and the reduced iodide species are reoxidized to I$_2$ at the LiCoO$_2$ cathode during the charge process.
Figure 5.3 The initial cycle charge/discharge profiles of LiCoO₂/Li coin half cells with 1 M LiPF₆ EC/EMC (1/2, v/v) containing various amounts of I₂.

Table 5.2 Charge (Q_{ch}), discharge (Q_{dis}) capacities and the columbic efficiency (CE) at the first three cycles of LiCoO₂/Li cells.

<table>
<thead>
<tr>
<th>I₂</th>
<th>1st cycle</th>
<th></th>
<th></th>
<th></th>
<th>2nd cycle</th>
<th></th>
<th></th>
<th></th>
<th>3rd cycle</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Q_{ch}</td>
<td>Q_{dis}</td>
<td>CE</td>
<td>Q_{ch}</td>
<td>Q_{dis}</td>
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<td>Q_{dis}</td>
<td>CE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[%]</td>
<td>[mAh]</td>
<td>[mAh]</td>
<td>[%]</td>
<td>[mAh]</td>
<td>[mAh]</td>
<td>[%]</td>
<td>[mAh]</td>
<td>[mAh]</td>
<td>[%]</td>
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<td></td>
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<tr>
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<td>98.2</td>
<td>4.88</td>
<td>4.87</td>
<td>99.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>5.72</td>
<td>4.83</td>
<td>84.4</td>
<td>5.01</td>
<td>4.82</td>
<td>96.2</td>
<td>4.90</td>
<td>4.82</td>
<td>98.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>8.51</td>
<td>4.64</td>
<td>54.5</td>
<td>5.20</td>
<td>4.74</td>
<td>91.2</td>
<td>5.03</td>
<td>4.75</td>
<td>94.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.4 The initial cycle charge/discharge profiles of graphite/Li coin half cells with 1 M LiPF₆ EC/EMC (1/2, v/v) containing various amounts of I₂.

Table 5.3 Charge ($Q_{ch}$), discharge ($Q_{dis}$) capacities and the cumbic efficiency ($CE$) at the first three cycles of graphite/Li cells.

<table>
<thead>
<tr>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{ch}$</td>
<td>$Q_{dis}$</td>
</tr>
<tr>
<td>I₂</td>
<td>[mAh]</td>
<td>[mAh]</td>
</tr>
<tr>
<td>0</td>
<td>6.12</td>
<td>5.26</td>
</tr>
<tr>
<td>0.03</td>
<td>6.15</td>
<td>5.24</td>
</tr>
<tr>
<td>0.1</td>
<td>6.19</td>
<td>5.28</td>
</tr>
</tbody>
</table>
5.3.2 Effects of I\textsubscript{2} as an additive on swelling behaviors

To determine the relationship between the swelling behavior and the state of charge (SOC), the thickness of a LiCoO\textsubscript{2}/graphite Al-pouch cell (760 mAh) was monitored as the cell was charged by linear sweep voltammetry (LSV) (Figure 5.5). During the LSV process at 25 °C, the current response in the range of 3.4–4.2 V was found to be correlated with the normal charge process, while the cell thickness scarcely changes. However, when the cell voltage exceeds 4.2 V, a new peak appears around 4.58 V along with a rapid increase in the cell thickness, which is ascribed to the overcharge current and the concomitant cell degradation. Importantly, when the temperature is raised to 90 °C, the cell thickness rises abruptly just above ca. 4.2 V, while the LSV is similar to that at 25 °C. This indicates that the LiCoO\textsubscript{2}/graphite cell is vulnerable to severe swelling when stored at 90 °C when the cell is in a fully charged state (i.e., SOC 100). This is consistent with previous reports claiming that LIB swelling dramatically increases when the SOC exceeds 80%.[1,5] From the fact that swelling at 90 °C starts to occur abruptly near 4.2 V (SOC 100), we inferred that the swelling can be suppressed if the cell voltage (or SOC) is reduced below 4.2 V even by a marginal amount (i.e., 50-100 mV). Accordingly, the feasibility of employing I\textsubscript{2} as an additive for lowering the cell SOC was examined in the next step.

Figure 5.5 Linear sweep voltammograms of LiCoO\textsubscript{2}/graphite pouch cells (760 mAh) and concomitantly measured cell thickness at 25 °C and 90 °C. Scan rate = 0.1 mV s\textsuperscript{-1}. 
The changes in the open-circuit voltage (OCV) during the high-temperature storage of fully charged LiCoO$_2$/graphite pouch cells were then compared at various I$_2$ concentrations (Figure 5.6). It was noted that the OCV drop becomes more evident with an increase in the I$_2$ content. While the control cell containing no I$_2$ additive exhibits a drop in the OCV of ca. 52 mV after 20 h of storage at 90 °C, the cell with 0.01 wt % I$_2$ exhibits a somewhat larger (75 mV) OCV change under identical storage conditions.

For cells with higher I$_2$ contents, the OCV drop is greater; the OCV falls to 4.05 V within 8 h for the cell with 0.05 wt % I$_2$, and the same OCV drop appears within 3 h for the cell with 0.1 wt % I$_2$. Therefore, the accelerated OCV drops observed in I$_2$-containing cells can be ascribed to the shuttling reaction of the I$_2$ additive. Also, the self-discharge by I$_2$ greatly depends on the storage temperature. The cells show much less of an OCV drop during storage at 60 °C (the dashed lines in Figure 5.6) than at 90 °C. This implies that the self-discharge by I$_2$ shuttling becomes significant only when the temperature is as high as 90 °C.

![Figure 5.6 Open-circuit voltage changes during the high-temperature storage of LiCoO$_2$/graphite pouch cells (760 mAh) containing various amounts of I$_2$. The cells were fully charged (SOC 100) before the storage. The storage temperatures were 60 °C (dashed lines) and 90 °C (solid lines).](image)
Finally, the impact of I2 on the swelling behavior of fully charged LiCoO2/graphite pouch cells during 6 h of storage at 90 °C was examined (Figure 5.7). In this test, 0.05 wt % I2 was employed because 0.01 wt % I2 was too small to induce a sufficient OCV drop (Figure 5.6), whereas 0.1 wt % I2 was too high to ensure normal charge/discharge behaviors. Note that the increased thickness of the cell with 0.05 wt % I2 (0.13 mm) is only one third of that of the control cell (0.36 mm). The recovery ratio of discharge capacities before and after storage at 90 °C was 92.0 % for the cell with the I2 additive, which is much higher than that of the control cell (80.1 %). The improved thermal stability achieved by the addition of I2 was also confirmed through electrochemical impedance spectroscopy (EIS) measurements of the cells before and after their storage. The addition of 0.05 wt % of I2 increases the cell impedance slightly before the storage (Figure 5.8a). However, after the storage (Figure 5.8b), the I2 additive significantly suppresses the rise of the semi-circle in the lower frequency region; this is related to the interfacial charge transfer reaction.[30,31] The results obtained thus far unequivocally suggest that I2 can serve as an electrolyte additive which effectively suppresses the swelling behavior and thermal degradation during storage at 90 °C. In addition, the cell with 0.05 wt % I2 exhibits cycle performance up to 400 cycles, comparable to the control cell (Figure 5.8c), which indicates that the I2 additive scarcely deteriorates the long-term cyclability of LIBs.

![Graph](image)

Figure 5.7 Thickness change during storage in an oven of LiCoO2/graphite pouch cells (760 mAh) with no additive (control) and 0.05 wt % I2. The cells were fully charged (SOC 100) before the storage.
Figure 5.8 Electrochemical impedance spectra of LiCoO$_2$/graphite pouch cells (760 mAh) with no additive (control) and 0.05 wt % I$_2$: (a) before and (b) after storage at 90 °C. (c) Cycle performances of pouch cells (760 mAh) with no additive (control) and 0.05 wt % I$_2$ at 25 °C.
5.3.3 Proposed mechanism for swelling prevention by the I$_2$ additive

In the previous sections, it was found that the effects of an addition of I$_2$ on the charge/discharge behavior are negligible after three cycles unless the I$_2$ amount is excessive (Figure 5.1 and Figure 5.2). It was also revealed that the self-discharge by I$_2$ is activated only when the cell is exposed to an abnormally high temperature (ca. 90 °C), whereas the I$_2$ shuttle reaction is insignificant at normal operation temperatures (< 60 °C).

To explain this temperature-responsive shuttle behavior of I$_2$, it is likely informative to refer to previous studies of the adsorption characteristics of I$_2$ and I$^-$ anion on solid electrode surfaces. There are numerous reports on the specific adsorption of I$^-$ on various metal surfaces,$^{[32-34]}$ including graphite electrodes.$^{[35,36]}$ It has also been reported that the oxidation of iodide species (I$^-$ and I$_3^-$) leads to the formation of an I$_2$ film layer on Pt and Ni electrode surfaces in both aqueous and propylene carbonate solutions.$^{[34,37,38]}$ Regarding the temperature-dependency of the iodide adsorption process, it was reported that the amount of iodide adsorbed onto organo-clay minerals decreases when the temperature exceeds 80 °C.$^{[39]}$

To confirm the adsorption behavior of iodide species, LiCoO$_2$ cathode and graphite anode surfaces were investigated by means of an XPS analysis. As shown in Figure 5.9a, a pristine LiCoO$_2$ cathode merely immersed in an I$_2$-containing electrolyte exhibits negligible iodine peaks. In contrast, the cathode retrieved from cycled LiCoO$_2$/graphite cells exhibits distinct I$_2$ peaks (I 3d$_{5/2}$ at 619.9 eV and I 3d$_{3/2}$ 631.1 eV)$^{[40]}$ The peak which appeared at 624 eV can be assigned to IO$_3^-$ or IO$_4^-$, possibly stemming from I$_2$ oxidation$^{[36,40]}$ but its magnitude is much smaller than those of I$_2$. A pristine graphite anode exhibits rather weak I$_2$ peaks which are scarcely altered after cycling (Figure 5.9b). In most current LIBs, the overall charge capacity of the cathode is designed to be lower than that of the anode to prevent possible Li deposition at the anode.$^{[41]}$ In this anode-limiting configuration, the cathode potential is higher than 3.5 V even in the fully discharged state (SOC 0)$^{[42,43]}$ Therefore, once the I$_2$ layer is formed on the cathode surface from the oxidation of iodide species (I$^-$ and I$_3^-$), it will remain there during the subsequent cycles (Figure 5.9a). In contrast, only the specifically adsorbed I$^-$ anion will be found at the anode, which explains the small amount of iodide on the anode in the XPS measurements (Figure 5.9b).
Figure 5.9 XPS spectra of (a) a pristine and a cycled LiCoO₂ cathode, and (b) a pristine and a cycled graphite anode. The pristine cathode and anode were immersed in an I₂-containing electrolyte and rinsed with DMC. The cycled cathode and anode were collected from cycled LiCoO₂/graphite coin cells.

Based on these prior reports, the temperature-activated latent shuttling behavior of I₂ can be rationalized, as schematized in Figure 5.10. The I₂ additive initially present in the electrolyte becomes adsorbed onto the electrode surface mostly as I₂ on the cathode, which is completed within a few initial cycles. The slightly higher impedance in an I₂-containing cell before the storage (Figure 5.8a) appears to be due to this I₂ adsorption on the cathode. Therefore, the concentration of the free I₂/iodide species in the electrolyte becomes negligible after a few initial cycles, thus showing no shuttling reaction. On the other hand, as the temperature is elevated above a threshold value (ca. 80–90 °C), the adsorbed I₂ is re-dissolved from the cathode into the electrolyte. Accordingly, the increased I₂ content will lead to enhanced shuttling and self-discharge reactions. The enhanced mobility of iodide species at an elevated temperature may also contribute to the shuttling reaction.

The threshold temperature and the threshold I₂ concentration, above which the shuttling reaction is activated, would depend on various cell parameters (i.e., the nature of the active materials, the electrode design, the cell size/capacity, and the relative amount of electrolyte to the active mass). Despite this complexity, this study suggests that there exists a proper I₂ amount that can maximize the thermal resilience of a given commercial LIB cell while minimizing the side effects (i.e., the failure of normal cell operation below the threshold
temperature). Our approach, which involves employing an I\(_2\) shuttle additive that induces reversible internal discharge, is a completely new concept which differs from previous approaches that rely on the passivation of the electrode/electrolyte interface either by a surface coating or by using electrolyte additives. Along with the low cost and environmental inertness of I\(_2\), the fact that only a small quantity (e.g., less than 0.1 wt %) is required makes I\(_2\) a promising electrolyte additive for thermally robust LIBs. The swelling-prevention strategy proposed in this study is expected to be readily applied to LIBs employing other cathode materials, including Ni-rich and high voltage (> 4.3 V) cathodes, which that are more vulnerable to high-temperature swelling.

![Figure 5.10 Schematic diagram of the temperature-responsive shuttle behavior of I\(_2\).](image)

**5.4 Conclusions**

This study demonstrated that when utilized at appropriate amounts, I\(_2\) can serve as an effective electrolyte additive to prevent the swelling of commercial 4 V LiCoO\(_2\)/graphite Al-pouch cells during storage at 90 °C. In this novel strategy to prevent swelling, self-discharge by I\(_2\) shuttling is activated only when a fully charged cell is exposed to a temperature of 90 °C, which lowers the SOC of the cell and renders it less prone to swelling. It was also confirmed that the I\(_2\) additive scarcely deteriorates the long-term cyclability while also scarcely increasing the electrochemical impedance of the LiCoO\(_2\)/graphite cells. The temperature-responsive shuttle mechanism of I\(_2\) was ascribed to the fixation of I\(_2\) via preferential adsorption on the cathode surface, which is facilitated during the charge process. The new strategy introduced herein has a number of critical advantages, including the low content levels (< 0.1 wt %), low cost, and environmentally friendly properties of I\(_2\). This
study also suggests a novel application of redox shuttle additives for swelling prevention in 4 V LIBs during high-temperature storage for the first time to the best of our knowledge.
5.5 References

[40] Distributed by the Measurement Services Division of the National Institute of Standards and Technology (NIST), Material Measurement Laboratory (MML), NIST is an agency of the U.S. Department of Commerce. http://srdata.nist.gov/xps/selEnergyType.aspx/, 2000 (accessed 16.04.21).
VI. A versatile sodium phosphate additive for enhanced thermal stability of spinel and layered cathodes of Li-ion batteries

6.1 Introduction

Current Li-ion batteries (LIBs) heavily depend on layered and spinel materials for cathodes because they provide conspicuous advantages, including high power and energy densities, and have been widely studied. Although LIBs have been successfully commercialized, a remarkable improvement in the energy densities of LIBs will be necessary to satisfy society’s needs for high energy density, for application such as electric vehicles (EVs) and grid storage. High energy density in a LIBs can be attained by increasing the reversible capacity of the electrodes, or by increasing the operating potential of the cathode. For example, in the case of commercially available spinel type LiMn$_2$O$_4$ (LMO), due to its superior electrochemical performance, low cost, and environmental inertness, LMO is considered a promising cathode material for LIBs. However, lithium hexafluorophosphate (LiPF$_6$)-based electrolytes are inevitably contaminated by a detrimental byproduct, hydrogen fluoride (HF), which causes fatal metal dissolution of cathode materials and unwanted side reactions on the anode materials. It is generally known that Mn dissolution is associated with a disproportionation which liberates soluble Mn$^{2+}$ into electrolyte: Mn$^{3+}$ (electrode) $\rightarrow$ Mn$^{4+}$ (electrode) + Mn$^{2+}$ (electrolyte). Then, the dissolved Mn$^{2+}$ moves to the anode and exacerbates degradation of the anode/electrolyte interface, which is revealed to be a key failure mechanism of LMO-based LIBs at elevated temperature.

Similarly, the spinel type LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) with high operating voltages (4.7 V vs. Li/Li$^+$) suffer from Mn dissolution and the severe oxidative decomposition of electrolyte solutions beyond the upper voltage limit of LiPF$_6$-carbonate electrolyte, around 4.3 V vs. Li/Li$^+$. As a result, large irreversible capacities are observed for the LNMO. In addition, increasing the cut-off voltage of LiNi$_x$Co$_{y}$Mn$_{z}$O$_2$ (NCM) would catalyze the decomposition reaction of the electrolyte due to its high oxidizing activity, resulting in severe capacity fading of the battery.
Functional additives are efficient and economic materials, which form a protective layer on the cathode and improve the thermal stability of various cathodes by preventing electrolyte decomposition in highly oxidizing environments. In recent years, various additives have reported that the long term stability is improved by using electrolyte additives that can suppress unwanted electrolyte decomposition via the formation of a protective layer on the cathode surface. For example, Li salt additives improves the long term stability both the cathodes and graphite anodes and tris (trimethylsilyl) borate and tris (trimethylsilyl) phosphate additives affects only the cathodes. The most recently reported tris (trimethylsilyl) phosphite is known to modify the cathode surface and remove HF from the electrolyte.

We herein report sodium phosphate (hereafter P2) additive, to scavenge fatal HF from electrolytes, and to eliminate severe electrolyte decomposition at high temperature. Furthermore, from an investigation of the surface chemistry on the SEI on various cathodes and anodes via X-ray photoelectron spectroscopy (XPS), we propose the possible mechanisms of effect of the P2 additive, improving the thermal stability of LiMn$_2$O$_4$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathodes in full- and symmetric-cells. In addition to, the P2 additive is expected to be universally applicable to many other LIB electrodes that similarly suffer from limitations in thermal stability.

6.2 Experimental

6.2.1 Chemicals and electrode preparation

The electrolyte with and without 1 wt% sodium phosphate monobasic (P2, Aldrich) was composed of commercially available 1.0 M LiPF$_6$ dissolved in a solvent mixture of ethylene carbonate (EC, Panaxetec) and ethyl methy carbonate (EMC, Panaxetec) in 3:7 volume ratio. For the electrochemical tests, the cathode electrodes were fabricated on Al foil using 90 wt% LiMn$_2$O$_4$ (LMO, POSCO ESM), LiNi$_{0.3}$Mn$_{1.7}$O$_4$ (LNMO, LG Chem), and LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811, ECOPRO) with 5 wt% polyvinylidene fluoride (PVdF) binder and 5 wt% conductive carbon. The specific capacities of cathode were LMO (1.30 mAh cm$^{-2}$), LNMO (1.17 mAh cm$^{-2}$), and NCM811 (2.60 mAh cm$^{-2}$), respectively. The composition of the graphite electrode was 95 wt% artificial graphite, 3 wt% PVdF binder, and 2 wt% conductive carbon. The specific capacity of the anode for
a full cell coupled with the cathodes. The microporous polyethylene film (PE, Tonen) was used as a separator, and its thickness was 20 μm.

6.2.2 Electrochemical measurements

To estimate the oxidation potential of the base and P2 electrolyte, linear sweep voltammetry (LSV) was employed with a three-electrode configuration. A Pt disk (area = 0.02 cm²) was used as the working electrode. Reference and counter electrodes were Li foil and Pt wire, respectively. Electrochemical experiments were carried out with a VSP potentiostat (BioLogic). Preparation in an Ar atmosphere glove box where H2O and O2 concentrations were kept below 5 ppm. The reduction behavior of the base and P2 electrolyte was examined using the differential capacity curve (dQ/dV vs. V) at the first lithiation process of graphite/Li coin cells at 0.1 C current.

For the battery tests, electrochemical tests were performed using 2032 coin-type cells assembled in an argon-filled glovebox. Full cells with graphite and LMO, LNMO, and NCM811 cathode were precycled at a rate of C/5, thereafter the cells were cycled at a current density of C/2 rate for 150 cycles at high temperatures. The cycle tests were carried out for LMO/LMO, LNMO/LNMO, NCM811/NCM811, and graphite/graphite symmetric cells at 60 oC at 0.5 C. The symmetric cells were fabricated by employing electrodes with a state-of-charge (SOC) of 50 collected from Li half cells that had been cycled three times. For the storage tests, fully charged full cells were stored at 60 oC. The discharge rate performance of the full cells were examined at 0.2 C CC/CV charge and at various discharge rates from 0.5 C to 5 C. The battery charge/discharge tests were carried out using a battery cycler (Toscato-3000, Toyo System) equipped with temperature chambers.

6.2.3 Material Characterization

After precycling and storage test, the cells were carefully disassembled in a glovebox to collect their electrodes. The electrodes were rinsed in dimethyl carbonate (DMC) to remove the residual LiPF6-based electrolyte and dried inside a glove box. (H2O ≤ 5 ppm, O2 ≤ 5 ppm, and temperature 25±1 oC). The surface compositions of the cathode electrodes (LMO, LNMO and NCM811) and graphite anodes were examined using X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Scientific). The amount of
manganese, nickel, and cobalt ions in the electrolyte that had come into contact with cathodes at 60 oC storage test was measured by means of atomic absorption spectroscopy (AA-7000, Shimadzu).

6.3 Results and discussion

6.3.1 Formation and property of the CEI layer on the cathodes

Generally, the cathode additive should be oxidized prior to main solvents of electrolyte.\(^{[23]}\) To evaluate the oxidation potential of the P2, linear sweep voltammetry (LSV) experiments were performed with a three-electrode cell. As shown in Figure 6.1a, the electrolyte containing P2 additive (hereafter P2 electrolyte) oxidizes from 4.25 V (vs. Li/Li'). In comparison, the electrolyte without P2 additive (hereafter base electrolyte) displays lower oxidation current than that of P2 electrolyte. Also, the oxidation current of P2 electrolyte is smaller after the first anodic scan, the P2 additive appears to modify the cathode surface during the first charging process. The results illustrate that P2 additive has a lower oxidation potential than carbonate solvents, which suggest P2 additive will decomposed before the main solvents of electrolyte. In addition, the oxidation products of P2 additive change the surface composition of the cathode.

To verify the presence of the surface film on the cathode, X-ray photoelectron spectroscopy (XPS) measurements were performed for the cathode electrodes cycled three times in base and P2 electrolytes. A Na 1s peak corresponding to NaH$_2$PO$_4$ (1072.0 eV) is clearly observed on the LNMO cathode cycled in P2 electrolyte, while it is absent on the cathode cycled in base electrolyte (Figure 6.1b). Figure 6.2 shows the P 2p XPS spectra for the cathodes with and without the P2 additive. A pronounced peak corresponding to NaH$_2$PO$_4$ containing compounds appeared at 134.10 eV, slightly lower than the binding energy of LiPF$_6$ (~137 eV) in the P2 electrolyte. This P-O group was produced by decomposition of P2 at the cathode; therefore, P2 contribute to the formation of the SEI on the cathodes. Only the LiPF$_6$ salt decomposition peak P-O (134.2 eV) of the LNMO cathode overlaps the peak position of the P2 electrolyte because of salt decomposition during high-voltage charging process. These clearly indicate that P2 additive forms a surface film on the cathodes via anodic decomposition. To examine the impact of P2 on the anode side, the differential capacity curves (dQ/dV vs. V) of graphite anodes in base and P2 electrolytes are presented in Figure 6.1c. During the first lithiation
process, the graphite anode in base electrolyte showed a distinct reduction peak at ca 0.62 V, which is attributed to the reduction of EC, and the concomitant formation of the solid electrolyte interphase (SEI) layer.[28-30] The graphite in the P2 electrolyte also exhibited a quite similar dQ/dV profile. In addition, no Na1s peak was observed on the graphite anode cycled in P2 electrolyte (Figure 6.1d). These verify that P2 hardly affect the SEI formation on graphite anodes.

Figure 6.1 (a) Linear sweep voltamograms of 1 M LiPF₆ EC/EMC (3/7, v/v) solutions with no additive and P2 additive. Pt (area = 0.02 cm²) working electrode. Scan rate was 50 mV s⁻¹. (b) Na 1s XPS spectra for the LNMO cathode precycled in base electrolyte and P2 electrolyte. (c) dQ/dV graphs of graphite anodes with base electrolyte and P2 electrolyte during the 1st cycle lithiation process. (d) Na 1s XPS spectra for the graphite anodes precycled in base electrolyte and P2 electrolyte.
6.3.2 The effect of P2 additive

The effect of the P2 additive in the electrolyte was examined by cyclic voltammograms (CVs). The HF titration was performed to directly measure the change of HF content in the electrolyte by addition of the P2 additive. However, there was a problem that the HF content can not be accurately measured by the conventional acid-base titration method because the P2 additive is acidic chemical in itself. To solve this problem, the amount of HF reduction by electrochemical experiments was indirectly measured. Figure 6.3a shows the maximum peak current of the CVs according to HF content on a Pt electrode in the base and P2 electrolyte.
Figure 6.3 (a) Maximum peak current of HF reduction CVs of 1 M LiPF₆ EC/EMC (3/7, v/v) solutions with no additive and P2 additive. F 1s XPS spectra of (b) cathodes and (c) graphite anodes after precycle at 25 °C.
Figure 6.4 Cyclic voltammograms of 1 M LiPF$_6$ EC/EMC (3/7, v/v) solutions with no additive and P2 additive. Pt (area = 0.02 cm$^2$) as a working electrode. Scan rate = 10 mV s$^{-1}$.

During the first cathodic scan, the reduction peaks appearing between 2.0 V and 3.0 V are known to be associated with HF reduction (Figure 6.4).[31] In our measurements, the initial HF concentrations of the base and P2 electrolyte were the same at 20 ppm, and two electrolytes showed almost similar peaks. To clearly distinguish electrolyte differences at various HF concentrations, both electrolyte was deliberately added with 200, 600, and 1000 ppm HF. It is found that the HF reduction currents in the P2 electrolyte are more effectively suppressed at high HF concentration: the current of HF reduction is decreased as the HF content is increased from 200 to 1000 ppm. This is because P2 electrolyte eliminates the HF in the electrolyte (HF + NaH$_2$PO$_4$ → NaF + H$_3$PO$_4$). Comparing the pKa values (pKa (HF) = 3.17, pKa (H$_3$PO$_4$) = 2.12), the reverse reaction is dominant in aqueous solutions, but it is expected that the forward reaction will be possible with organic solvent systems.

To investigate the surface chemistry mechanisms of the cathode with and without the P2 additive, XPS was performed after the precycle at 25 °C. Figure 6.3b and c shows the F1s XPS spectra for the cathode and anode with and without the P2 additive, respectively. The F 1s XPS spectra of Figure 6.3b and c show two major peaks; one corresponds to the P-F (687 eV) bond formed by LiPF$_6$ decomposition and the other is attributed to LiF (685 eV) created by the reaction of HF with Li cation. The LiF content of P2 electrolyte on the surface of LMO and NCM811 cathodes was much lower than that of the base electrolyte, it means that the P2 electrolyte effectively reduces LiF formation by decreasing HF from the electrolyte. In the case of LNMO
cathodes, the LiF content of P2 electrolyte was slightly lower than that of the base electrolyte due to the high operating voltage. In addition, a metal dissolution experiment was conducted to compare HF differences with and without P2 additive. A fully lithiated (state of charge 0, SOC 0) cathodes were immersed in the electrolyte and stored at 60 °C for 48 h. The amount of transition metal ions in the base and P2 electrolyte were measured using atomic absorption spectrometry (Figure 6.5). The P2 electrolyte had a relatively low transition metal ion content compared to the base electrolyte, and the amount of manganese from NCM811 electrode is negligible. This is because the HF scavenging effect of P2 additive is enough to suppress the transition metal dissolution from the LMO, LNMO cathodes at 60 °C.

![Figure 6.5](image_url) A comparison of transition metal dissolution behavior from the bare (a) LMO, (b) LNMO, and (c) NCM811 cathode electrodes with and without a P2 additive. Cathode electrodes were stored in the base electrolyte at 60 °C for 2 days.

### 6.3.3 Cycling and storage performances

Figure 6.6 shows an improvement in the cycling stability and a decrease in accumulated irreversible capacity of full cells with P2 additive. A high accumulated irreversible capacity indicates severe parasitic reactions in full cells.[32] In the case of LMO full cells, the discharge capacity retention with P2 electrolyte was drastically improved compared with the base electrolyte from 20.74 % to 49.50 % at 60 °C. Moreover, a very low accumulated irreversible capacity was obtained for the full cell with P2 electrolyte. The capacity retention of LNMO full cells were similar in the base and P2 electrolyte, but the accumulated irreversible capacity was much lower in the P2 electrolyte. This suggests that more parasitic reactions are occurring with base electrolyte although similar capacity retention is observed.[33] The capacity of the base electrolyte faded during cycling
and had a very unstable, high accumulated irreversible capacity. These parasitic reactions are likely promoted by the traces of HF unavoidably present in electrolyte. This is expected to be due to undesired electrolyte decomposition at the cathode cycled with a high temperature (55 °C) and high voltage in a full cell and the loss of reversible capacity by manganese metal deposition on the graphite. We assume that the metal ions dissolved out of the cathode cause the capacity of a full cell to fade considerably because the dissolved metal ions migrate toward the graphite anode under the deposition of metal ions leading to degradation of graphite anode. This finding suggests that severe oxidative decomposition of the electrolyte caused by the high charge cutoff voltage and the dissolution of metal ions by HF attack are effectively reduced by using the P2 additive.

In the case of layered NCM811 cells, capacity degradation and irreversible capacity of base electrolyte were not as large as those of the spinel cells, however, the evaluation of cycle performance was not able to be continued due to the continuous charging during the CV charging range in 99th cycle. The P2 electrolyte showed improved cycle performance and efficiency at 60 °C.

Figure 6.6 (a) Cycle performance and (b) accumulated irreversible capacity of the LMO/graphite, LNMO/graphite, and NCM811/graphite full cells. Charging and discharging with 0.5 C current followed by constant voltage.
To further clarify the effect of phosphate on the P2 additive, the cycle performance at high temperature was carried out with an additive in which NaH$_2$PO$_4$ was replaced with LiH$_2$PO$_4$ (Figure 6.7). The performance of LiH$_2$PO$_4$ additive was not as good as that of P2 additive but was superior to that of base electrolyte. As a result, the superior performance of P2 additive is due to dihydrogen phosphate ion (H$_2$PO$_4^-$).

![Figure 6.7](image)

Figure 6.7 (a) Cycle performance and (b) accumulated irreversible capacity of the LMO/graphite, LNMO/graphite, and NCM811/graphite full cells. Charging and discharging with 0.5 C current followed by constant voltage.

In addition, the rate capabilities of the base and P2 electrolyte were assessed by measuring discharge (delithiation) capacities at a series of current densities up to 5 C at 25 oC. The P2 electrolyte exhibited equivalent or superior rate capability (Figure 6.8). This suggests that the P2 additive contributes to the improvement of the high temperature performance without adversely affecting the charge transfer.
Figure 6.8 (a) Discharge rate capability of LMO/graphite, LNMO/graphite, and NCM811/graphite full cells.

Figure 6.9 Cycle performance of the (a) LMO, (b) LNMO, (c) NCM811, and (d) graphite symmetric cells at 60 °C. Charging and discharging with 0.5 C current followed by constant voltage.
To clarify the effect of P2 additive on the anode and cathodes, the cycling performances of LMO, LNMO, NCM811, and graphite symmetric cells at 60 °C are presented in Figure 6.9. The capacity retention of LMO symmetric cells at a rate of C/2 was dramatically improved from 56.44% to 86.04% by using the P2 additive. P2 additive forms a protective surface layer and scavenges HF that effectively suppresses Mn dissolution and electrolyte oxidative decomposition at high temperature during cycling. In the case of LNMO symmetric cells, they were examined at harsh temperature, resulting in a significant degradation in cycle performance, although the P2 additive exhibited better capacity retention. Unlike the LMO and LNMO symmetric cells, a comparison of the reversible capacity of the NMC811 and graphite symmetric cells showed that the discharge capacity of the P2 electrolyte is slightly superior to that of base electrolyte at 60 °C during 100 cycles. The degradation of NCM811 is mainly due to the formation of Ni^{2+} on the surface of the cathode, not the metal dissolution.\cite{34} It prevents the formation of Ni^{2+} through the formation of P2-derived film and also alleviates the electrolyte oxidation (Figure 6.10).

In the case of graphite symmetric cells, P2 additive does not modify the SEI components but the suppression of SEI degradation due to the reduced HF in the electrolyte improves the high temperature cycle performance. The F 1s spectra of Figure 6.3c show LiF created by the reaction of HF with the SEI components, such as Li$_2$CO$_3$ (2HF + Li$_2$CO$_3$ $\rightarrow$ 2LiF + H$_2$O + CO$_2$). In the case of the graphite precycled in the P2 electrolyte, the LiF peak was discernibly lower. This means that P2 effectively mitigates LiF formation by eliminating HF from the electrolyte, as depicted in Figure 6.3a.

![Figure 6.10 Ni 2p XPS spectra of NCM811 cathode after storage test at 60 °C.](image-url)
To further understand the effect of P2 additive on the cathode surface, a high temperature storage OCV change test was conducted. The potential drop during storage was a direct measure of the electrolyte oxidation occurring at the cathode side.\textsuperscript{35} The high temperature storage performance of LMO, LNMO, and NCM811 full cells with and without P2 additive was investigated at 60 °C, as displayed in Figure 6.11a. There was a significant open-circuit voltage (OCV) drop in the full cells with the base electrolyte. It is generally accepted that the poor cycling performance of the LMO and LNMO cells originate from the dissolution of manganese metals from spinel cathode into electrolyte. However, unlike the base electrolyte, the P2 electrolyte led to a
slight OCV drop in the full cells. This indicates that the P2-derived cathode layer is thermally stable and robust enough to prevent continuous electrolyte oxidative decomposition. In addition, the P2-originated passivation layer hinders the dissolution of transition metal ions from the cathode and thereby avoids the detrimental effects of the dissolved transition metal ions in the cells. Indeed, XPS results show a much lower content of Mn on the graphite electrode of the full cell cycled in the P2 electrolyte (Figure 6.11b), which provides evidence for the effective inhibition of transition metal dissolution in the P2 electrolyte. In short, the main reasons for improved storage performance are that the content of HF in the P2 electrolyte is lower than that of the base electrolyte and P2 additive forms surface coatings to mitigate metal dissolution and soluble Mn$^{2+}$ formation at spinel cathode surface. In the case of NCM811, the metal eluted from the graphite surface could not be identified because the degradation mechanism of layered NCM811 is different from metal dissolution of spinel cathode.

The surface of the NCM811 surface was observed by using XPS in order to identify the main reason of the deterioration of the nickel-rich electrode due to the reduction of the nickel. The increasing intensity of Ni$^{2+}$ (858 eV) in the surface is observed by XPS of the base electrolyte after storage test. These Ni$^{2+}$ species have originated from the reduction of Ni$^{4+}$ surface species. On the contrary, the intensity of Ni$^{2+}$ in the P2 electrolyte are much lower than those of the base electrolyte after storage. In other words, the reduction process of Ni$^{4+}$ to Ni$^{2+}$ on the base electrolyte during storage is more severe, which is the possible trigger for the chemical reactions to form NiF$_2$. The HF can react with Ni$^{2+}$ ions produced during the discharge process which results in the formation of NiF$_2$ on the cathode. Since the P2 additive can act as a scavenger for HF in the electrolyte, the formation of NiF$_2$ on the cathode with P2 additive could be suppressed and thus OCV decreasing could be minimized. Although HF is not entirely removed from the P2 electrolyte, the P2-derived SEI layer is expected to block the HF attack toward the cathode, as seen in the schematic representation of Figure 6.12. The P2 electrolyte can scavenge HF and forms P2-derived SEI layer, which suppresses the metal dissolution from the spinel cathodes and electrolyte oxidation at high temperature, leading to superior thermal stability.
Figure 6.12 A conceptual scheme depicting the beneficial effects of P2 additive. The P2 electrolyte can scavenge HF and forms P2 additive derived CEI layer, which otherwise exacerbates the metal dissolution from the spinel cathodes and electrolyte oxidation at high temperature, leading to superior thermal stability.

6.4 Conclusions

We report P2 additive for improving thermal stability of LMO, LNMO, and NCM811 cathode materials, which eliminated HF from the electrolyte and modified the cathode surface without effect of the graphite anode. The P2 additive improved the high temperature cycle and storage performance dramatically. Along with the versatile advantages regardless of the type of cathodes, it is expected that P2 additive can be extended to various active materials for current and next generation LIB, where thermal stability is very important. At the same time, phosphate derivatives are also good candidates for future investigation.
6.5 References


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Ⅶ. Analysis of physicochemical properties and superior rate performance of superconcentrated salt electrolytes

7.1 Introduction

Recently, Yamada group reported super-saturated acetonitrile (AN) solutions (> 4 M) as a promising for Li-ion battery (LIB) electrolytes exhibiting ultrafast-charging character, contrary to the general belief that AN electrolytes fail to operate Li metal anodes due to their poor reductive stability.[1]

![Figure 7.1 Charge–discharge profiles of a natural graphite/Li cell with 4.2 M LiTFSI/AN electrolyte at C/10 rate.](image)

Figure 7.1 Charge–discharge profiles of a natural graphite/Li cell with 4.2 M LiTFSI/AN electrolyte at C/10 rate.

According to the Yamada group’s report, a graphite anode displays a reversible charge-discharge behavior in 4.2 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/AN electrolyte as shown in Figure 7.1. It was claimed that during the first lithium intercalation into graphite, TFSI\(^-\) anions, instead of AN solvents, are predominantly reduced to form a stable solid electrolyte interphase (SEI) layer.[1] Furthermore, 4.5 M lithium bis(fluorosulfonyl)imide (LiFSI)/AN electrolyte exhibited much faster charge-rate capability than a conventional carbonate-based electrolyte (Figure 7.2).
Figure 7.2 (a) Lithium intercalation voltage curves of a natural graphite/Li cell with 4.5 M LiFSI/AN and commercial 1.0 M LiPF<sub>6</sub>/EC:DMC (1/1, v/v) electrolytes at various C-rates (C/20, C/2, 1C, and 2C) at 25 °C. (b) Reversible capacity of natural graphite in the two electrolytes at various C-rates and 25 °C. Charge and discharge were conducted at the same C-rate without using a constant-voltage mode at both ends of charge and discharge, and the charge (lithium deintercalation) capacity was plotted.[1]

It is widely known that the Al corrosion issue is a major bottleneck for the imide salt electrolytes. Figure 7.3 shows chronoamperograms of an Al electrode at 4.5 V in 3–6 M LiFSI/AN electrolytes. In 3 M and 4 M electrolytes, the anodic current substantially increased with time, which is due to anodic Al corrosion reaction. On the other hand, 5 M and 6 M LiFSI/AN electrolytes resulted in remarkably decreased Al oxidation currents. The suppressed Al corrosion was ascribed to the fact that the free solvent molecules responsible for dissolution ability is eliminated through coordination to Li<sup>+</sup> ions in such a concentrated electrolyte.[2]
The physicochemical properties of LiFSI/AN solutions are shown in Table 7.1. 5–6 M LiFSI/AN solutions exhibit the ionic conductivity as high as 3–7 mS cm\(^{-1}\), which is in commercially acceptable range. However, the viscosity dramatically increases above 5 M, which may lead to poor wetting of polyolefin separators.

**Table 7.1 Physicochemical properties of LiFSI/AN solutions at 30 °C.**\(^{[2]}\)

<table>
<thead>
<tr>
<th>Concentration(^{[3]}) [mol dm(^{-3})]</th>
<th>Molar ratio (AN/LiFSI)</th>
<th>Density [g cm(^{-3})]</th>
<th>Ionic conductivity [mS cm(^{-1})]</th>
<th>Viscosity [mPa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>17</td>
<td>0.89</td>
<td>50</td>
<td>0.69</td>
</tr>
<tr>
<td>3.0</td>
<td>4.7</td>
<td>1.14</td>
<td>29</td>
<td>4.0</td>
</tr>
<tr>
<td>4.0</td>
<td>3.1</td>
<td>1.26</td>
<td>16</td>
<td>9.0</td>
</tr>
<tr>
<td>5.0</td>
<td>2.1</td>
<td>1.37</td>
<td>7.1</td>
<td>37.7</td>
</tr>
<tr>
<td>6.0</td>
<td>1.5</td>
<td>1.48</td>
<td>3.3</td>
<td>153</td>
</tr>
</tbody>
</table>

In this study, the claimed effects of superconcentrated salts/AN electrolytes were scrutinized. First, the ionic conductivity and reductive stability against Li metal are examined. Second, the fast-charge capability of the superconcentrated LiFSI/AN electrolytes are investigated in relation to the charge protocol and the active mass loading of the graphite electrodes. Finally, the effects of salt concentration on the anodic corrosion of Al and SUS are re-investigated.
7.2 Experimental

7.2.1 Chemicals and electrode preparation

Acetonitrile and LiTFSI were purchased from Aldrich. Battery grade LiFSI salt and 1 M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, v/v) were provided by Panaxetec. The natural graphite electrode was fabricated on Cu foil (10 μm thick) using polyvinylidene fluoride (PVdF) binder (10 wt%) with a coin cell capacity of 0.7 mAh (an active material loading of 1.3 mg cm$^{-2}$). The artificial graphite electrode was fabricated on Cu foil (10 μm thick) using polyvinylidene fluoride (PVdF) binder (3 wt%) and conductive carbon (2 wt%) with a coin cell capacity of 2.0 and 3.0 mAh (an active material loading of 4.0 and 5.5 mg cm$^{-2}$).

7.2.2 Electrochemical measurements

For the battery tests, 2032 coin cells were employed by integrating the same graphite electrode mentioned above and Li metal with a polyethylene (20 μm, Tonen) and glass fiber separators. The SEI formation behavior was examined by differential capacity (dQ/dV) curveduring the first lithiation process of the graphite/Li coin cells at 0.05 C constant current (CC). Charge and discharge tests of the graphite/Li cells were conducted via two different protocols: (1) According to the Yamada group [1], the test was conducted at the same C-rate without using a constant voltage (CV) mode at both ends of charge and discharge. (2) Following the conventional protocol, the discharge rate performance was examined at 0.2 C CC/CV charge and at various discharge rates from 0.2 C to 5 C. The charge rate capability was examined at 0.2 C CC discharge and at various charge rates from 0.2 C to 5 C. To quantify the charging performances, the ratio of CC charge capacity to total charge capacity was calculated. The battery tests were carried out using a battery cycler (Toscat-3000, Toyo System) equipped with temperature chambers. Electrochemical impedance spectroscopy (EIS) measurements were carried out for graphite/Li half cells and graphite/graphite symmetric cells with a VSP potentiostat (BioLogic) over a frequency range from 300 kHz to 10 mHz with an amplitude of 5 mV.

For the corrosion study, all the electrochemical experiments were carried out using a three-electrode systems with a flooded cell (polyethylene round bottle) with 2.5 ml±0.1 of electrolyte in an Ar-filled glove box. An Al rod (0.07 cm2) and SUS rod (0.07 cm2) were used as a working electrode. Li foil and Pt wire were
used as a reference electrode and counter electrode, respectively. The Al and SUS working electrodes were polished on emery paper (#1200, 15 μm grit size). Cyclic voltammetry (CV) was performed over 3–6 V (vs. Li/Li+) with a scan rate of 10 mV s⁻¹. The ionic conductivities of electrolytes were measured at 25 ºC with an ionic conductometer (Thermo Scientific). Before each measurement, the electrolyte sample was kept for 30 min at a given temperature.

7.3 Results and discussion

7.3.1 Ionic conductivity and reductive stability against Li metal

The ionic conductivities of LiFSI/AN electrolytes are presented in Table 2.2. 5 M LiFSI/AN solution shows ionic conductivity of 7.6 mS cm⁻¹ despite its high viscosity. The measured value (7.6 mS cm⁻¹ at 25 ºC) is similar slightly to the reported value (7.1 mS cm⁻¹ at 30 ºC).[2]

<table>
<thead>
<tr>
<th>LiFSI Concentration (mol dm⁻³)</th>
<th>Conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>47.0</td>
</tr>
<tr>
<td>2.0</td>
<td>48.5</td>
</tr>
<tr>
<td>3.0</td>
<td>33.4</td>
</tr>
<tr>
<td>4.0</td>
<td>16.6</td>
</tr>
<tr>
<td>5.0</td>
<td>7.6</td>
</tr>
</tbody>
</table>

As a visible indicator of reductive stability, we monitored the degradation behaviors of lithium metal stored in LiPF6/carbonate, LiTFSI/AN, and LiFSI/AN solutions (Figure 7.4). Concentrated (> 3 M) LiPF6/AN electrolytes were solidified with significant heat generation. The lithium metal was found to be highly unstable in all the electrolytes except 5 M LiFSI/AN; the lithium metal was dissolved and the electrolytes turned yellow.
within 24 h. AN is supposed to be reduced by lithium metal to produce a highly toxic free cyanide, as follows.

\[ \text{CH}_3\text{CN} + 2\text{Li} \rightarrow \text{CH}_3\text{+} + \text{CN}^- + 2\text{Li}^+ \]

Also, the degradation of lithium metal was accelerated when the ratio of electrolyte/Li metal is lowered to be comparable to that in the coin cells (Figure 4.4b). This implies that the electrolyte depletion would be severe in the coin half cells.

### (a) 5 ml Electrolytes + Li metal (0.5 cm X 0.5 cm)

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>1M LiPF$_6$ in AN</th>
<th>1M LiTFSI in AN</th>
<th>3M LiTFSI in AN</th>
<th>5M LiTFSI in AN</th>
<th>1M LiFSI in AN</th>
<th>3M LiFSI in AN</th>
<th>5M LiFSI in AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>discoloration time</td>
<td>Immediately</td>
<td>2 hours</td>
<td>24 hours</td>
<td>24 hours</td>
<td>2 hours</td>
<td>2 hours</td>
<td>2 hours</td>
</tr>
</tbody>
</table>

### (b) 400 ul Electrolytes + Li metal coin size (1.54 cm$^2$)

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>1M LiPF$_6$ in AN</th>
<th>1M LiTFSI in AN</th>
<th>3M LiTFSI in AN</th>
<th>5M LiTFSI in AN</th>
<th>1M LiFSI in AN</th>
<th>3M LiFSI in AN</th>
<th>5M LiFSI in AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>discoloration time</td>
<td>Immediately</td>
<td>Immediately</td>
<td>Immediately</td>
<td>2 hours</td>
<td>Immediately</td>
<td>Immediately</td>
<td>Immediately</td>
</tr>
</tbody>
</table>

Figure 7.4 Chemical reactivity of lithium metal in LiPF$_6$/AN, LiTFSI/AN, and LiFSI/AN solutions at room temperature. (a) 0.5 x 0.5 cm$^2$ Li metal in 5 ml electrolytes and (b) Li coin (1.54 cm$^2$) in 0.4 ml electrolytes.

### 7.3.2 The 1$^{st}$ cycle behaviors in superconcentrated AN electrolytes

The differential capacity (dQ/dV) curves of thin graphite/Li cells (0.8 mAh) during the first charge (lithiation) process in 1 M LiPF$_6$/carbonate, 4.2 M LiTFSI/AN, and 4.5 M LiFSI/AN are presented in Figure 7.5. During the first lithiation of graphite anodes, the reduction peaks appearing above 0.4 V are known to be associated with electrolyte/additive reduction, which leads to SEI formation. In our measurements, 1 M LiPF$_6$/EC:DMC (1:1, v:v) displayed a reduction peak at ca. 0.7 V and the 4.5 M LiFSI/AN showed a distinct
reduction peak at ca. 1.2 V, which are attributed to the reduction of EC and LiFSI, respectively. The 4.2 M LiTFSI/AN exhibited a broad reduction peak at 1.2 V in addition to some reduction peaks around 0.3-0.5 V, which indicates that SEI layer derived in LiTFSI/AN is not as robust as that formed in the other two electrolytes. For these reasons, 4.2 M LiTFSI/AN electrolyte displayed the lower coulombic efficiency than the others (Table 7.3 and 7.4).

Figure 7.5 Differential capacity (dQ/dV) curves of graphite/Li half cells with 1 M LiPF6 in EC/DMC (1/1, v/v), 4.2 M LiTFSI in AN, and 4.5 M LiFSI in AN electrolytes. (a) PE and (b) Glass fiber separators.

Table 7.3 Charge (Q_{ch}), discharge (Q_{dis}) capacities and the coulombic efficiencies (\eta_{1st}) at the first cycle of graphite/Li cells (PE separator).

<table>
<thead>
<tr>
<th>1st cycle (PE separator)</th>
<th>Q_{ch} [mAh g^{-1}]</th>
<th>Q_{dis} [mAh g^{-1}]</th>
<th>\eta_{1st} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M LiPF6 in EC/DMC (1/1, v/v)</td>
<td>371.3</td>
<td>323.8</td>
<td>87.2</td>
</tr>
<tr>
<td>4.5 M LiFSI in AN</td>
<td>355.2</td>
<td>324.6</td>
<td>91.4</td>
</tr>
<tr>
<td>4.2 M LiTFSI in AN</td>
<td>382.0</td>
<td>307.4</td>
<td>80.5</td>
</tr>
</tbody>
</table>

Table 7.4 Charge (Q_{ch}), discharge (Q_{dis}) capacities and the coulombic efficiencies (\eta_{1st}) at the first cycle of graphite/Li cells (Glass fiber separator).

<table>
<thead>
<tr>
<th>1st cycle (Glass Fiber separator)</th>
<th>Q_{ch} [mAh g^{-1}]</th>
<th>Q_{dis} [mAh g^{-1}]</th>
<th>\eta_{1st} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M LiPF6 in EC/DMC (1/1, v/v)</td>
<td>405.8</td>
<td>349.0</td>
<td>86.0</td>
</tr>
<tr>
<td>4.5 M LiFSI in AN</td>
<td>393.0</td>
<td>353.0</td>
<td>89.8</td>
</tr>
<tr>
<td>4.2 M LiTFSI in AN</td>
<td>492.9</td>
<td>355.0</td>
<td>72.0</td>
</tr>
</tbody>
</table>
7.3.3 Rate capability

The rate capability of thin graphite/Li cells (0.8 mAh) in 1 M LiPF$_6$ EC/DMC (1/1, v/v), 4.2 M LiTFSI AN, and 4.5 M LiFSI AN are compared in Figure 7.6. The charge (lithiation) and discharge (delithiation) were conducted at the same C-rate following Yamada group’s protocol. 4.5 M LiFSI/AN electrolyte exhibited superior charge rate capability at all C-rates to the other electrolyte systems, which is consistent with Yamada group’s results.[1] It is noted that compared to 1 M LiPF$_6$/carbonate, 5 M LiFSI/AN displays reduced overpotential at the beginning of discharge, which is mainly determined by IR drop and charge transfer overpotential. Because the ionic conductivities of the two electrolytes are similar to each other, the different overpotential can be attributed to the reduced charge transfer overpotential in 5 M LiFSI/AN.

![Figure 7.6 Rate capability of thin graphite/Li cells (0.8 mAh) with (a) PE and (c) glass fiber separators. Charge (lithiation) and discharge (delithiation) voltage profiles of the cells with (b) PE and (d) Glass fiber separators.](image)

- 99 -
In 4.2 M LiTFSI/AN, the reversible capacity significantly decreases with increasing C-rate, which seems to be due to its low ionic conductivity (0.98 mS/cm) or its high reactivity with Li metal (Figure 7.4). Figure 7.6b and 6d show voltage profiles at 2 C rate of the cells with PE and glass fiber separators, respectively. The cell with glass fiber separator exhibited higher charge and discharge capacities in both 1 M LiPF₆ EC/DMC and 4.5 M LiFSI/AN electrolytes, which can be ascribed to the reduced IR drops resulting from the glass fiber separator.

Figure 7.7 show the rate performances of thick graphite/Li half cells measured according to Yamada’s protocol. In contrast to the fact that in the thin graphite cells, 4.5 M LiFSI/AN exhibited lower rate performance. Recently, it was reported that as the loading level of the electrode increases, the ion transport within electrode pores becomes dominant rate-determining factor.[3,4] Considering this, it seems that the beneficial effect of 4.5 M LiFSI/AN in the charge transfer overpotential is diluted in the high-loading graphite electrode of which rate capability is more influenced by the ion transport within electrode pores.

![Graph showing rate capability and voltage profiles](image)

Figure 7.7 (a) Rate capability and (b) voltage profiles of thick graphite/Li cells (5mAh) with glass fiber separators. Charge and discharge were conducted according to Yamada’s protocol (only CC charge and discharge).
7.3.4 EIS analysis

The effect of electrode loading on the electrochemical impedance spectroscopy (EIS) of the graphite/Li cells are examined as shown in Figure 7.8. The thin graphite cell with 4.5 M LiFSI/AN exhibits significantly lower $R_{ct}$ that 1 M LiPF$_6$ in EC/DMC (1/1, v/v). This supports the fast-charge character is mainly due to the lower $R_{ct}$. However, even with a thick electrode, $R_{ct}$ is small, but $R_{ion}$ is too large due to the lower ionic conductivities of 4.5 M LiFSI/AN electrolytes. For thicker graphite cells, no significant difference in $R_{tot}$ ($R_{ion} + R_{ct}$) values between 1 M LiPF$_6$/carbonate and 4.5 M LiFSI/AN are observed. These results are consistent with the mitigated fast-charge performances shown in thick graphite cells.

Figure 7.8 Nyquist plots of Graphite/Graphite symmetric cells with (a) thin graphite (1.6 mAh), and (b) thick graphite (5 mAh).
7.3.5 Al and SUS corrosions

The cyclic voltammograms (CVs) of Al in 4.5 M and 6.0 M LiFSI/AN are compared in Figure 7.9. The anodic corrosion current begins to rise steeply above 5 V at the first anodic scan and keeps growing even after the scanning direction is reversed at 6.0 V, which indicates severe Al corrosion commonly observed in lithium imide solutions. Yamada group claimed that Al corrosion in 5 M LiFSI/AN is remarkably suppressed up to 4.5 V. Our study, however, reveals that Al corrosion problem still remains in super-saturated LiFSI/AN when the potential is increased above 4.5 V.

Figure 7.9 Cyclic voltammograms of Al electrodes at the first, second, and third cycles in (a) 4.5 M and (b) 6 M LiFSI in AN.

In the case of SUS, 1 M LiPF₆/carbonate do not show the counter-clockwise current response at the first cycle (Figure 7.10). In addition, the current at the subsequent cycles keeps decreasing in both solutions, manifesting their excellent passivating nature against Al oxidation. However, in 6.0 M LiFSI/AN (Figure 7.11), the anodic corrosion current begins to rise steeply around 4 V at the first anodic scan. This implies that SUS corrosion is even more severe than Al corrosion and it will be a problem in the coin cell tests.
Figure 7.10 Cyclic voltammograms of Al electrodes at the first, second, and fifth cycles in LiPF$_6$ in EC/DEC (1/2, v/v).[6] 

Figure 7.11 Cyclic voltammograms of SUS electrodes at the first, second, and third cycles in 6 M LiFSI in AN. 

6 M LiFSI in AN

- SUS electrode
7.4. Conclusions

In this study, superconcentrated LiFSI/AN electrolytes were re-investigated focusing on its beneficial effects claimed in the previous reports.[1,2]

- The lithium metal is highly unstable in all the electrolytes tested in this study except 5 M LiFSI/AN electrolyte.

- The superconcentrated 4.5 M LiFSI/AN electrolyte exhibited fast-charge capability only when the thin graphite cell (< 1mAh) is tested via Yamada protocol (only CC charge mode). The fast-charge is not observed for thick graphite cells (≥ 2mAh).

- EIS study confirmed that the superior fast-charge performance of 4.5 M LiFSI/AN originates from much lower charge transfer barrier at the graphite/electrolyte interface, which is possibly related to the unique solution structure of the concentrated electrolytes. However, a very large $R_{\text{ion}}$ eliminates the fast charging effect of the high loading level graphite because of the low ionic conductivity of the superconcentrated electrolytes.

- Contrary to Yamada group’s claim, Al corrosion problem still remains in super-saturated LiFSI/AN. In addition, SUS corrosion is found to be more severe than Al corrosion, which should be addressed for this electrolyte to be considered in 4 V LIB cathodes.
7.5. References


요 약 문

고성능 리튬 이온 전지용 기능성 전해액 개발

본 논문은 고성능 리튬 이온 전지를 위한 새로운 첨가제와 코팅법 및 초고농도 전해액에 대한 연구이다. 폴리도파민 코팅을 흑연 음극에 적용하였고, 첨가제의 경우, 흑연 음극 성능 개선 첨가제, 양극 성능 개선 첨가제, 부피 평장 억제를 통한 안정성 항상 첨가제들을 개발하였다. 또한 희석 촉진 성능을 가진 초고농도 전해액 (LiFSI/AN)에 대한 분석을 진행하였다. 이를 정리하면 다음과 같다.

(1) 리튬 이온 배터리 (LIB) 용 흑연 음극에 폴리도파민 (PD) 코팅을 적용하였다. 폴리도파민 코팅은 기존의 전극 코팅 방법에 비하여 매우 간편하고 친환경적이며, 가격이 빠른 장점이 있다. PD 코팅 흑연 음극은 기존의 흑연 음극보다 항상된 리튬 이온의 탈/삽입 기능을 가능하게 함으로써 빠른 충/방전 성능을 보였으며, 향상된 고온 수명 성능을 보였다. 이는 흑연 음극의 solid electrolyte interphase (SEI) 층 아래쪽에 형성되어 있는 PD 층의 염기성 성질이 흑연 음극의 퇴화를 가져오는 HF 를 제거하고 리튬 이온의 탈/삽입을 보다 쉽게 해준다는 것을 밝혀냈다.

(2) 새로운 SEI 첨가제로써 3-fluoro-1,3-propane sultone (FPS)를 연구하였다. FPS 는 광범위한 온도 범위에서 리튬 이온 전지의 상용화된 첨가제인 vinylene carbonate (VC)와 1,3-propane sultone (PS) 보다 우수한 수명 성능을 나타내었다. 또한 FPS 는 VC 와는 대조적으로 우수한 열적 안정성을 보였다. 높은 산화 안정성, 우수한 열적 안정성을 바탕으로 FPS 는 기존의 VC 첨가제를 뛰어넘을 수 있는 첨가제로 제안하였다.

(3) 소량의 아이오딘 (I2)를 첨가제로 사용하여 상업용 4V LiCoO2/graphite 과우치 셀의 고온 (90 ℃) 평장을 방지할 수 있음을 입증하였다. 완전히 충전된 전지는 90 ℃ 고온에 노출되면 아이오딘 첨가제의 서열 작용에 의한 자가 방전이 활성화되어 전지의 state of charge (SOC)가 낮아지고 이는 평장을 억제하여 안정성을 높일 수 있다.

(4) LiPF6 를 염으로 사용하는 전해액에서 부산물로 발생하는 HF 를 제거하고 흑연 음극에 영향을 주지 않으며, 다양한 양극 물질의 열적 안정성을 향상시키는 NaH2PO4 (P2) 첨가제를 개발하였다. P2 첨가제는 고온 수명 성능 및 저장 성능을 획기적으로 향상시켰으며, 양극 물질의 종류에 관계없이 복잡하게 사용할 수 있는 장점이 있다. 또한 흑연 음극에 영향을 주지 않는 첨가제이기 때문에 흑연 음극 성능 개선용 첨가제와 혼용할 수 있는 장점이 있다.
전기차 시장이 급속도로 커짐으로써 리튬 이온 전지의 고속 충전 성능 개선이 매우 시급한 현재, 초고농도 전해액 (>4.5 M LiFSI/AN)이 활발히 연구되고 있다. 기존의 카보네이트 전해액보다 낮은 이온전도도를 가지지만 더 빠른 충전 성능을 나타낸다고 알려져 있는데, 상용화된 로딩 레벨의 초연 음극에서는 낮은 이온전도도와 전하 이동 저항의 큰 증가로 인해 카보네이트 전해액보다 낮은 수준의 고율 충전 성능을 보이며, 집전체로 사용되는 알루미늄 부식 및 분리막의 낮음 젖음성 문제 등 개선하여야 할 방향성을 연구하였다.

핵심어: Li-ion batteries, Polydopamine, FPS, I2, P2, additives, LiFSI, AN