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**Study on the Effect of LiNO_3 on Solid Electrolyte Interface
Structure and Electrolyte Degradation in Ether-based Low-
concentration Electrolyte for Anode-free Lithium Metal
Battery**

(低濃度エーテル系電解液を用いた負極フリーリチウム金属電池の固体電解質
界面構造および電解質劣化における LiNO_3 の影響に関する研究)

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2025

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Chapter 1

Introduction

1.1 General Introduction

Energy is an indispensable element for the operation of modern society. As global demand for energy continues to grow, traditional fossil fuels still dominate, but their risk of depletion and environmental issues, such as the emission of large amounts of greenhouse gases, have prompted the search for more environmentally friendly and sustainable energy solutions. Among many alternative energy technologies, lithium battery technology is seen as a very promising option due to its high energy density and lower environmental impact. The commercial application of lithium-ion batteries (LIBs) has completely transformed the markets for portable electronic devices, mobile communications, and even electric vehicles (EV). Especially in the development of EV, LIBs not only offer a way to reduce dependence on fossil fuels but also drive technological innovation toward lower carbon emissions. Although existing LIB technology is widely used in multiple fields, its energy density is still unable to meet all future high-energy demand markets, such as long-distance EV and large-scale energy storage systems. Therefore, researchers and engineers are developing more efficient lithium battery technologies, such as lithium-metal, lithium-air (Li-O₂) and lithium-sulfur (Li-S) batteries,^{1,2} which promise to provide energy densities far exceeding existing LIBs as shown in **Figure 1-1**.

The theoretical energy densities of Li-O₂ and Li-S batteries are 3505 Wh kg⁻¹ and 2600 Wh kg⁻¹, respectively, much higher than traditional LIBs (about 387 Wh kg⁻¹). This potential for high energy density makes Li-O₂ and Li-S batteries have great application prospects in EV and renewable energy storage fields. However, these technologies still face some key technical challenges, including improving battery cycle life, addressing safety issues, and reducing production costs. Future research will continue to explore how to optimize the electrochemical performance of Li batteries, achieving higher energy output and longer service lives. In addition, improvements in environmental impact assessments and battery recycling technologies will also be an indispensable part of Li battery research to ensure the sustainable development of this technology. Thus, Li battery technology is not only a solution to today's energy challenges but also a key technology for future energy transitions.

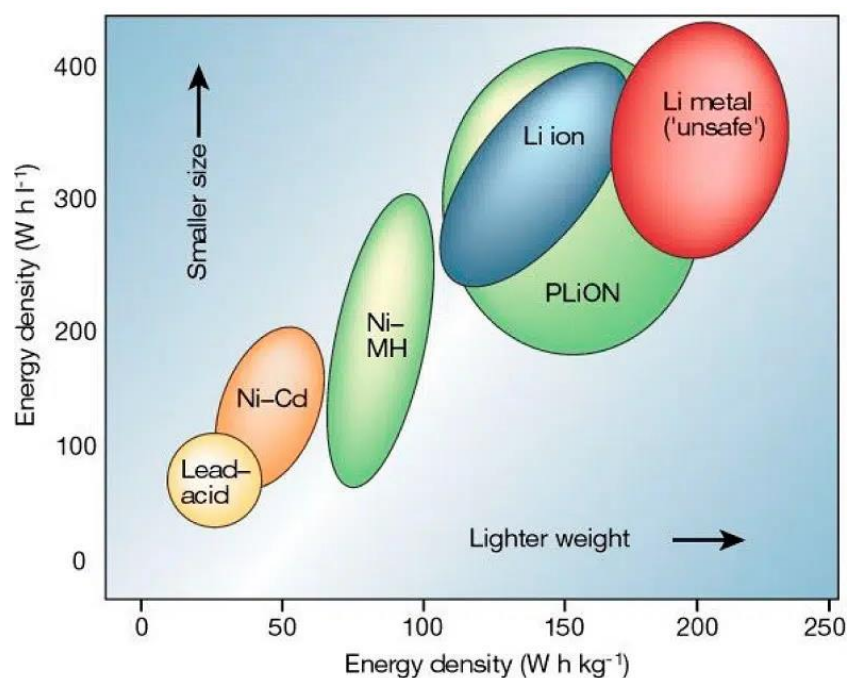


Figure 1-1. Comparison of volumetric energy densities (Wh L^{-1}) and specific energy densities (Wh Kg^{-1}) of different rechargeable batteries.²

1.2 Lithium-based Secondary Batteries

1.2.1 Lithium-ion Batteries (LIBs)

LIBs have become the dominant technology for portable electronics, EV, and renewable energy storage due to their high energy density, long cycle life, and relatively lightweight design. The first commercial LIB was introduced by Sony in 1991, revolutionizing the energy storage industry by providing a rechargeable alternative to traditional lead-acid and nickel-cadmium batteries.³ As shown in **Figure 1-2**, LIBs operate based on the movement of Li ions between the anode and cathode through an electrolyte during charging and discharging processes. The typical LIB consists of three key components: the anode (usually made from graphite), the cathode (commonly LiCoO_2 , or other Li metal oxides such as LiFePO_4 and $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})\text{O}_2$), and the electrolyte immersed in a separator in between cathode and anode, which is typically a Li salt dissolved in an organic solvent, such as the most commonly used 1 M LiFP_6 in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) in a 1:1 volume ratio.⁴ The graphite anode possesses a layered structure that enables the intercalation and deintercalation of Li ions with minimal irreversible changes. The cathode materials for LIBs adopt a layered, spinel, or olivine structure, which provides specific pathways or channels for the lithiation and delithiation of Li ions during the charging and

discharging processes while maintaining structural stability. During charging, Li ions migrate from the cathode to the anode through the electrolyte, storing energy in the process. During discharging, these ions move back to the cathode, releasing energy that can be used to power electronic devices. In particular, the electrolyte undergoes electrochemical decomposition on the graphite surface during the initial charging, leading to the deposition of insoluble products that form a layer known as the solid electrolyte interphase (SEI). A well-formed SEI, characterized by good Li ion conduction ability and mechanical stability, acts as an effective passivation film, preventing further reduction of the electrolyte components. The stable SEI generated can enhance the cycle stability of LIBs, contributing significantly to their commercialization.⁵

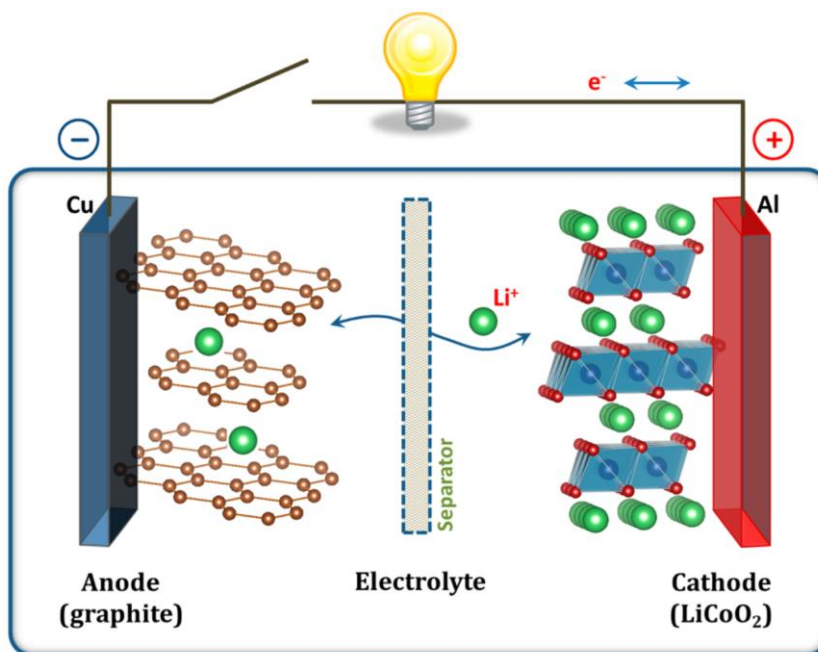


Figure 1-2. Schematic illustration of the typical LIBs configuration, where LiCoO₂ and graphite are used as cathode and anode materials, respectively.⁶

LIBs have a long cycle life, often exceeding 1,000 charge-discharge cycles before significant capacity degradation occurs.^{7,8} In the meantime, LIBs have a relatively low self-discharge rate, no memory effect, and do not contain toxic components like lead or cadmium. Advances in technology have enabled fast-charging capabilities, allowing LIBs to be charged to 80% capacity in very short time, depending on the specific design.^{9,10} However, LIBs suffer from capacity degradation due to side reactions within the cell, and LIBs are prone to thermal runaway, a condition where excessive heat leads to a self-sustaining exothermic reaction, potentially causing fires or explosions.^{5,11,12} This risk is exacerbated if the battery is damaged, improperly charged, or exposed to

high temperatures. In addition, the cost of raw materials like Li, cobalt, and nickel makes LIBs more expensive than some other types of rechargeable batteries.¹³ Moreover, even in recent year the recycling of LIBs is not yet widely implemented, leading to concerns over waste and resource depletion.¹⁴

In conclusion, LIBs have significantly influenced modern technology, enabling the development of lightweight, high-performance devices and vehicles. While they offer numerous advantages, including high energy density and long cycle life, challenges such as safety risks, environmental impact, and resource limitations must be addressed. Ongoing research aims to develop safer, more sustainable, and cost-effective alternatives or improvements to the current LIBs technology.

1.2.2 Lithium Metal Batteries (LMBs)

While some EV utilizing LIBs have already been commercialized and the market is developing rapidly in recent year, LIBs cannot fulfill the demands for massive applications such as electric vehicles because of an energy density limit of around 250 Wh kg⁻¹.^{15,16} Hence, the development of next-generation lithium-based batteries with higher energy density and lower costs is necessary to extend the driving range of EV further. The initial investigation into the electrochemical properties of Li as an anode was reported in the early 20th century, and practical advantage of LMBs was proposed in 1970s.^{3,17} The biggest difference between LMBs and LIBs is that, unlike LIBs which use a graphite anode, LMBs utilize Li metal as the anode (**Figure 1-3**), which possesses a very low redox potential (-3.04 V vs. standard hydrogen electrode) and a very high theoretical capacity (3860 mAh g⁻¹).¹⁸ This significant difference offers the potential for much higher energy density, which makes LMBs a promising candidate for next-generation batteries, particularly for applications requiring long-range and high-performance. For the cathode side, the Li intercalation compounds used in LIBs can also be applied in LMBs, while a sulfur electrode or air electrode (usually a rich pore structure, such as carbon nanotubes, Ketjen black et al.) can replace the intercalation compounds for the purpose of making Li-S battery and Li-O₂ battery, respectively.¹⁹

However, the research and development on LMBs have proceeded slowly since then due to the safety issues of using highly reactive metallic Li for anode, which readily reduces electrolyte causing its degradation, and finally exhaustion of both Li metal and

electrolyte.^{19–21} During the cycling of LMBs, Li plating and stripping naturally occur at the Li metal/electrolyte interface (for LIBs this only occurs under harsh charging conditions, such as overcharge, charge at low temperatures, etc.),²² where the deposited Li can form various surface morphologies, including mossy, granular, or whisker-like (i.e. dendritic) structures. In particular, the Li dendrite formation growth causes the instability of the Li metal/liquid electrolyte interface, including the more fragile and unstable SEI structure compared to the SEI in LIBs. As shown in **Figure 1-3** the dendritic formations ultimately are detrimental to cycling efficiency and battery safety, as they can cause huge capacity loss by creating electrically isolated Li ("dead Li") and may even trigger internal short circuits and explosion hazards if they penetrate the separator. These problems have prevented LMBs from entering the commercial market. Therefore, controlling the morphology of the Li-deposited surface is crucial for the successful development of LMBs, with a focus on minimizing or eliminating dendrite formation and promoting smoother, less harmful microstructures, such as mossy or particulate morphologies.^{22,23}

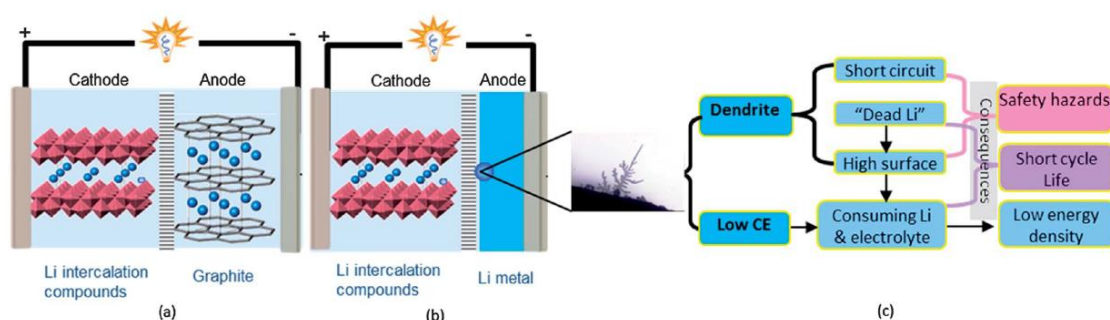


Figure 1-3. Schematic diagram comparison of (a) LIBs and (b) LMBs; (c) the typical morphology of Li dendrites and the major issues related to dendrites and low Coulombic efficiency.¹⁹

1.2.3 Anode-free Lithium Metal Batteries (AFLMBs)

As discussed above, thorny problems including Li dendrite formation and growth will cause the poor efficiency of Li plating/stripping and the danger of short-circuiting for LMBs. Although adding excess Li can usually compensate for the consumed Li storage, this will reduce the energy density advantage of LMBs and artificially extend the cycle life of the battery, disabling a correct evaluation of battery performance.²⁴ For the above reasons, anode-free lithium metal batteries (AFLMBs) are considered as a potential alternative to LMBs.^{24–29}

AFLMBs, also called “anode-less lithium metal batteries”, “lithium metal-free batteries (LMFBs)”, “zero-excess lithium metal batteries (ZELMBs)” by different researchers.³⁰ An AFLMB can be simply defined by removing the Li metal anode of LMB during cell assembly, and only a bare current collector such as copper is paired, which is used as a substrate for Li deposition to create a Li anode after initial charging. In principle, the negative to positive electrode capacity (N/P) ratio in AFLMB is 0 and 1 after cell assembly and after initial charging, respectively, meaning that all Li resources in the anode come from the cathode. During the initial charging and discharging, Li ion will deposit on the current collector as Li metal, then strip and intercalate back into the cathode. Therefore, the use of Li metal can be fully minimized, leading to the substantially reduced battery’s weight and volume and improved battery’s safety. Owing to this, the energy density can be greatly enhanced compared to LIBs and LMBs, which is the most attractive feature of AFLMBs (**Figure 1-4**).^{24,31–33} Additionally, there is no excess Li for an as-fabricated AFLMBs and the performance is dependent on Li plating/stripping efficiency, which will enable a more realistic evaluation of capacity loss mechanisms.^{24,34} It should be noted that, since the initial plating of Li metal will automatically produce a “Li metal anode” on the Cu surface, the behavior of the initial cycle for an AFLMB usually differs significantly from that of the following cycles.²⁴

Despite the above advantages, the research bottleneck in AFLMBs mainly originates from the quick capacity drop during initial state and the diminished Coulombic efficiency over battery cycling due to the zero-excess Li storage.²⁴ Since an AFLMB does not have the host for deposited Li, the first charging may cause over 20% volume expansion.³³ This will fundamentally reduce the energy density of AFLMBs. In particular, due to the limited Li inventory (low negative to positive electrode capacity (N/P) ratio) in AFLMBs, Li plating on the anode usually takes place less evenly, hence the mechanical breakage of SEI as well as Li dendrite growth during the stripping and further plating, which often occurs in LMBs, can be more easily found in AFLMBs.^{35,36} Therefore, lean lithium metal batteries (LLMBs), which use a minimal amount of Li metal on the anode, are proposed recently to provide “a compromise solution” to address this issue.³⁷ LLMBs have comparable energy density with ALFMBs while it can avoid the problem of Li nucleation barriers that causes irregular Li morphology during the initial plating on bare Cu current collector surface, therefore reducing the growing Li dendrite. However, the unique advantages of AFLMBs regarding energy

density and manufacturing are still remarkable, since LLMBs inevitably sacrifice some energy density benefit, and the handling of fragile Li metal is not required in AFLMBs to save the manufacturing cost.

The following section will carefully discuss the main challenges that AFLMBs studies are facing with. Generally, the strategies and techniques to develop practical AFLMBs share many similarities with those in LIBs and LMBs. Nevertheless, current opinions on the improvement of AFLMBs performance are basically focused on the rational modification of electrolyte and current collector.³⁶



Figure 1-4. The schematic comparisons of LIB, LMB and AFLMB. LCO, NMC and LFP are the abbreviation of LiCoO_2 , $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y})\text{O}_2$ and LiFePO_4 , respectively.

1.3 Main Challenges in AFLMBs

1.3.1 Uneven Lithium Nucleation and Growth

The uneven Li metal nucleation and the growth over extended charge-discharge cycles can lead to the formation of Li dendrites that further react with the electrolyte. The proliferation of these dendrites not only lowers CE but also poses safety risks, which can impede the broader adoption and the commercialization of AFLMBs.³⁸ To mitigate this issue, it is essential to inhibit the growth of Li dendrites.

It is generally accepted that there are two types of Li nucleation, which are the instantaneous nucleation and the progressive nucleation,^{39,40} They are then followed by either two-dimensional (2D) or three-dimensional (3D) growth of Li metal.⁴⁰ The

instantaneous nucleation corresponds to the formation of the nuclei at all active sites instantly at the beginning of deposition, followed by an eventual growth. The progressive nucleation corresponds to the continuous and simultaneous nucleation and growth of the nuclei during deposition. **Figure 1-5** shows the illustration of the two Li nucleation types.

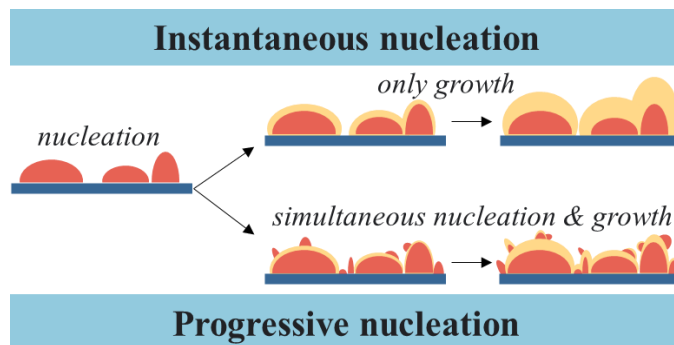


Figure 1-5. Schematic illustration of the two Li nucleation types.

To estimate the mechanism of Li nucleation and growth, the chronoamperometric current-time (j - t) curves can be analyzed by the Scharifker and Hills (SH) model, which is a traditional mathematical model expressed by the following normalized dimensionless equations (**Equation 1-1** and **1-2**).^{41,42}

For the 3D instantaneous nucleation:

$$\left(\frac{j}{j_{max}}\right)^2 = \frac{1.9542}{t/t_{max}} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_{max}} \right) \right] \right\}^2 \quad (1-1)$$

For the 3D progressive nucleation:

$$\left(\frac{j}{j_{max}}\right)^2 = \frac{1.2254}{t/t_{max}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_{max}} \right)^2 \right] \right\}^2 \quad (1-2)$$

Where j_{max} stand for the maximum current observed at time t_{max} . The non-dimensional j/j_{max} vs. t/t_{max} are commonly employed to identify the type of nucleation, followed by diffusion-controlled growth, by comparing theoretical predictions with experimental data. Deviations from these theoretical models before and after J_{max} can indicate other electrochemical processes, such as electrolyte decomposition (E.D.) related side reactions, that simultaneously occurring with the 3D nucleation and diffusion-controlled growth of Li.⁴³

In the chronoamperometric tests, initial potential is instantly stepped to the target potential where the specific reduction or oxidation reaction occurs, which prompts the system from a non-reaction state or steady state to a transient state. This invariably leads to a current transient before reaching the next steady state, governed by the rate of mass

transfer of ions to the electrode surface, as outlined by the Cottrell equation. For simple diffusion-controlled reactions, the current j as a function of time t follows the Cottrell equation (**Equation 1-3**).^{44,45}

$$j = \frac{nFAC_0\sqrt{D}}{\sqrt{\pi t}} \quad (1-3)$$

Where n is the number of electrons transferred per molecule of reactant in the reduction or oxidation reaction, F is the Faraday constant (96485 C/mol), A is the electrode area, C_0 is the initial bulk concentration of the electroactive species being reduced or oxidized, D is the diffusion coefficient. This equation describes how the current decays inversely with the square root of time, indicative of a diffusion-controlled process.

In the year of 2019, Thirumalraj et al. proposed a model called “the Li-SEI model” and employed it to fit the j - t transients of Li plating/stripping.⁴⁶ This model was developed based on the Cottrell equation, while it further describes quantitatively the mechanism of SEI formation/crack associated with the 3D instantaneous nucleation and diffusion-controlled (3D-DC) process of Li. This is, as far as we know, the first model used in discussing complex electrode/electrolyte interface condition for battery application. It is modified from the theoretical 3D-DC model proposed by Palomar-Paradavé et al. where the reduction of protons during cobalt electrodeposition was discussed.^{43,47,48} As indicated by **Equation 1-4**, the time-dependent total current $j_{total}(t)$ can be expressed as the sum of the current from Li plating, $j_{Li}(t)$ and the current from the decomposition of electrolyte $j_{E.D.}(t)$, where the latter is usually a result of SEI crack. The physical meanings of the parameters in the above equations are listed in **Table 1-1**.

In addition, both the “Li-SEI model” or the Palomar-Paradavé’s model describe the mechanism of metal deposition accompanied by the reductive side reaction, which can be categorized to the electrochemical redox process with diffusion-controlled currents as is described in the Cottrell equation. Therefore, the applied range of the “Li-SEI” model could be tentatively extended to include Li plating (anodic process) and Li stripping process, albeit in the exact opposite direction of considering Li nucleation.

$$j_{total}(t) = j_{Li}(t) + j_{E.D.}(t), \quad j_{Li}(t) = \frac{a}{\sqrt{t}}(1 - e^{-ct}), \quad j_{E.D.}(t) = d(1 - e^{-c(t - \frac{1-e^{-Nt}}{N})}) \quad (1-4)$$

Where

$$a = \frac{nFC\sqrt{D}}{\sqrt{\pi}}$$

$$c = N_0\pi D \sqrt{\frac{8\pi MC}{\rho}}$$

$$d = n_{E.D.} F k_{E.D.} \sqrt{\frac{2MC}{\pi\rho}}$$

Table 1-1. The physical meaning of the parameters.

nF	molar charge transferred during Li plating (C mol^{-1})
D	diffusion coefficient of Li^+ through SEI ($\text{cm}^2 \text{s}^{-1}$)
C	bulk concentration of electrolyte (mol cm^{-3})
M	molar mass of Li metal (g mol^{-1})
ρ	density of plated Li metal (g cm^{-3})
N_0	number of Li nucleation sites (cm^{-2})
N	density of Li nuclei (cm^{-2})
$n_{E.D.}F$	molar charge transferred during E.D. (C mol^{-1})
$k_{E.D.}$	rate constant of E.D. due to SEI fracture ($\text{mol cm}^{-2} \text{s}^{-1}$)

From the above description of Li nucleation and growth models and mechanisms, it can be clearly seen that the Li plating and stripping is strong relevant to dendrite growth, SEI stability, and subsequent electrolyte degradation (**Figure 1-6**), which applies to the use of different substrates/current collector or different electrolytes.⁴⁶ Under this circumstance, current collector modification is very crucial to achieve the homogeneity of Li plating and stripping. As one of the most commonly used current collectors, Cu serves a crucial role in lithium-based batteries owing to its excellent conductivity and stability. However, it also tends to encourage uncontrolled Li plating, leading to issues such as dendrite formation and the development of disconnected Li layers, which negatively impact the battery's performance and safety.

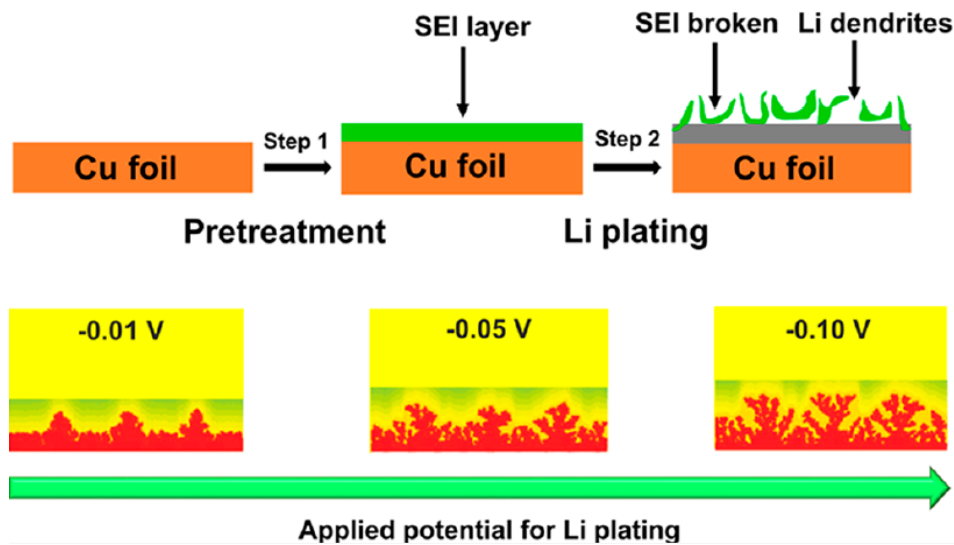


Figure 1-6. Schematic illustration of Li nucleation and growth metal accompanied by SEI fracture during Li plating on bare Cu foil current collector at various applied potentials.⁴⁹

Furthermore, visualization techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and optical microscopy (OM) have been applied to directly investigate the nucleation and growth of Li metal and its dendrites. For example, mechanisms of Li dendrites growth and short-circuiting were explored by Huang et al. using OM, revealing the role of SEI layer as an insulating barrier between two electrodes during short circuits.⁵⁰ Specifically, Li plating/stripping at the initial stage exhibited a relatively smooth morphology on both the Cu and Li surfaces. However, this was followed by the formation of dendrites, leading to an internal short circuit and the accumulation of dead Li. Interestingly, during the short-circuit observed at plating or stripping on the Cu electrode, the cell voltage was not zero but slightly negative or positive respectively, indicating an SEI resistance between two contacted electrodes (**Figure 1-7**).

Although these techniques enable *in situ* visualization of Li dendrites and dead Li, they are limited by high-vacuum condition or electron beam damage. On the other hand, the advanced transmission X-ray Microscopy (TXM) offers a non-destructive alternative, enabling high-resolution imaging under ambient conditions.⁵¹ For instance, Hagos et al. successfully visualized Li plating/stripping dynamics, showing the inhomogeneous growth and shrinkage of mossy-like Li takes place upon Li plating/stripping under several lower and higher current densities, which presents a faster growth and stripping from the bottom and the top, respectively, causing the stacking of dead Li (**Figure 1-8**).⁵²

In conclusion, the *in situ* techniques like OM and TXM can serve as an effective tool for real-time dynamic visualization and quantitative analysis of Li plating/stripping processes on different substrates, which can significantly contribute to the advancement of battery technologies including AFLMBs.

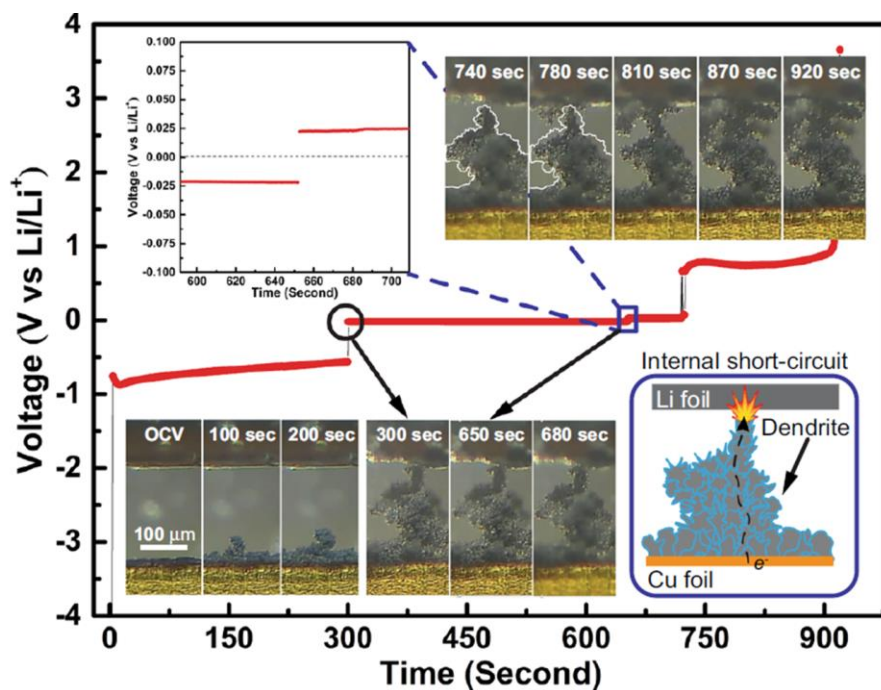


Figure 1-7. *In situ* OM observation of Li plating/stripping on a Cu electrode at an extremely high current density (500 mA cm^{-2}) to illustrate short-circuit behavior.⁵⁰

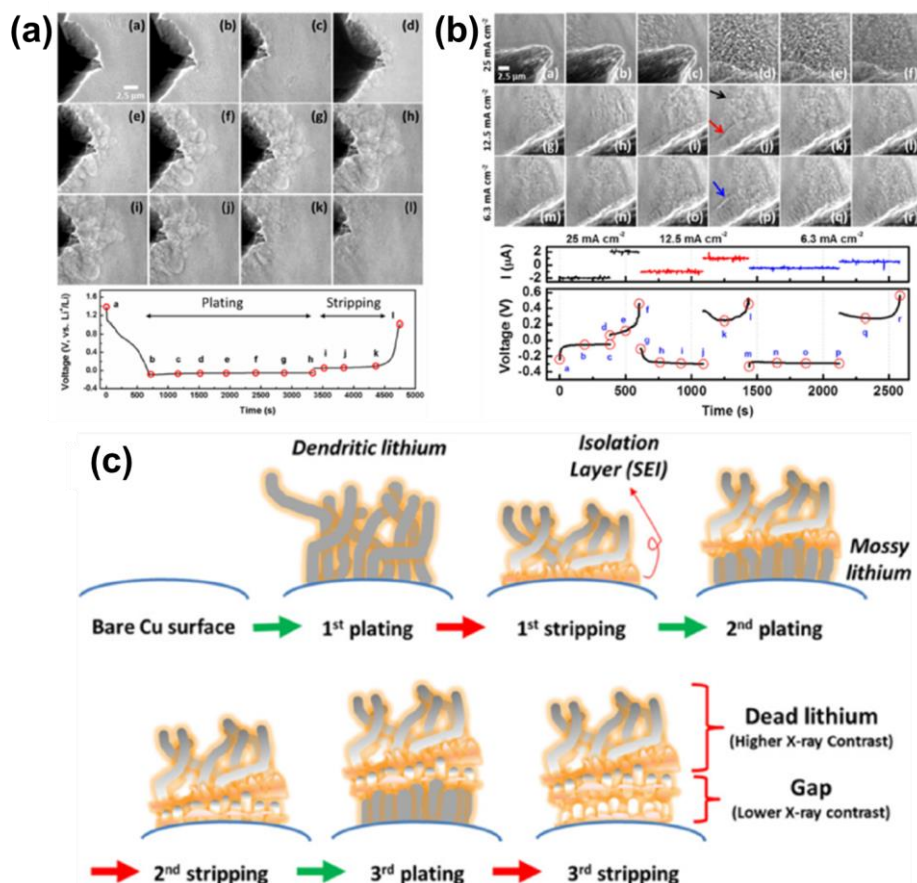


Figure 1-8. *In situ* TXM images at various stages of (a) one Li plating/stripping cycle at 1 mA cm^{-2} and (b) during first, second and third cycles at different current densities; (c) Schematic illustration showing the mechanism of dead Li growth upon cycling.⁵²

1.3.2 Complex SEI Layer Formation and Reconstruction

An SEI layer was first identified as a spontaneous reaction product on Li metal by Peled et al.⁵³ In general, the dominant electrode reactions at the anode of the Li metal-based battery involve the parasitic reactions (e.g. the electrochemically and chemically breakdown of the solvent and Li salts) and the electrochemical plating and stripping of Li. Particularly during the Li plating, the low potential and high reactivity of Li causes electrolytes - comprising solvents, Li salts, or additives - to decompose, which is the main source of electrolytes loss. Consequently, an SEI layer made up of insoluble decomposition products forms on the anode as a result of electrolyte degradation. Typically, solvent molecules provide organic species, while anionic group reduction products form inorganic species in the SEI (**Figure 1-9**). Since the potential of Li is above the LUMO of most common organic electrolytes, the SEI formation is basically unavoidable.⁵⁴ On the other hand, the SEI layer is found to be ionically conductive but electronically insulating, which can serve as a crucial barrier that prevents direct contact between deposited Li and the electrolyte, thereby enhancing battery stability including subsequent CE performance.^{5,55,56}

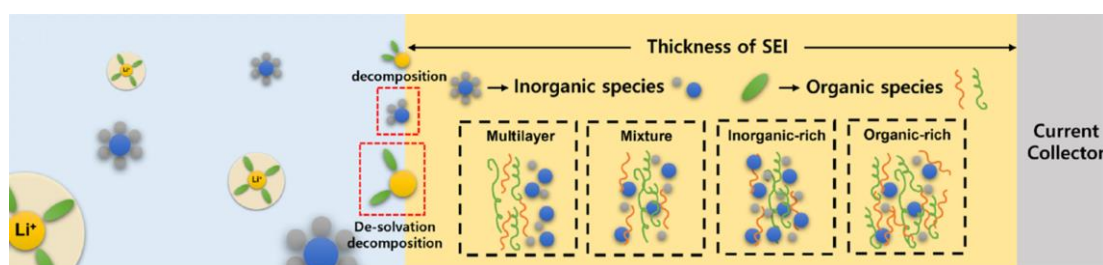


Figure 1-9. A diagram showing the structure and components of the SEI layer components.³²

Depending on different electrochemical stages, the formed SEI layers in AFLMBs can be categorized as follows (**Figure 1-10**): A “native-SEI (n-SEI)” layer first forms right after cell assembly but before applying bias voltage, which is composed of some Cu oxides and the inorganic products from chemically reduced electrolyte components.⁵⁷ Moreover, another SEI layer is formed over bare Cu after applying voltage but before the initial Li plating, which can be defined as a “pre-SEI” layer.⁵⁸ Since there is no pre-formed Li metal for AFLMBs, the formation of pre-SEI is more dependent on cathode-liberated Li and is strongly affected by the interaction with current collector. During the process of Li plating, an “additional-SEI (add-SEI)” forms simultaneously with Li nucleation due to the contact of Li metal with the liquid electrolyte. Hence, the fundamental difference between pre-SEI and add-SEI lies on the

different substrates (Cu or Li metal). Moreover, a newly constructed SEI layer can be found after the first Li stripping and the breakage of the above SEI layers, which is called as “subsequent-SEI (s-SEI)” layer.⁵⁰

As shown in **Figure 1-10**, Li plating/stripping usually occurs beneath the pre-formed n-SEI layer and pre-SEI layer, but if these surface layers are unstable and fragile, the distribution of plated Li will be inhomogeneous,³⁵ causing the growth of Li dendrite and the isolated “dead Li” to penetrate the SEI layers, followed by a construction of the s-SEI layer. Meanwhile, the sudden morphological change from Cu current collector to the freshly deposited Li will also likely cause a dramatic reconstruction in the chemical composition of SEI.⁵⁹ These processes open a pathway of continuously consuming both Li and electrolyte, resulting in poor CE.^{60–62} Therefore, the favorable SEI layers should not only ensure fast Li ion conduction but also be electrically insulated to block further decomposition of electrolytes. However, compared to LIBs and LMBs, the SEI layers are more problematic in AFLMBs particularly due to the instability of initially formed SEI layer on the Cu surface and the influence of initial Li metal plating on the Cu substrate which takes place by Li ions transition through the pre-formed SEI layer.

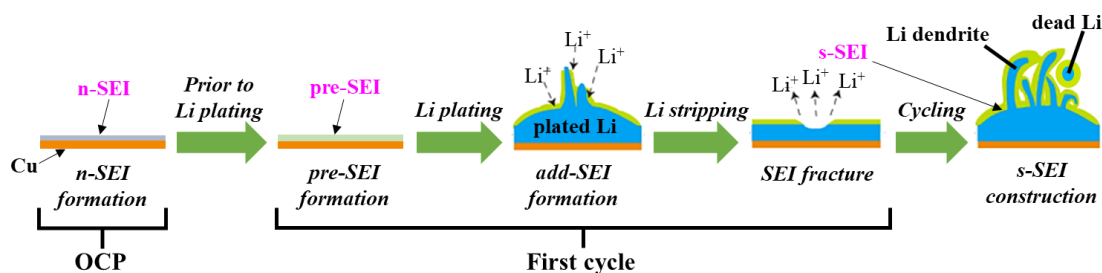


Figure 1-10. Schematic illustration of the formation of different types of SEI layers in AFLMBs.

Compared with LIBs and LMBs, the SEI layer in AFLMBs is often thicker, more dynamic, and compositionally complex due to the lack of a stable Li metal substrate. It is prone to mechanical fracturing during Li stripping, which exposes fresh Li and leads to additional SEI growth.^{31,32} While strategies like electrolyte engineering and current collector modifications have been proposed to mitigate SEI instability, the challenges remain significant compared to LIBs and LMBs. The absence of a pre-formed Li anode in AFLMBs fundamentally alters the SEI formation dynamics, demanding innovative solutions to achieve stable cycling performance.

Considering the complicated SEI layers formation and evolution, as well as the change of metallic substrates beneath SEI before and after initial Li deposition in AFLMBs, careful investigations that can distinguish these SEI layers in terms of the

compositional and structural properties are required. Olana et al. used *in situ* diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS) to investigate surface reactions and the resultant SEI components on both Cu foil and Li metal anode.⁶³ The research demonstrates that the decomposition of LiTFSI and LiNO₃ contributes to the formation of SEI layers. On Li anode, LiTFSI decomposed at open circuit potential (OCP) to form intermediate species, which further reduced during cycling to form smaller inorganic SEI species (**Figure 1-11(a)**). On Cu anode, LiTFSI remained stable at OCP, while during cycling, its reduction led to the formation of inorganic components as well (**Figure 1-11(b)**). Meanwhile, both Cu and Li anode exhibited decomposition of LiNO₃ at OCP, producing LiNO₂ and likely Li₂O. The further reduction during cycling forms Li₃N. It was also found that the SEI on Cu is generally thinner and less reactive due to the lack of direct Li-metal interaction at the initial stages.

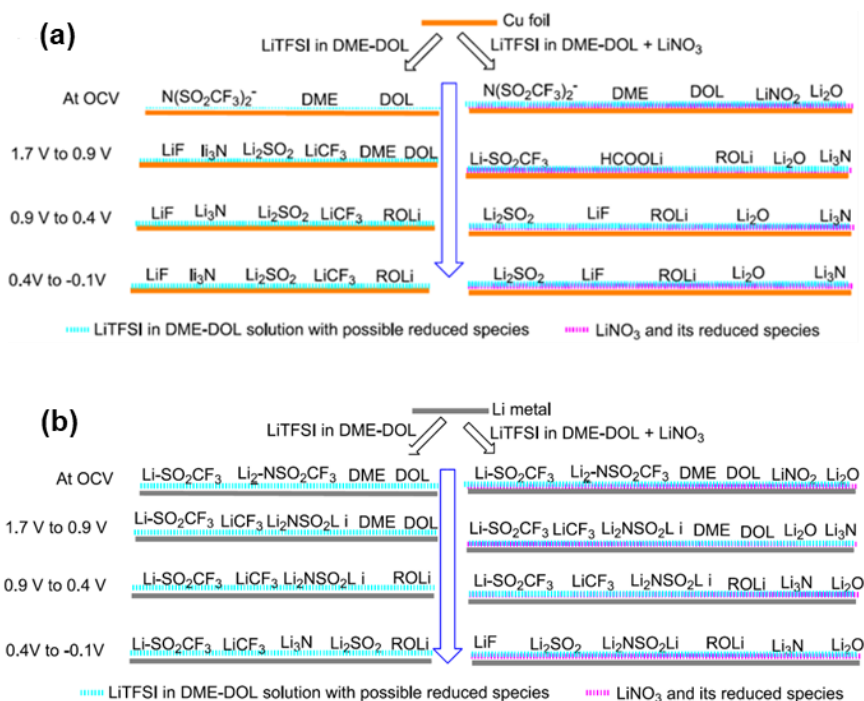


Figure 1-11. Illustration of SEI formation during linear sweep voltammetric (LSV) scanning in cathodic direction on (a) Cu metal and (b) Li metal based on *in situ* DRIFTS difference spectra analysis. The electrolytes contain LiTFSI salt dissolved in DME (1,2-dimethoxyethane) and DOL (1,3-dioxolane), with or without the addition of LiNO₃.⁶³

Moreover, by adopting Raman spectroscopy, Schmitz et al. confirmed a uniform distribution of Li₂CO₃ and a nonuniform distribution of Li₂C₂ during Li plating in a LiPF₆/EC + DEC (diethyl carbonate) electrolyte using Cu as current collector, highlighting the characteristics of SEI components over plated Li metal.⁶⁴ Recently, Gu et al. utilized depth-sensitive plasmon-enhanced Raman spectroscopy (DS-PERS) to observe the step-by-step formation of the SEI layer, first on a Cu current collector and

then on freshly deposited Li.⁵⁹ Their findings challenged the conventional view, which either neglects the SEI formation on Cu or assumes that the SEI on Cu remains unchanged after Li deposition. DS-PERS revealed that SEI forms sequentially on both Cu and Li, undergoing substantial chemical and structural transformations. Based on this, they developed a cycling protocol that encourages a favorable SEI formation pathway, significantly improving the performance of AFLMBs. (**Figure 1-12**).

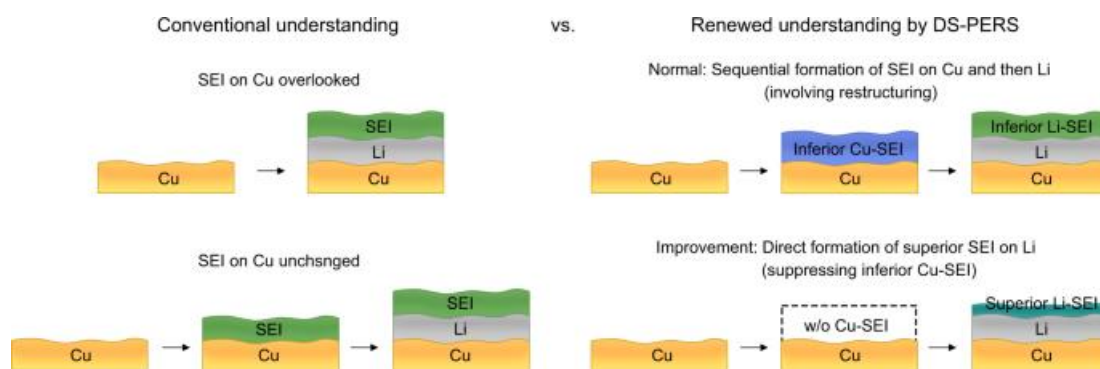


Figure 1-12. Schematics of conventional and renewed understandings of SEI layer formation and evolution for AFLMBs.⁵⁹

The mass change on the electrode surface is another critical information related to SEI formation and evolution. Despite some advances have been made in LIBs regarding the investigation on the *in situ* mass change during SEI formation and evolution, very little attention has been paid towards the LMBs including AFLMBs. Liu et al. studied the formation and re-oxidation process of SEI on graphite electrode in LIBs by quartz crystal microbalance (QCM) technique.⁶⁵ **Figure 1-13** depicts different stages of SEI formation during cathodic scan and re-oxidation during anodic scan. It was found that electrolyte decomposition and SEI formation occur in regions II and III, followed by further reduction and growth of the SEI layer in region IV. The mass accumulation was analyzed in relation to the specific chemical components forming the SEI, such as LiF and Li alkyl carbonates. The mass loss during anodic scan was attributed to the re-oxidation of Li alkyl carbonates. Their study provides valuable insights into the reversibility and stability of the SEI components during the early stages of battery cycling, which could possibly be applied in AFLMBs studies as well.

Meanwhile, studies on the structural integrity of SEI have been limited. Under this circumstance, the enhanced QCM-D (with dissipation monitoring) further offers insights into the viscoelastic properties of non-rigid interphases, providing additional data on SEI characteristics like thickness, viscosity, and modulus in different electrolyte environments.^{66,67} Chai et al. studied the mechanical properties of the SEI in LMBs

using QCM-D.⁶⁸ They compared SEI formation in 3 different organic electrolytes, namely propylene carbonate (PC), EC/DEC and tetraethylene glycol dimethyl ether (TEGDME), and revealed that the SEI in carbonate electrolytes formed as a two-layer structure, with a rigid layer followed by a viscoelastic one, whereas in TEGDME a single rigid layer was formed. It was also found that the SEI layer formed in TEGDME solvent is thinner but more rigid, which contributed to a better electrochemical performance (**Figure 1-14**). Their study further demonstrates the promising prospects of QCM technique in the study of the SEI layer.

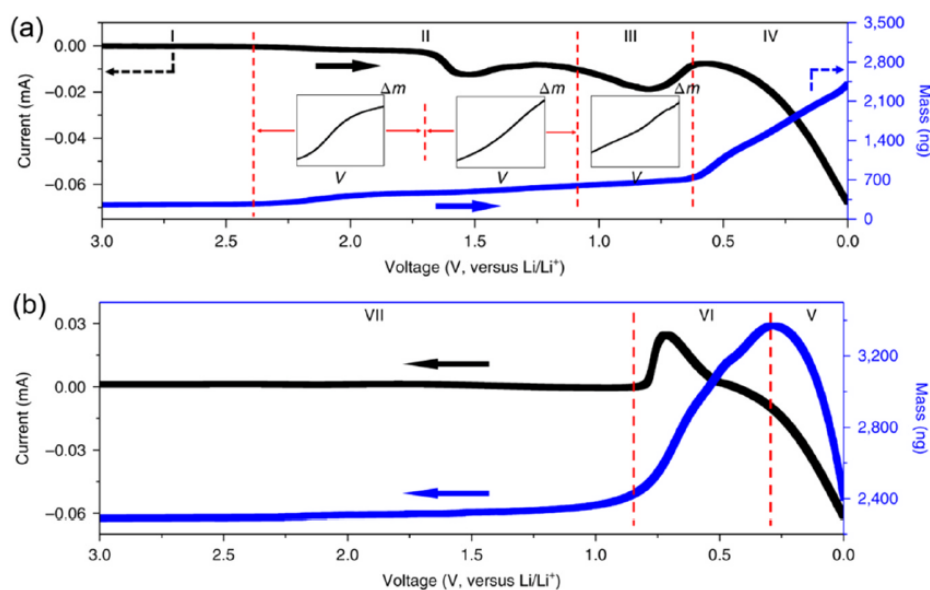


Figure 1-13. Cyclic voltammetry (CV) curves for (a) cathodic and (b) anodic scans (black) of the fresh graphite electrode at a scan rate of 1 mV/s within the voltage range of 0 to 3.0 V, along with the corresponding mass deposit responses on the graphite electrode (blue) captured by QCM. The solid black arrows indicate the scanning direction for CV, while the solid blue arrows show the scanning direction of QCM measurements.⁶⁵

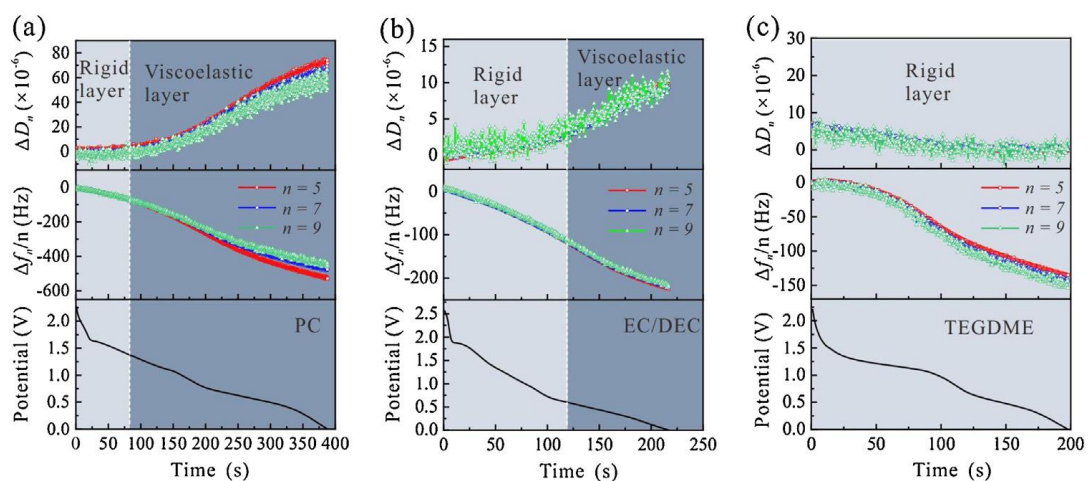
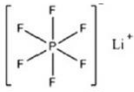
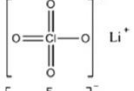
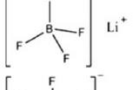
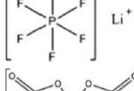
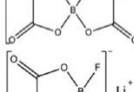
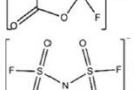
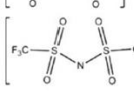
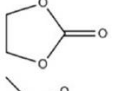
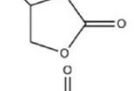
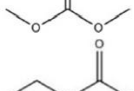
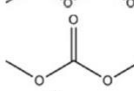
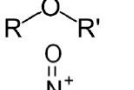
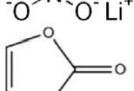
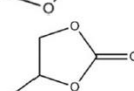


Figure 1-14. The changes in energy dissipation (ΔD_n) and normalized frequency shift ($\Delta f_n/n$) measured by QCM-D, along with the working electrode potential during the initial discharge at 0.1 mA/cm² from OCP to 0 V, in the (a) PC, (b) EC/DEC, and (c) TEGDME based electrolytes with 1 M LiClO₄.⁶⁸

1.3.3 Electrolyte Decomposition (E.D.)

E.D. is another very critical problem to be solved in AFLMBs. The electrolyte components subject to the decomposition can involve not only Li salts but also solvent molecules and additives. **Table 1-2** summarizes the E.D. products from the commonly used electrolyte components.

Table 1-2. Summary of reduction products of Li salts, solvents, and additives.⁶⁹ Notes that M represents not only Li but also sodium and potassium.

Types	Name	Molecular structure	Reduction products in SEI
Li Salts	LiPF ₆		LiF, Li _x PF _y O _z , P _x F _y , Li ₂ O
	LiClO ₄		Li ₂ O, LiClO ₃ , LiClO ₂ , LiCl
	LiBF ₄		Li ₂ CO ₃ , LiF
	LiAsF ₆		Li ₂ CO ₃ , LiF, Li ₂ O, As ⁰
	LiBOB		Li ₂ C ₂ O ₄ , LiBO ₂ and Li ₂ CO ₃ , and polymeric moieties
	LiDFOB		Li ₂ CO ₃ , LiF, Li ₂ C ₂ O ₄ , LiBO ₂ , and polymeric moieties
	LiFSI		Li ₃ N, Li ₂ N ₂ O ₂ , Li ₂ S, Li ₂ SO ₄ , LiF, Li ₂ O, and polymeric moieties
	LiTFSI		Li ₃ N, Li ₂ S, Li ₂ SO ₄ , LiF, Li ₂ O, and polymeric moieties
Solvents	EC		(CH ₂ OCO ₂ M) ₂ , MCH ₂ CH ₂ OCO ₂ M, M ₂ CO ₃ , polycarbonate, and other alkyl carbonates
	PC		M ₂ CO ₃ , polycarbonate CH ₃ CH(OCO ₂ M)CH ₂ OCO ₂ M, and other alkyl carbonates
	DMC		CH ₃ OM, CH ₃ OCO ₂ M, and other alkyl carbonates
	DEC		CH ₃ CH ₂ OM, CH ₃ CH ₂ OCO ₂ M
	EMC		ROM (R = CH ₃ CH ₂ , CH ₃), CH ₃ OCO ₂ M
	ethers		CH ₃ M, CH ₃ OM, and ethereal oligomers
Additives	LiNO ₃		Li _x NO _y , Li ₂ O, Li ₃ N
	VC		oligomers containing repeated —CH=CH— units, (CHOCO ₂ M) ₂ , (CH=CHOCO ₂ M) ₂
	FEC		MF, M ₂ O, polycarbonate, and other alkyl carbonates

Notably, the massive emergence of E.D. is basically due to the cracking of an unstable SEI layer that causes the exposure of deposited Li metal to the bulk electrolyte. Although the solid products from E.D. will automatically construct a renewed SEI layer over the cracked one, the newly formed SEI layer can still suffer from the same problem (i.e., instability) due to the uncontrolled and irregular E.D. process, resulting in a continuous cycle of cracking and E.D. occurrence.

In the case of AFLMBs, E.D. can occur over Cu current collector prior to the initial Li plating. But it should be noted that this occurs in a Li-deficient environment, which may render an incomplete decomposition of electrolyte.

For instance, many researchers have investigated the decomposition mechanisms of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI).^{70,71} **Figure 1-15** shows the predicted decomposition pathways of LiTFSI. As a first step, two possible bond cleavage are proposed: the one is the N–S cleavage, and the other is the S–C cleavage. Both occurs as a result of an electron addition that causes the local distribution of electron near the S atom, leading to the instability and subsequent breaking of either N–S or S–C bond. The overall reduction produces some larger components like $\text{Li}_2\text{NSO}_2\text{CF}_3$ and LiSO_2CF_3 and a variety of smaller inorganic species including Li_3N , Li_2O , Li_2S , Li_2S_2 , Li_2SO_3 , $\text{Li}_2\text{S}_2\text{O}_4$, LiF , LiCF_3 , etc. These species are insoluble and contribute to the formation of a passivation layer on the electrode.

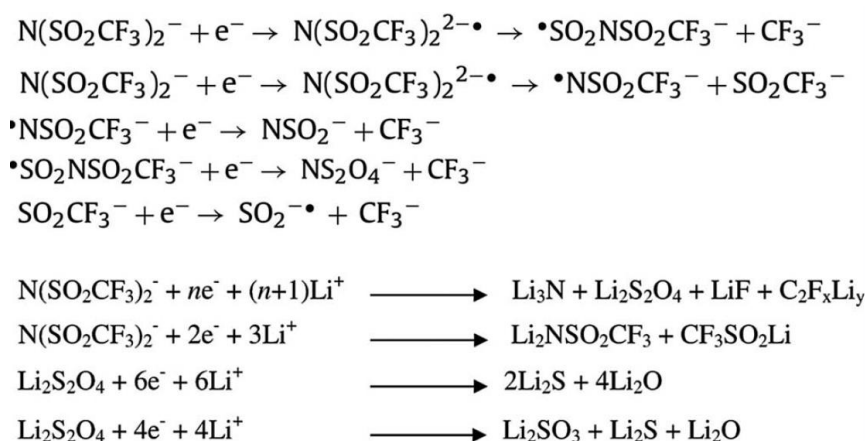
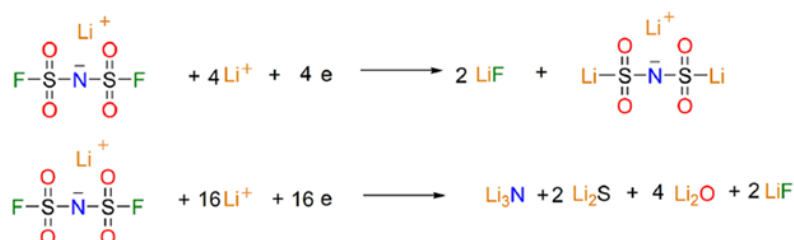


Figure 1-15. Possible reduction reactions of LiTFSI in non-aqueous solutions.^{70,71}

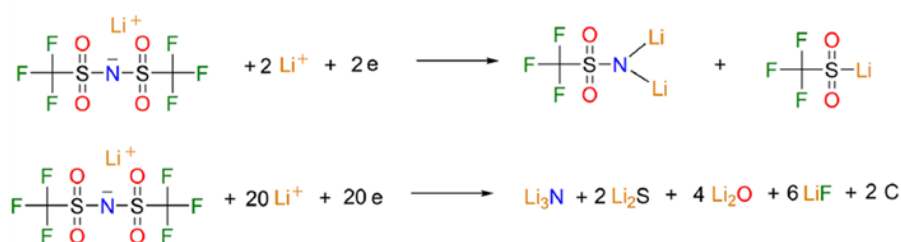
The decomposition process of another Li salt called lithium bis(fluorosulfonyl)imide (LiFSI) has also been previously studied. Meanwhile, as a famous solvent used in LMBs, DME has demonstrated greater resistance to decomposition caused by the Li-metal anode compared to other organic solvents like

cyclic ethers and carbonates. However, it can still undergo the decomposition due to the strong reactivity of Li especially under the radical attack, or due to certain electrochemical conditions especially at low potentials. Eshetu et al. summarized the reductive reaction schemes of the two Li salts (LiFSI, LiTFSI) and DME solvent (**Figure 1-16**).⁷² For each Li salt, the upper reaction is thought to occur on Cu surface, which demonstrates the preferential cleavage of S–C for LiFSI and N–S for LiTFSI among all bonds in the molecule. The lower reaction undergoes based on the deposited Li surface, showing a more thorough reduction with 16-electron transfer for LiFSI and LiTFSI. Regarding DME solvent reduction mechanism, a two-electron reduction reaction (the upper reaction) was proposed by Aurbach et al.,⁷³ identifying methoxy lithium (CH_3OLi) and $\text{H}_2\text{C}=\text{CH}_2$ as key species involved in SEI formation. Another type of two-electron reduction mechanism was also proposed (the lower reaction).⁷⁴ This reaction leads to the formation of $\text{H}_2\text{C}=\text{HC}-\text{O}-\text{CH}_3$, CH_3OLi , and LiH . The formation of ROLi like species is confirmed in many studies as the common feature in DME electrochemical degradation on Li electrode.⁷⁵

4e and 16e reduction of LiFSI



2e and 20e reduction of LiTFSI



2e reduction of DME

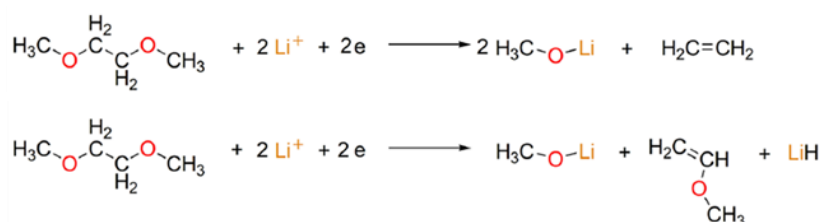


Figure 1-16. Proposed mechanism for the reduction of the electrolyte components including LiFSI, LiTFSI and DME.⁷²

Camacho-Forero et al. theoretically studied the decomposition of DME in depth. **Figure 1-17** shows the predicted degradation pathway of DME via their theoretical calculation, which is thermodynamically favorable under a one-lithium-radical attack. Two reaction pathways are considered: one involving the cleavage of the C–O bond near the middle carbon (C_m–O) and the other near the terminal carbon (C_t–O). Their results suggest that C_m–O bond cleavage (pathway α) is more favorable, both thermodynamically and kinetically, than C_t–O bond cleavage (pathway β) which involves significantly higher activation energies in the subsequent steps. The pathway α leads to the formation of Li ethylene complexes and CH₃OLi. The study provides insights into the initial steps of DME decomposition in Li-rich environments, helping to explain the formation of key decomposition products observed in simulations.

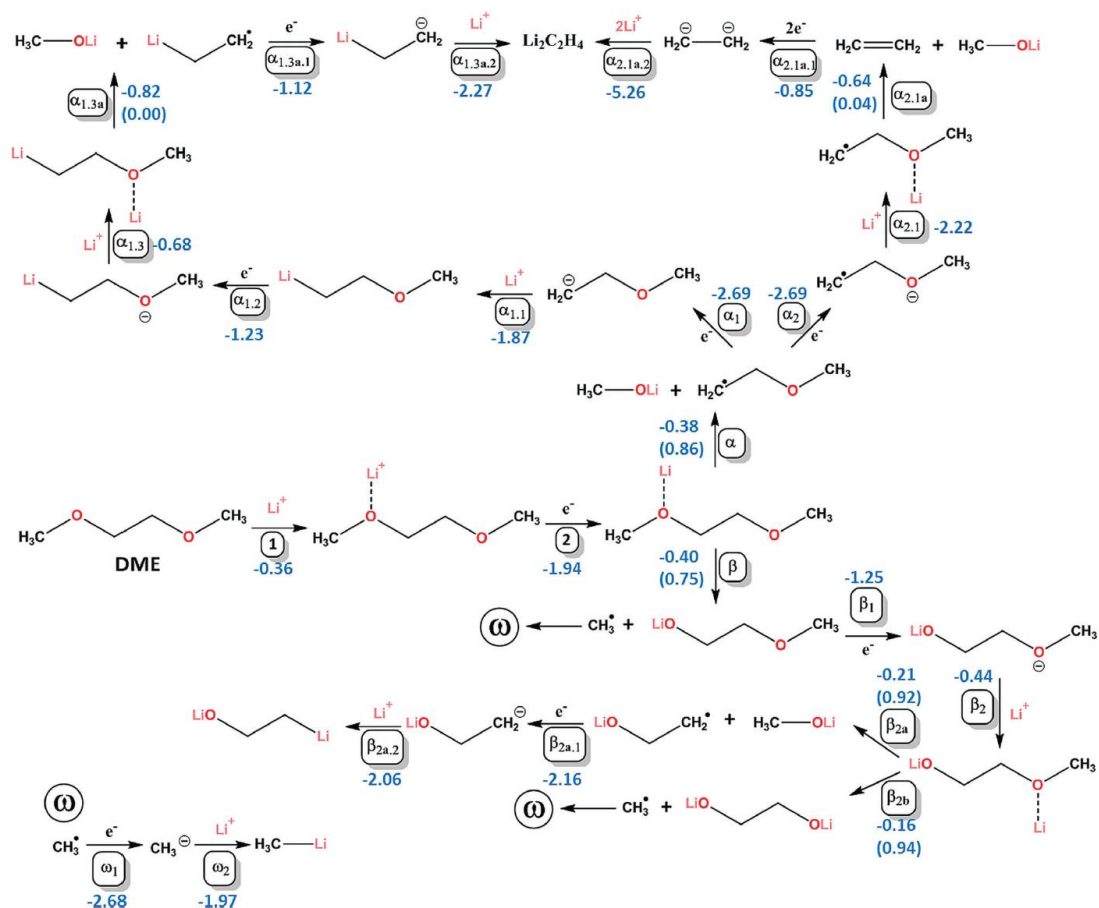


Figure 1-17. A thermodynamically favorable reaction pathway for DME decomposition via Li radical attacks, leading to the cleavage of C–O bond. The reaction energies (ΔE₀) and kinetic activation barriers (in parentheses) are calculated in eV using the B3PW91/6-311++G(p,d) method.⁷⁶

Another typical ether solvent is TEGDME, or called tetraglyme elsewhere. TEGDME has been widely used in Li-O₂ batteries, which are a promising candidate for next-generation energy storage, but the practical use has been limited by low stability

AFLMBs, such differences between DME and TEGDME are subject to change, which though requires further investigation due to the very few reports on the application of TEGDME in LMBs, let alone AFLMBs.^{79,80}

The above discussions on E.D. are based on the decomposition of individual electrolyte components (either Li salts or solvent molecules), while the interaction between different species is also plausible. As shown in **Figure 1-19**, a theoretical study demonstrated the overall charge distribution in the DME-based 1 M electrolyte.⁷⁶ Before 10 ps (with a total charge $\leq -4|e|$), nearly all excess electrons are absorbed by LiFSI/LiTFSI, which accounts for their early decomposition. Then, DME molecules begin to take up the newly introduced electrons, as evidenced by a step-like increase between 10 and 22 ps. In the case of the 1 M LiFSI solution, any additional charge after this point is absorbed by the DME molecules, explaining the stability of the $\text{N}(\text{SO}_2)_2$ fragment formed during LiFSI reduction. In contrast, a sudden charge transfer occurs toward the LiTFSI fragments in the 1 M LiTFSI solution between 22 and 25 ps, which coincides with a drop in the charge on the electrolyte side. This is linked to the defluorination of $\text{CF}_3\text{SO}_2\text{N}$ during this period. For DME molecules in the 1 M LiTFSI solution, the total charge starts to increase around 25 ps, corresponding to a redox reaction involving one of the molecules. After this, the solvent predominantly absorbs any additional charge supplied to the system.

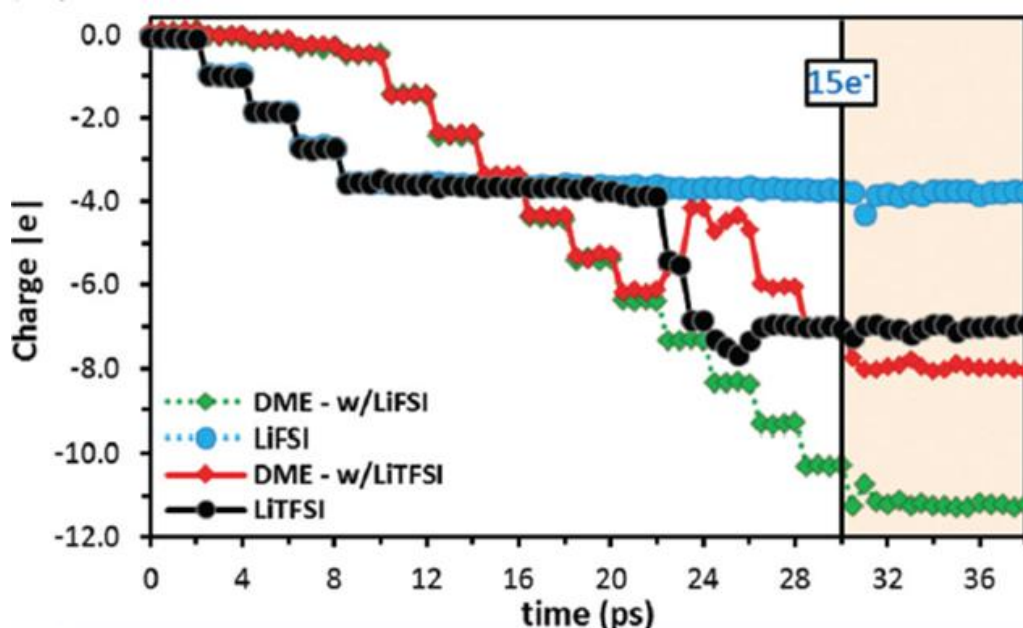


Figure 1-19. Charge evolution from AIMD simulations with sequential addition of electrons: Time evolution of DME and LiFSI/LiTFSI total charge (and fragments formed from their decomposition). The total number of DME in both 1 M solutions are the same.⁷⁶

In 2023, Wu et al. experimentally studied the interaction between LiFSI and DME by applying mass spectroscopy. **Figure 1-20** is the mechanism of the predicted interaction, where the FSI⁻ anion initially undergoes reduction, gaining two electrons and two Li ions to form LiF and a compound labeled as Li(FSO₂NSO₂Li) via S–F bond cleavage. LiF and a portion of Li(FSO₂NSO₂Li) remain in the SEI, acting as solid components that passivate the Li surface. While the other portion of Li(FSO₂NSO₂Li) reacts with the DME solvent to produce soluble compounds like Li(FSO₂NSO₃CH₃) and Li(FSO₂NSO₃CH₂CH₂OCH₃), which dissolve into the electrolyte and may contribute to further degradation of the SEI over time. This mechanism highlights how interactions between the anion (FSI⁻), Li ions, and the DME solvent can lead to the formation of both solid and soluble by-products that impact the stability of the SEI layer.

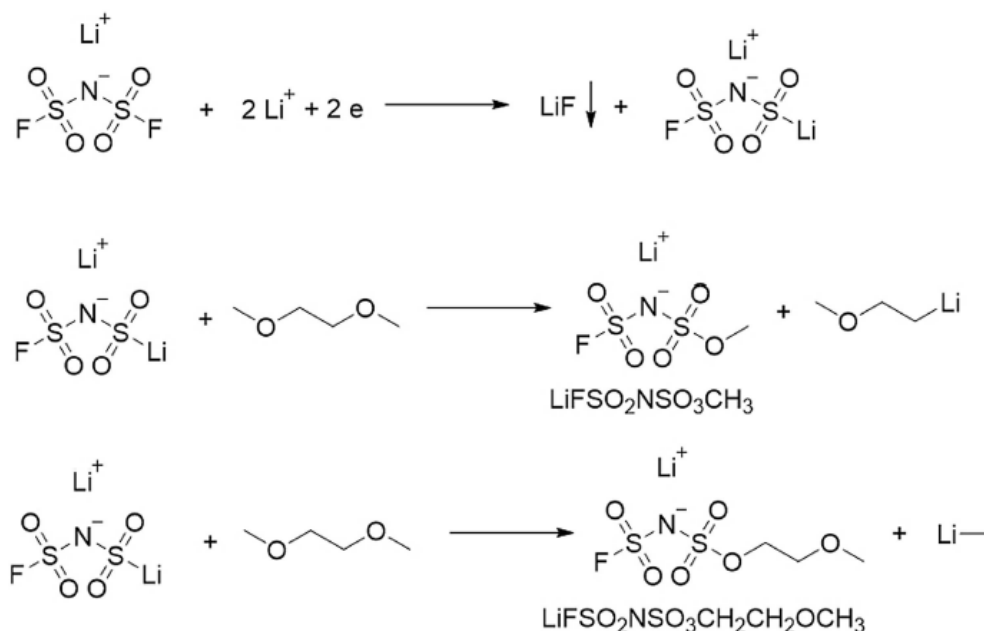


Figure 1-20. The proposed mechanism for the interaction of LiFSI with DME solvent via mass spectroscopy.⁸¹

1.4 Electrolyte Modifications to Improve AFLMBs Performance

Current countermeasures to address the challenges in AFLMBs can generally be categorized into three aspects: electrolyte design, current collector modification, and test condition optimization. Among them, electrolyte engineering can be regarded as the most important route for developing high-performance AFLMBs, which is highly associated with the morphology of deposited Li metal and the properties of SEI layer.

Given that the composition and characteristics of the SEI significantly influence E.D. progress and therefore, the overall battery performance, tailoring the SEI's properties emerges as an effective approach. Thus, optimizing electrolyte formulations stands out as the most effective approach to stabilize the SEI layer to suppress the occurrence of E.D.

1.4.1 Solvent

Overall, the liquid electrolytes used in AFLMBs can be divided into two main categories: conventional carbonate electrolytes such as EC, DME and DEC, which have been extensively studied in LIBs due to their wide electrochemical window (> 4.5 V vs. Li/Li^+), and ether electrolytes like DME, TEGDME and DOL, which still possess many unknown properties.^{82,83} The growing interest in ether-based electrolytes stems from their superior compatibility with Li metal. This can lead to reduced dendrite formation and higher Li stripping efficiency, providing benefits for AFLMBs. (see **Table 1-3**).⁸³ In particular, the SEI formed in ether electrolytes is more flexible and stable than that in carbonate electrolytes, which suffer from fragile SEI structure. Furthermore, it was found that fluorinated ether solvent based electrolytes, which form stable LiF -rich SEI layers, offer advantages such as high mechanical strength, reduced side reactions, and better oxidation stability.^{84,85}

However, achieving higher energy density requires a battery to operate at higher voltages, making the use of high-voltage cathodes desirable for better performance. The challenge lies in the fact that ether-based electrolytes typically exhibit lower oxidation stability compared to conventional carbonate electrolytes. Therefore, the primary focus should be on enhancing the oxidation tolerance of ether-based electrolytes. Moreover, the high production costs limit the large-scale use of ether-based electrolytes as well. Recent efforts therefore focus on developing cost-effective co-solvent systems that combine fluorinated solvents with ether electrolytes.⁸⁶

Table 1-3. Comparison of carbonate-type and ether-type solvents.

Solvent type	Carbonate	Ether
Examples	EC, DEC, DMC, etc.	DME, TEGDME, DOL, etc.
Advantages	High oxidation stability (> 4 V)	Good Li compatibility (less dendrite) High cathode stability
Disadvantages	Low reduction stability (reacting with Li)	Oxidation instability (< 4 V)

1.4.2 Lithium Salts

The Li salts generally applied in AFLMBs contain inorganic and organic salts. Inorganic Li salts include lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium nitrate (LiNO_3), etc. Organic lithium salts include LiFSI, LiTFSI, lithium difluoro(oxalato)borate (LiDFOB), lithium triflate (LiCF_3SO_3), etc. LiFSI and LiTFSI are two typical organic Li salts widely used in Li-based batteries. Both FSI^- and TFSI^- anions have two stable conformers (*cis*- and *trans*-forms) with small energy differences,^{87,88} The only difference in chemical structure between the two anions is that FSI^- contains fluorosulfonyl groups ($-\text{SO}_2\text{F}$) and TFSI^- contains trifluoromethylsulfonyl groups ($-\text{SO}_2\text{CF}_3$), while the resultant properties and performance characteristics are quite distinct. The F–S bond in LiFSI is weaker than the C–S bond in LiTFSI, leading to faster hydrolysis and lower heat resistance for LiFSI. Additionally, both LiFSI and LiTFSI have very high solubility and can easily absorb moisture from the air, requiring strict sealing during handling to ensure electrolyte quality. As for applications, LiTFSI improves low-temperature performance in electrolytes, but as LiFSI has risen in prominence, it has gradually replaced LiTFSI due to its superior properties and is now widely used. Recently, LiFSI is often combined with ionic liquids in electrolytes for the application of Li-based batteries.⁸⁹

In general, the modification of Li salts in the electrolyte can be categorized into the following: dual-salt electrolytes,²⁶ high-concentration electrolytes (HCEs),^{25,27} and localized high-concentration electrolytes (LHCEs).⁹⁰

1.4.2.1 Dual lithium salts

In general, inorganic Li salts possess high ionic conductivity and electrochemical stability, while using organic Li salts can achieve high thermal and chemical stability.³¹ As a promising alternative, the inorganic-organic dual Li-salt electrolytes combine the advantages of inorganic Li salts (e.g. LiPF_6 , LiBF_4 , LiNO_3), and organic Li salts (e.g. LiDFOB , LiFSI, LiTFSI).

Beyene et al. investigated 2 M LiFSI + 1 M LiTFSI in DME/DOL (1:1, v/v).²⁶ The dramatic CE performance enhancement for this dual-salt electrolyte was observed compared to the concentrated single-salt (3 M TFSI) electrolyte, which was attributed to the formations of a more compact inorganic-rich SEI layer owing to the reductive

decomposition of FSI⁻ anion (**Figure 1-21**). Weber et al. studied the LiDFOB + LiBF₄ dual-salt electrolyte by using an FEC:DEC (1:2, v/v) solvent mix, and found that 80% of the initial capacity was retained for 80 to 90 cycles when a practical concentration (~1.2 M) was adopted (**Figure 1-22**).²⁸ Their result was quite remarkable considering that it was achieved in a practical large-area pouch cell under lean electrolyte conditions. Rodriguez et al. used 1 M LiNO₃ coupled with 1 M LiFSI in glyme and achieved the inhibition of Li dendrite growth and high Li plating capacity retention. Their study demonstrated the advantage of reducing the Li salt concentration while retaining good CE performance for the application of dual salt electrolyte in AFLMBs.³⁴

Dual-salt electrolytes have gained popularity in recent AFLMBs studies due to their ability to enhance the performance of electrolytes while reducing costs compared to concentrated electrolytes. These dual-salt solutions are increasingly favored in the latest electrolyte designs for advanced battery technologies.

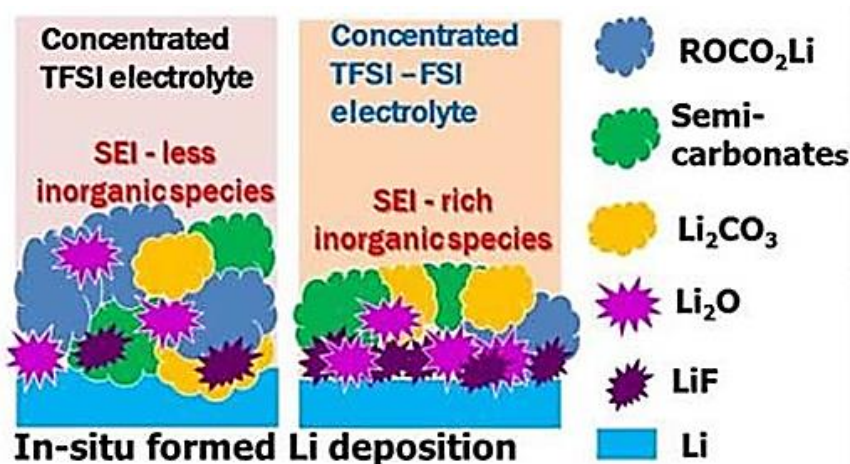


Figure 1-21. The estimated SEI formed the concentrated TFSI electrolyte and the concentrated TFSI-TFSI dual-salt electrolyte.²⁶

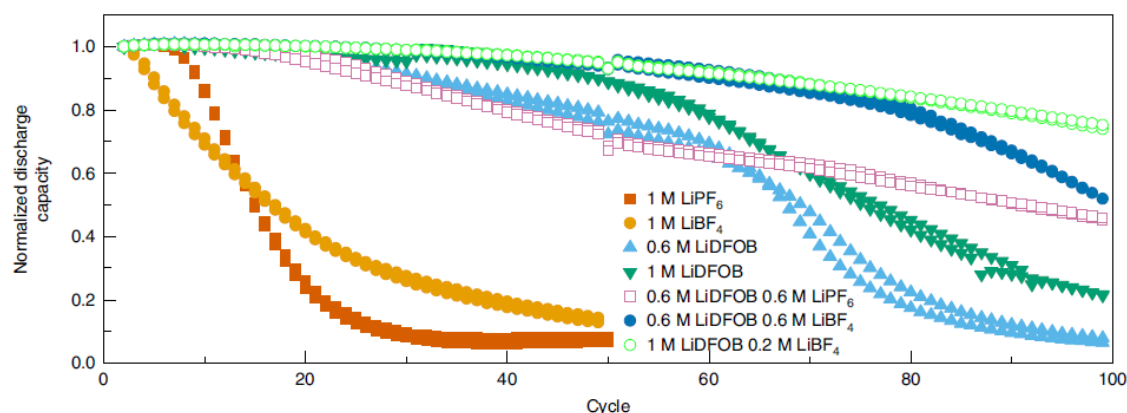


Figure 1-22. Capacity retention for anode-free pouch cells using electrolytes with different single- and dual-Li salts.²⁸

1.4.2.2 Lithium salt concentration

As discussed in Section 1.4.1, the ether-based electrolytes usually possess low oxidation stability. A common approach to address this issue is to increase the Li salt concentration of the electrolyte. Previously, efforts to optimize electrolyte composition have largely focused on adjusting its concentration. Typically, electrolytes in the range from 1.0 to 1.2 M are used, as these concentrations offer a balance between desirable properties such as ionic conductivity, viscosity, and stability. However, in the past decades there has been growing interest in electrolytes with highly-concentrated Li salts, as they promote the formation of a stable SEI layer that helps preventing Li dendrite growth.^{91–93}

The ratio of solvent to Li salts plays a crucial role in influencing the composition and properties of the SEI layer. As shown in **Table 1-4** and **Figure 1-23**, for the HCEs (usually with a concentration higher than 4 M) an anion-involved solvation structure forms, meaning there is increased interaction between Li ions and anions. This leads to the creation of inorganic-rich SEI layers that are more rigid and can prevent further electrolyte decomposition, thereby improving the electrolyte's oxidation stability. In contrast, in dilute electrolytes (less than 3 M), the excess of free solvent molecules results in a solvation structure where Li ions interact more with solvent molecules. This leads to the formation of organic-rich SEI layers, which are fragile and unstable. It should be noted that, the terminology “concentration” in this thesis is a relative concept in batteries' research over past decades,⁹⁴ since 3 M can be regarded as remarkably concentrated in other fields such as surface chemistry.

On the other hand, higher electrolyte concentration comes with trade-offs, because it will increase viscosity, which instead lowers the ionic conductivity. In addition, HCEs require a larger quantity of Li salt, increasing the weight of battery and therefore, reducing its energy density. Moreover, the cost of Li salt, which could account for over 50% of the total cost of conventional electrolytes, makes high concentrations more expensive than dilute ones.⁹⁵ Thus, it might be a good choice for the future research to put more attentions back on the electrolytes with considerably low concentrations (e.g., even less than 0.5 M). Correspondingly, the major challenge in using dilute electrolytes is finding ways to resolve unstable solvent-derived SEI, to improve the overall performance. Under this circumstance, modifying their solvation structure is necessary.

Table 1-4. The comparison of concentrated and dilute electrolytes.

Electrolyte type	Concentrated (> 4 M)	Dilute (< 3 M)
Advantages	Improved oxidation stability	Cost-effective
	Anion-involved solvation (Stable SEI)	Retaining high energy density Higher ionic conductivity
Disadvantages	High cost Reduced energy density Less conductive	Free solvent dominated (Unstable SEI)

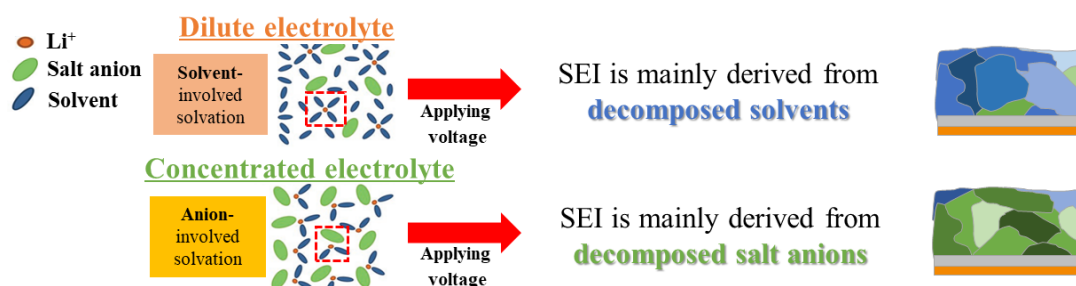


Figure 1-23. Schematic illustration of different SEI layers formed in dilute and concentrated electrolytes, respectively.

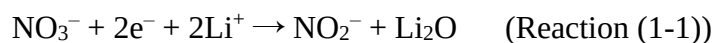
1.4.3 Additives

Conventional electrolytes in Li-based batteries consist of conductive Li salt(s) and solvent that can completely dissolve the Li salt(s). Additionally, incorporating a small amount of electrolyte additives can significantly enhance the battery's performance.^{96,97} The concentration of electrolyte additives is usually quite low, often ranging from as little as 0.1% to 5% by weight of the total electrolyte composition. Despite their small quantities, these additives have a significant impact on the performance and safety of the battery. Typically, they can effectively modify the behavior of the electrolyte, such as enhancing ionic conductivity, improving thermal stability, forming protective layers on the electrodes, or preventing undesirable side reactions. On the other hand, using them in larger quantities could lead to undesirable effects, including increased viscosity of the electrolyte or other negative impacts on the battery's performance and lifespan. Therefore, precise formulation and balancing of these additives are crucial for achieving optimal battery performance.

Basically, there are two types of additives, i.e. inorganic additives (such as LiNO_3 , LiAsF_6 and AlCl_3) and organic additives (such as vinylene carbonate (VC), and FEC). The lowest unoccupied molecular orbital (LUMO) energy of the additives is usually lower than that of other electrolyte components so that they can be preferentially

reduced on Li metal anode to form more conductive and robust SEI components. LiNO₃ is one of the most commonly used inorganic additives,^{98–102} which is mainly because of its low cost and the capability to upregulate the SEI characteristics. The LUMO energy of LiNO₃ is -1.42 eV, so it has the priority to be reduced by Li metal than other Li salt(s) in the electrolyte.⁷⁹

LiNO₃ is commonly used as an additive in the Li-S batteries to protect the Li anode from reacting with polysulfides.⁷¹ Additionally, it has been shown to enhance performance in Li-O₂ batteries.¹⁰³ According to the previous studies, LiNO₃ forms a protective layer consisting of ionic conductive Li_xNO_y, and some oxidized polysulfides, which helps reduce the polysulfide shuttle effect and thereby improves the CE performance.^{104,105} It was also found by Cui et al. that the synergetic effect of LiNO₃ and polysulfides plays an important role in preventing dendrite formation and enhancing overall battery efficiency.¹⁰⁶ Furthermore, it was reported that adding LiNO₃ as a co-salt to LiFSI can regulate the morphology of plated Li from dendritic Li to spherical Li to suppress the undesired reaction area between Li and the free solvent.^{107,108} In the case of adopting LiTFSI with LiNO₃ additive, the coordination of TFSI⁻ anions with Li⁺ can be strengthened, and the decomposition of TFSI⁻ anions can be facilitated to generate low electronic conductive components such as LiF or Li₂CO₃.¹⁰⁹ Jaumann et al. discussed the function of LiNO₃ in depth and discovered that the addition of LiNO₃ to ether-based electrolyte solutions (DME/DOL) enhances the electrochemical reversibility of silicon/carbon electrodes by forming a protective SEI layer composed of R-NO₂ species (R represents the organic components) via **Reaction (1-1)**:



This layer prevents the decomposition of the conductive salt LiTFSI but does not inhibit DOL decomposition.¹¹⁰ In addition, the presence of Li₂O is linked to improved long-term cycling stability. In contrast, high concentrations of LiF are associated with lower reversibility, challenging the common assumption of its positive impact on SEI stability (**Figure 1-24**).

However, it should be mentioned that, although there have been many studies on LiNO₃ additive applied in Li-based batteries, the investigations on its function in the Li-deficient batteries like AFLMBs are still limited, particularly when using bare Cu as current collector.^{99–101,111}

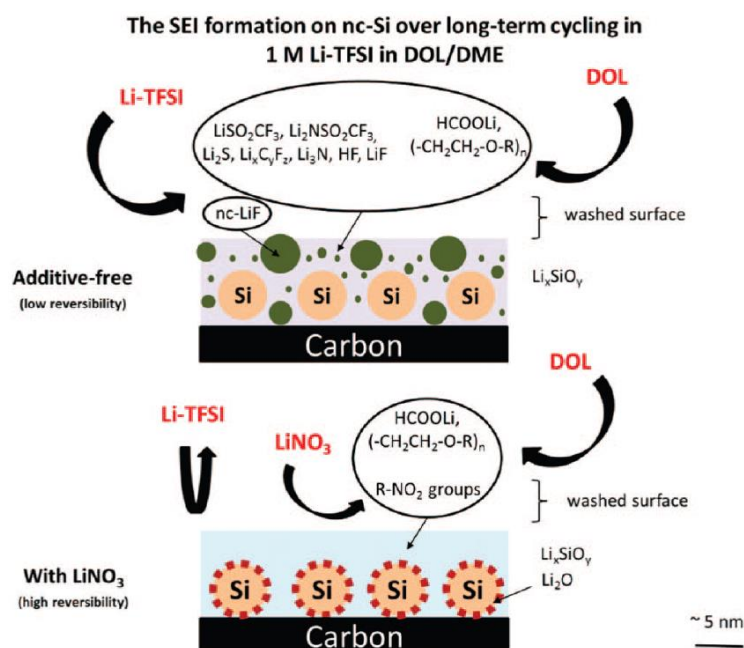


Figure 1-24. Schematic illustration of the SEI formation mechanism on the nanostructured silicon/carbon electrode after prolonged cycling in 1 M LiTFSI in DOL/DME, with respect to the addition of LiNO₃.¹¹⁰

1.4.4 Future Direction of Developing Ether-based Electrolytes

Basically, the future development of ether-based electrolytes should focus on the following key aspects:

1. Improved Li solvation by anions: In electrolytes containing solvent and Li salt, anions compete with solvent molecules to solvate Li ions, leading to three types of solvation structures, namely SSIP (solvent-separated ion pairs), CIP (contact ion pairs), and aggregates (AGG). From SSIP to AGG, more anions interact with Li instead of solvent molecules.

2. High oxidation stability: To be applied in high-voltage batteries, electrolytes must possess strong oxidation resistance.

3. Low concentration: Reducing the concentration of electrolytes can help lower costs, making them more economically feasible for large-scale use.

4. Non-fluorinated electrolytes: Although fluorinated ethers can improve SEI composition by forming LiF-rich layers, their uncertain environmental impact poses a risk for large-scale commercialization.

Overall, modifying the solvation structure is key to minimizing electrolyte

decomposition. While increasing electrolyte concentration has been the traditional method, recent advancements suggest using weakly-solvated ether electrolytes (WSEE),^{112–114} which takes the opposite route by maintaining a low salt concentration. WSEE electrolytes, despite their low concentration, can still create an anion-involved solvation environment, similar to highly concentrated electrolytes. They use less polar solvents, which suppress the interaction between Li and solvent molecules, facilitating the formation of CIP or even AGG solvation structures (**Figure 1-25**).

However, it is important to note that while WSEE offers similar benefits to highly concentrated electrolytes, the fundamental difference is that WSEE still contains many free solvent molecules due to its low concentration. The current challenge with WSEE lies in its limited compatibility with high-voltage cathodes like NMC. Most WSEE formulations cannot yet tolerate the high voltages required, and the underlying mechanisms of WSEE are not fully understood, requiring further research.⁹⁴

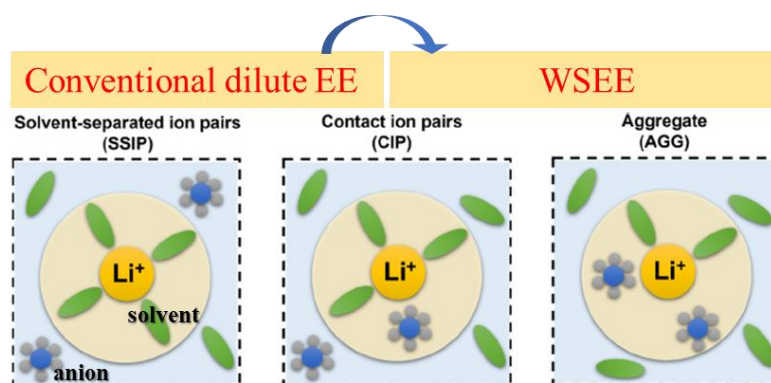


Figure 1-25. Schematic comparison of conventional dilute ether-based electrolytes and the WSEE.⁹⁴

1.5 Objective and Overview of This Thesis

The objective of this thesis is to study the fundamental processes at the electrode/electrolyte interface, focusing on SEI layers, Li plating/stripping and E.D. reactions in the low-concentration ether-based electrolyte system for AFLMBs, while Li||Cu was used resembling the anode side. In particular, the SEI layers and the E.D. process are highly interdependent, creating either a virtuous cycle or a vicious cycle during charge and discharge cycling. In other words, developing a robust SEI can suppress the progression of E.D., while understanding the E.D. mechanism can contribute to the construction of a more stable SEI structure. This thesis majorly aims at resolving the main problems regarding both SEI layers and E.D. process (e.g., the

compositional and morphological change of SEI, and the severe E.D. occurring on Li metal) through the modification of electrolytes. The investigations were conducted by controlling the potential and applying *in situ* techniques to monitor the potential-dependent progress of surface components (SEI species, E.D. products, etc.). Particular focuses were placed on:

1. Low concentration (< 3 M) electrolytes, in which the underlying problems in SEI layers and E.D. are more prominent;
2. The initial stage of cycling, particularly the first cycle which lays the fundamental groundwork and can have a profound impact on subsequent cycles;
3. The roles of LiNO_3 as an additive and a co-salt that have not been discovered.

In **Chapter 1**, the background and challenges in AFLMBs research, and the electrolyte modification methods to address these challenges, from a viewpoint of fundamental interfacial sciences, is reviewed.

In **Chapter 2**, information about chemicals, principles of characterization methods, instrumental setups, as well as experimental parameters and conditions are given.

In **Chapter 3**, the change of mass, surface roughness, and the species of the adsorbed layer (n-SEI and pre-SEI) over Cu electrode surface at OCP and as a function of applied potential prior to initial Li plating was preliminarily examined in the low-concentration TEGDME-based electrolytes dissolving LiTFSI and LiNO_3 . The total concentration was set as 0.4 M to particularly focus on the solvent-derived adsorbed layer formation mechanism, where organic species play an important role. The investigation was performed at a slow scan rate of 1 mV/s to enable clearer identification of organic and inorganic products and an assessment of their impacts. Additionally, the roles of LiNO_3 as an additive and as a co-salt were explored and compared. Using QCM combined with CV, surface mass changes and roughness variations were analyzed, and a potential-dependent shift in surface composition affected by the ratio of LiNO_3 (namely, w/o LiNO_3 , LiNO_3 as an additive, and as a co-salt) was confirmed by the MPE change. FT-IRAS revealed the formation of organic species at OCP and during cathodic scanning, demonstrating the major role of LiNO_3 in accelerating the decomposition of TEGDME and regulating the surface species of the adsorbed layer on the Cu surface prior to initial Li plating.

In **Chapter 4**, the effects of operating potential range, electrolyte concentration,

and LiNO_3 additive on the SEI layer structure and Li plating/stripping efficiency was investigated in low-concentration TEGDME-based electrolytes (0.4 M and 2.0 M of LiTFSI). Techniques such as CV, QCM, XPS, SERS, EIS, and SEM analysis were employed. Key findings include the identification of an “oxidative subsequent SEI” (OSS) formation process and its impact on surface morphology as well as Li plating/stripping efficiency. It was found that LiNO_3 addition or blocking OSS greatly enhanced the stability of CE performance during cycling, while increasing LiTFSI concentration from 0.4 M to 2.0 M alone did not function well. Further investigation revealed the protective role of Li_2O in improving SEI stability under the relatively low concentration of 0.4 M, and the presence of LiNO_3 was found to preserve Li_2O and prevent its oxidation to Li_2O_2 , which is the guarantee of stability. At the higher concentration (2.0 M) with LiNO_3 additive, LiF became the decisive SEI species, further enhancing the CE.

In **Chapter 5**, two common Li salts, LiFSI and LiTFSI, were combined with LiNO_3 as the co-salt in DME-based electrolytes to investigate the E.D. mechanisms during initial-cycle Li plating/stripping of Li||Cu half-cell. The total concentration was set as 1.2 M in an attempt to highlight the decomposition of both Li salts and solvent. First, E.D.-derived charges were extracted during initial Li plating/stripping via a method called “multi-step chronoamperometry (MUSCA)” and the non-linear fitting with the modified approach of the “Li-SEI model”, while QCM was used to separate mass changes related to E.D. process. Spectroscopic techniques (SERS and FT-IRAS) were employed to analyze potential-dependent variations in the surface major chemical species and propose possible E.D. reactions associated with initial Li plating. Lastly, the charge ratios of each electrochemical E.D. reaction were calculated and discussed. The differences between single-salt and dual-salt electrolytes, with particular emphasis on the effect of LiNO_3 as the co-salt, were carefully evaluated. This chapter highlights that LiNO_3 played a crucial role by preventing the reduction of LiFSI/LiTFSI into smaller inorganic by-products. It also promoted the interaction between LiFSI/LiTFSI and DME solvent by facilitating the substitution of functional groups within the Li salts by DME fragments, increasing the charge ratio of salt-solvent interactions in the E.D. process during the initial Li plating/stripping.

In **Chapter 6**, the overall conclusions of this thesis and potential directions for future research are presented.

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Chapter 2

Experimental

2.1 Materials

The Cu disc ($\phi 16 \text{ mm} \times 0.2 \text{ mm}$ in thickness, $\geq 99.96\%$) was purchased from Takeuchi Metal Foil & Powder Co., Ltd. The Cu - deposited quartz crystal was purchased from Seiko EG&G Co., Ltd. The Cu round plate ($\phi 10 \text{ mm} \times 5 \text{ mm}$ in thickness, 99.999%) was purchased from E-Metals Co., Ltd. All types of Cu as electrodes were rinsed with concentrated acetic (denoted as c-HAc, Wako Pure Chemical Industries) for 10 min at room temperature and thoroughly dried by Ar flow prior to all measurements.¹ The pre-treated Cu electrode was assembled with Li ribbon (Sigma Aldrich, 99%) in order to construct the Li||Cu half-cell for a variety of electrochemical measurements.

Lithium-battery-grade lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%), lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.9%), 1,2-dimethoxyethane (DME, 99.5%) and tetraethylene glycol dimethyl ether (TEGDME, $>98\%$) were purchased from Kishida Chemical Co., Ltd. The corresponding formula of the chemicals are shown in **Figure 2-1**. All the solvents were stored with 4A molecular sieves for at least 7 days before use. The Li salts (LiFSI and LiTFSI) were completely dissolved in the solvent (DME or TEGDME) and stirred overnight to make homogeneous solutions with different concentrations in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.5 \text{ ppm}$, $\text{O}_2 < 0.2 \text{ ppm}$). Lithium nitrate (LiNO_3 , $>99.95\%$, Kanto Chemical Co., Inc.) was either added as an additive into the single-salt electrolytes, or as a second salt to prepare the dual-salt electrolytes. The water content in these electrolytes was all less than 30 ppm by Karl-Fischer titration (model: CA-21, Mitsubishi Chemical Analytech Co., Ltd.).

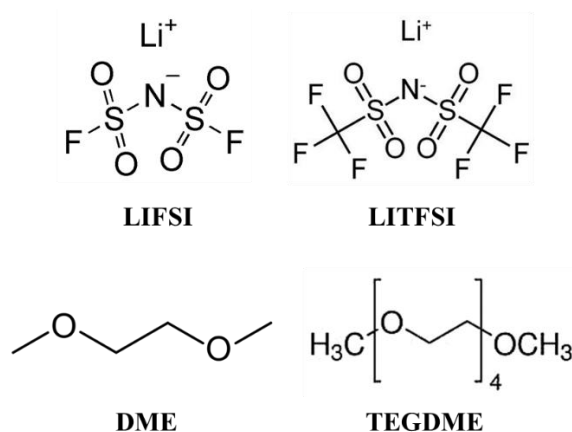


Figure 2-1. Chemical formula of LiFSI, LiTFSI, DME and TEGDME.

2.2 Cyclic Voltammetry (CV)

2.2.1 Introduction of CV

CV is a widely used electrochemical technique for studying the redox behavior of electrodes and electrolyte stability in lithium-based batteries. Regarding LMBs or AFLMBs studies, CV provides insights into the kinetics of lithium plating and stripping, helping to evaluate reversibility and Coulombic efficiency (CE). By analyzing current peaks, CV reveals the potential at which Li deposits and dissolves and allows identification of key processes like SEI formation and electrolyte decomposition. However, its effectiveness is influenced by scan rate, electrode surface condition, and ion transport limitations, requiring careful optimization of experimental parameters for accurate interpretation.

2.2.2 Parameters of CV measurements

CV measurements were conducted using the HZ-7000 system (Hokuto Denko Corporation) in the glovebox. A PTFE-made three-electrode cell was used, with the Cu disc as working electrode and Li ribbon as counter and reference electrode (**Figure 2-2**). The measurement conditions include a fixed scanning rate of 1 mV or 10 mV/s, and a potential range not larger than -0.5 V to 3.2 V vs. Li/Li⁺. In this study, the Coulombic CE of Li plating/stripping in the Li||Cu half-cell was calculated by **Equation 2-1**:

$$CE = \frac{Q(\text{stripping})}{Q(\text{plating})} \times 100\% \quad (2-1)$$

where $Q(\text{stripping})$ and $Q(\text{plating})$ represent the charges consumed during Li stripping and in Li plating, respectively, obtained by integrating peak areas in the current density vs. time curves.

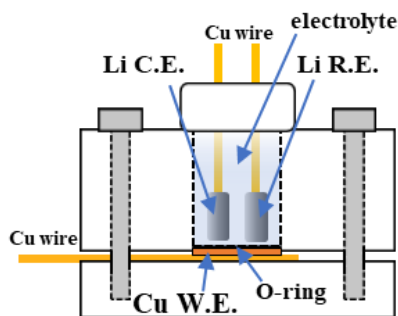


Figure 2-2. Schematic illustration of CV cell. W.E.: working electrode; C.E.: counter electrode; R.E.: reference electrode.

2.3 Chronoamperometry (CA)

2.3.1 Introduction of CA

CA is a widely used electrochemical technique in battery research that provides valuable insights into the reaction kinetics and transport properties of battery materials. This method involves applying a step change in potential to an electrochemical cell and measuring the resulting “current transients” as a function of time. CA is particularly useful for studying the behavior of electrode materials under conditions that mimic the rapid changes in potential experienced during battery charging and discharging.^{2,3}

CA is based on the control of the electrode potential over time. Initially, a sudden and constant potential is applied to the electrode, triggering electrochemical reactions at the electrode surface. This potential step changes the electrochemical environment, causing either oxidation or reduction of species depending on the direction of the applied potential. The resulting current-time transient displays a characteristic decay pattern: the current spikes initially due to excess charge carriers, then decreases as the concentration of reactive species at the electrode surface declines. This response, measured as a function of time, reflects the kinetics of the reactions and diffusion processes, providing insight into the reaction mechanisms. Furthermore, CA can help in the evaluation of electrode stability under rapid charging conditions, determination of the electrodeposition behavior and mechanism, study of degradation mechanisms, assessment of the effects of different electrolytes and additives on the performance of the battery, etc.⁴⁻⁷

2.3.2 Parameters of CA measurements

The electrochemical cell used for CA measurement was same as that used for CV measurement. **Figure 2-3** shows the program for a specialized CA method called multiple potential step chronoamperometry (MUSCA).^{8,9} This program involved totally 60 potential steps, resembling the continuous CA tests during Li plating and stripping. Specifically, 20 different applied potentials ranging from -10 mV to -200 mV were selected to simulate the Li plating during negative scanning (cathodic process), 20 different applied potentials ranging from -200 mV to -10 mV were selected to simulate the Li plating during positive scanning (anodic process), and 20 different applied potentials ranging from 0 mV to 200 mV were selected to simulate the Li stripping. The

potential interval was set as 10 mV.

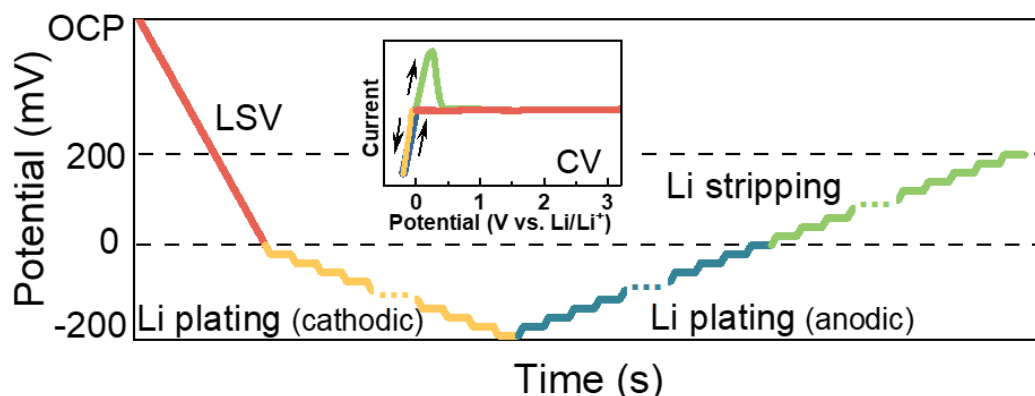


Figure 2-3. The program setting of time-dependent potential variation for CA measurements. LSV stands for linear sweep voltammetry. The inset indicates the equivalent CV measurement for a better understanding of the CA measurement program setting.

2.4 Quartz Crystal Microbalance (QCM)

2.4.1 Introduction of QCM

QCM is a highly sensitive method capable of detecting surface mass changes as minute as a few nanograms by measuring shifts in the resonance frequency of a quartz crystal sensor.¹⁰ Coupled with electrochemical techniques like CV, this method allows for real-time tracking of growth and dissolution of surface layers, such as the formation of organic lithium salts in the SEI layer.^{11,12}

The application of QCM in electrochemistry works by measuring mass changes on an electrode during electrochemical processes.^{13–15} The electrode consists of a thin AT-cut crystal, positioned approximately 35 degrees to the x-axis, and coated with a metallic film on both sides. QCM operates on the principle of the piezoelectric effect in quartz crystals.^{16,17} When an alternating current is applied, it induces oscillations in the quartz. These oscillations can be influenced by the addition or removal of rigid substances on the electrode's surface. The resulting frequency changes of oscillations can be tracked in real time, allowing for the analysis of various interactions at the electrode, such as metal deposition and oxidation processes.

The mass change (Δm) on the working electrode surface can be converted from the recorded frequency change using the Sauerbrey equation (**Equation 2-2**):¹⁸

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (2-2)$$

where f_0 and Δf are the fundamental resonant frequency and the change in frequency

(Hz) respectively, Δm is the mass change (μg), A is the active electrode area deposited on the crystal (cm^2), ρ_q is the density of quartz (2.648 g/cm^3), and μ_q is the shear modulus of quartz ($2.947 \times 10^{11} \text{ g/cm}\cdot\text{s}^2$). The f_0 and A values for the Cu quartz electrode used in this study are 9.04 MHz and 0.196 cm^2 , respectively. Therefore, Δm on the crystal surface can be determined for a given Δf during a QCM experiment.

Apart from its function as a nanogram mass sensor, QCM can also be used to analyze the surface roughness change by detecting resonant resistance ΔR , the increase of which causes energy loss during oscillation.^{19,20} It has been found that ΔR is influenced by surface roughness, that is to say, when the electrolyte is trapped by the roughened surface layer formed on the electrode, the damping of shear-mode vibration will lead to the increase of ΔR .^{21,22} **Figure 2-4** shows an equivalent circuit of quartz crystal electrode, by which the QCM can achieve the synchro recording of mass change and surface roughness change.

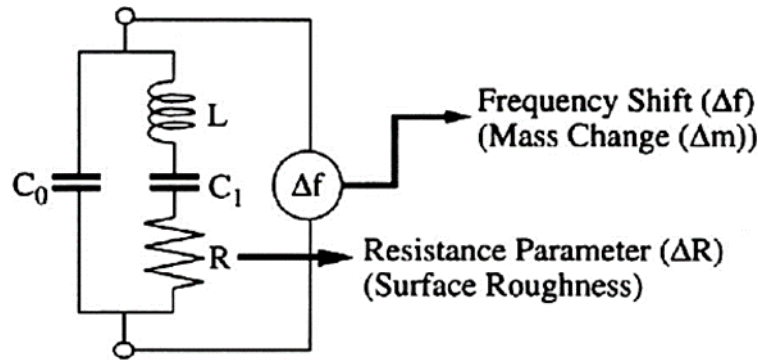


Figure 2-4. An equivalent circuit of quartz crystal electrode under shear-mode vibration. The symbol L , C_0 , and C_1 represent the mass, elasticity modulus, and the inherent static capacitance, respectively, in a real mechanical vibration of the electrode.²³

It should be noted that, the deviation could occur when applying above Sauerbrey equation to study an electrolyte/electrode interface, in which the influence of density and viscosity of electrolyte due to the contact with electrode surface should be considered.^{24,25} Under such circumstances, the measured Δf is expressed by **Equation 2-3**:

$$\Delta f = \Delta f_m + \Delta f_{\eta\rho} \quad (2-3)$$

Where Δf_m is due to the actual deposited product, and $\Delta f_{\eta\rho}$ is the viscosity-induced frequency change due to electrolyte contact which is obtained from **Equation 2-4**:²⁴

$$\Delta f_{\eta\rho} = -f_0^{3/2} \sqrt{\frac{\rho_L \eta_L}{\pi \rho_q \mu_q}} \quad (2-4)$$

where ρ_L and η_L are the density and viscosity of the electrolyte, which are subject to

change during measurement. In the meantime, it is known that the high viscosity of electrolyte can easily cause an increase of ΔR .²³ Therefore, ΔR is also dependent on ρ_L and η_L (**Equation 2-5**):

$$\Delta R = \frac{A\sqrt{2\pi f_0 \rho_L \eta_L}}{k^2} \quad (2-5)$$

where k is called electromechanical coupling factor, which is a specific value for each electrolyte.²⁵ By combining Equation (4) and (5), one can get the following equation (**Equation 2-6**):

$$\Delta f_{\eta\rho} = -\frac{f_0 \Delta R k^2}{A\pi\sqrt{2\rho_q \mu_q}} \quad (2-6)$$

in which the initial R and $f_{\eta\rho}$ values can be confirmed as soon as the electrode is immersed in the electrolyte, while the latter is the difference between the resonant frequencies before and after immersing electrolyte, respectively. Then k can be determined according to Equation (2-6), and thereafter, the real-time $\Delta f_{\eta\rho}$ during measurement can be obtained with the recorded ΔR . In this study, the measured Δf was converted into Δf_m for calculating the real mass change.

With the derived Δm from QCM measurements and the charge (Q) obtained by the integration of current during the concurrent electrochemical measurements, the mass-to-charge ratio, which is called MPE (mass change per mole of electrons), can be obtained as per Faraday's law (**Equation 2-7**):²⁶

$$MPE = \frac{\Delta m}{Q/(nF)} \quad (2-7)$$

Where nF is the molar charge transferred. With the obtained of MPE values, one could not only predict possible reactions on the electrode surface but also discuss the reversibility of the redox couples including Li plating and stripping process.

Note that although QCM is a surface sensitive technique, the mass growth or reduction cannot be fully attributed to the surface reactions, since either the deposits produced by reactions in bulk electrolyte or the physical disconnection of unreactive species on the electrode surface can also account for the mass change. This might hinder the correct MPE estimation in some cases. Therefore, the combination of QCM with other surface-sensitive chemical species detecting techniques (e.g. Raman spectroscopy) is required to ensure the reliability of MPE analysis.

2.4.2 Parameters of QCM measurements

In the present study, the QCM measurement was carried out using the QCA-922 system (Seiko EG&G Co., Ltd.) during the CV scanning. A customized three-electrode electrochemical cell made of a PTFE bottom and a glass chamber was used. An AT-cut quartz crystal deposited by Cu thin films (fundamental resonant frequency: 9.04 MHz) was used as working electrode, and Li ribbon was used as counter and reference electrode (**Figure 2-5**). The Cu quartz electrode was rinsed with c-HAc for 10 min and thoroughly dried by argon flow prior to the experiment. The QCM cell was kept for 30 min before each measurement to stabilize the open circuit potential (OCP), Δm , and ΔR . The gate time for the experiment was 0.1 s. During the electrochemical process, the values of Δm and ΔR were simultaneously recorded.

In Chapter 3 and 4, QCM coupled with CV measurements were carried out at a scan rate of 1 mV/s and 10 mV/s, respectively. In Chapter 5, QCM measurements were mainly conducted during initial Li plating and stripping by the MUSCA method (see **Figure 2-3**), where different potentials were applied starting from -10 mV to -200 mV and reversed to 200 mV at 10 mV intervals.

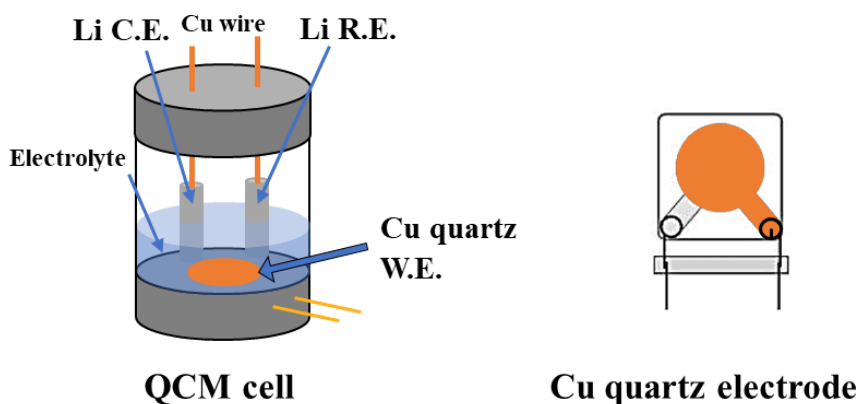


Figure 2-5. Schematic illustration of QCM cell and Cu quartz electrode.

2.5 Surface-enhanced Raman spectroscopy (SERS)

2.5.1 Introduction of SERS

SERS is a technique that amplifies the Raman signals of molecules near rough metal surfaces, allowing for the detection of single molecules.^{27,28} The enhancement is primarily attributed to two mechanisms: electromagnetic mechanism and chemical mechanism.^{29–31}

The electromagnetic mechanism (EM) is the dominant mechanism in SERS, which enhances the Raman signals through the interaction of molecules with the electric fields around metal particles like Pt, Au, Ag and Cu. When an incident light hits the surface, it excites localized surface plasmon resonance (LSPR), which amplifies the Raman signals. If the frequency of the incident light is close to the resonance frequency of these surface plasmons, the local electromagnetic fields are significantly enhanced, thereby increasing the intensity of the Raman scattering by factors up to 10^{10} or more. Rough metal surfaces or specifically arranged nanoparticles (when the distance between nanoparticles is less than 10 nm) create the “hot-spots”, where these plasmons are localized, producing significant enhancement of signal.^{32–35} For instance, as depicted in **Figure 2-6(a)**, Raman-active analyte molecules situated in the gap between the two close metal nanoparticles exhibit stronger Raman signals compared to those on a single metal surface, highlighting the role of these “hot-spots”.³⁶

The chemical mechanism (CM) involves the actual chemical interactions between the Raman-active analyte molecules and the metal nanoparticles when the molecules chemisorb onto the metal surface, causing the transfer of electrons between them (**Figure 2-6(b)**).³⁶ This can form a new chemical entity or charge-transfer complex, altering the electronic structure of the molecule, which can lead to changes in the polarizability of the molecule during the Raman scattering process, thus enhancing the Raman signal. The CM typically results in an increase in Raman signal by a factor of up to 10^3 , and its effect is highly specific to the molecular structure and the nature of the metal surface involved. Although the enhancement from CM is generally weaker than that from EM, CM still plays a crucial role in SERS.³⁷

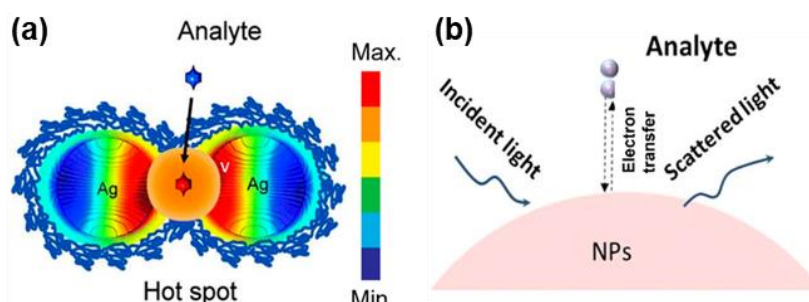


Figure 2-6. Schematic of two mechanisms contributing to SERS effect: (a) electromagnetic enhancement and (b) chemical enhancement.³⁶

In the present study, Cu metal was selected as the SERS substrate instead of commonly used metals like Au and Ag, because this can mimic the actual working condition of the anode side of AFLMBs by adopting the Li||Cu half-cell configuration.

Furthermore, Cu can serve as a cost-effective alternative for certain SERS applications. While not as efficient as Au or Ag, Cu still can support LSPR and exhibit decent plasmonic properties that can be utilized for SERS.^{38–40}

2.5.2 SERS substrate preparation

Cu plate was electrochemically roughened by a “cathodic deposition method”⁴⁰ in 0.4 M H₂SO₄ + 0.2 M CuSO₄ aqueous solution by using a plate-type three-electrode electrochemical cell (**Figure 2-7(a)**) with the HZ-7000 potentiostat. The surface area of Cu plate exposed for roughening was about 50 mm². The counter electrode was Cu wire (serving as an anode) and the reference electrode was Ag/AgCl (sat. NaCl). The Cu plate cathode was polarized at *ca.* -0.5 V vs. Ag/AgCl for around 75 min to ensure a deposition towards a certain direction. The roughened Cu plate was cleaned by ultrasonication in Mill-Q water for 10 min to remove surface contamination, and was stored in glovebox for further use. The scanning electron microscope (SEM) images indicate the co-existence of roundish (ϕ 200~500 μ m) with some longitudinal (1~4 μ m) flowerlike redeposited metallic Cu on the roughened Cu plate (**Figure 2-7(b)**).

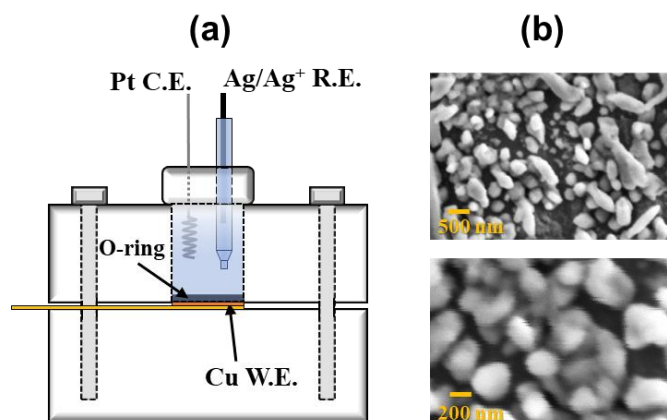


Figure 2-7. (a) Schematic illustration of typical three-electrode electrochemical cell for Cu SERS substrate roughening; (b) SEM images of Cu SERS substrate surface after roughening.

2.5.3 Parameters of *in situ* SERS measurements

The *in situ* SERS spectra was recorded with a confocal microscope spectrometer (RamanTouch-VIS-NIR) in a super-dry room (water contents < 0.1 ppm, Shinryo Corp.). A 10 $\times$ long working distance lens (Olympus America Inc.) was used to observe and locate the surface of electrode. A homemade PTFE three-electrode cell was used,

where the roughened Cu disc was used as the working electrode, and Li ribbon was used as counter and reference electrode (**Figure 2-8**). The 785 nm laser was irradiated through a quartz window ($\phi 10\text{ mm} \times 1\text{ mm}$ in thickness) onto the electrode surface with an exposure time of 10 s. The grating was set as $300\text{ grooves mm}^{-1}$ with a spectral resolution of 3.5 cm^{-1} .

In Chapter 4, the SERS spectra of the first CV cycle were recorded during the negative scanning from OCP to -0.5 V at 10 mV/s (OCP, 1.5, 0.8, 0.1, 0, -0.1 , -0.5 V), followed by the positive scanning up to 2.2 V at 10 mV/s (0.5, 1.5, 2.2 V), and a subsequent scanning up to 3.2 V at 1 mV/s to carefully check a specific oxidation reaction. From the second to the 10th CV cycle scanned between 3.2 V and -0.5 V at 10 mV/s , the spectra were recorded at -0.5 V of the second, third, 5th and 10th cycles. The working electrode potential was kept constant for 3 min before each SERS measurement. A Gaussian-Lorentzian (pseudo-Voigt) function was chosen to deconvolute the Raman peaks at designated regions in order to calculate the integrated peak intensities.

In Chapter 5, the SERS spectra were recorded during the initial cycle by the MUSCA method, with a focus on the region of -200 mV to 200 mV vs. Li/Li^+ where Li plating and Li stripping occur: a negative potential step (-50 , -100 , -120 , -140 , -160 , -180 , -200 mV), followed by a positive potential step (-180 , -160 , -140 , -120 , -100 , -50 , 50 , 100 , 200 mV). The SERS spectra were successively recorded at each potential.

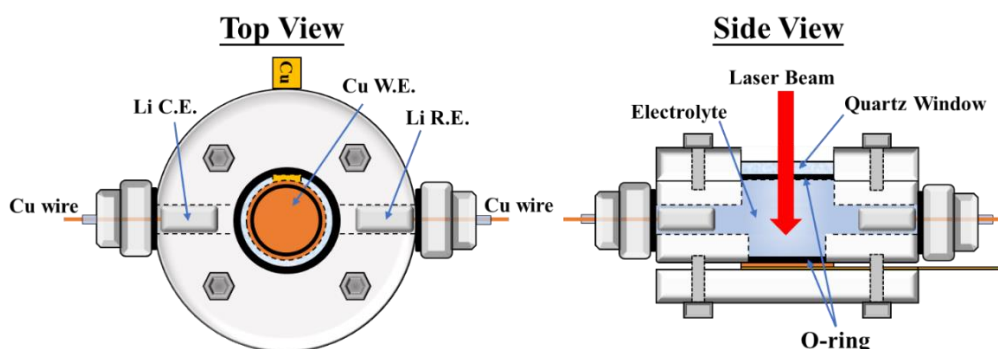


Figure 2-8. Schematic illustration of *in situ* SERS cell.

2.6 Fourier-Transform Infrared Reflection Absorption Spectroscopy (FT-IRAS)

2.6.1 Introduction of FT-IRAS

Fourier-transform infrared (FTIR) spectroscopy is a valuable tool for investigating

changes in chemical bonds and molecular structures in polymers and organic compounds, including in SEI layers. It has been extensively applied to study electrochemical reactions and the dynamic processes occurring at the electrolyte/electrode interface in lithium-based batteries including AFLMBs.⁴¹ Vibrational infrared radiation can be utilized in different methods to gather analytical data from interfaces. Some of the key techniques include transmission infrared spectroscopy, attenuated total reflection infrared spectroscopy (ATR-IR), diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS), infrared reflection absorption spectroscopy (IRAS), etc.

IRAS was first introduced by Bewick et al. for the use of studying electrochemical interfaces. They developed the electrochemically modulated (EM)-IRAS technique, which uses very thin-layer electrochemical cells (1 to 5 μm in thickness) to reduce IR absorption by the bulk electrolyte.⁴² This method measures the difference in the electrode/electrolyte interface at two different potentials, making it effective when adsorbate structures change with applied potential. As an alternative, polarization modulation (PM)-IRAS takes advantage of the fact that p-polarized IR radiation is absorbed more by thin layers on electrodes than s-polarized radiation, allowing researchers to determine the orientation of adsorbed species.⁴³ Unlike SERS, IRAS spectroscopy has the advantage of being applicable to a broader range of metal surfaces. However, a key challenge with IRAS is separating surface-adsorbed species from those in the bulk electrolyte, often requiring subtraction of bulk electrolyte spectra to isolate surface information.^{44,45}

In IRAS, infrared light is directed from the solution side, and the reflected light from the electrode surface is measured. The electrode is pressed against the cell window, reducing the electrolyte layer to μm level for accurate measurement. Common window materials include CaF_2 , ZnSe , and Si , which are transparent to infrared light and insoluble in water. However, it was found in this study that ZnSe can react with organic electrolyte solutions upon applying bias voltage, generating dark-color chemical species that devitrifies the window surface.

A key aspect of IRAS is using p-polarized light at a large incident angle, which creates a strong electric field perpendicular to the metal surface (E_{surf} in **Figure 2-9(a)**). This field enhances absorption by absorbed molecules. In contrast, s-polarized light undergoes phase inversion upon reflection, producing no electric field, and thus no

absorption by surface molecules occurs (**Figure 2-9(b)**).⁴⁶ When measuring with electrodes, the refraction of light at the window-solution interface must be considered. For the most commonly used CaF_2 windows, an incident angle of 60 to 65° is typically used. A polarizer is inserted to select p-polarized light, minimizing background interference from s-polarized.

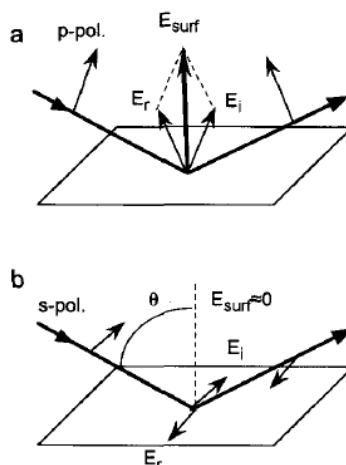


Figure 2-9. Reflection of (a) p-polarized and (b) s-polarized lights at metal surface. E_i and E_r : electric fields of incident and reflected light, respectively; E_{surf} : the generated strong electric field by p-polarized light.⁴⁶

2.6.2 FT-IRAS electrode preparation

The Cu electrode ($\phi 10 \text{ mm} \times 5 \text{ mm}$ in thickness) for IRAS measurements was polished by the #2000 sandpaper to remove the scratches on the surface, followed by cleaning with ultrasonication in Mill-Q water for 2 min to clear away the remaining Cu granules on the electrode surface. The obtained electrode was dried and buff polished by alumina polishing abrasive (nominal particle size: 0.05 μm , Baikowski Co., Ltd.) on the pad to obtain the mirror-like surface. Finally, the electrode was washed by Mill-Q water again and stored in the glovebox for further use.

2.6.3 Parameters of *in situ* FT-IRAS measurements

In situ FT-IRAS measurements were conducted in a three-electrode cell with a glass-made cell body for accommodating Cu working electrode and Li counter and reference electrode, and a PTFE-made bottom plate for fixing the prism (**Figure 2-10**). The hemicylindrical CaF_2 prism ($\phi 25 \text{ mm}$, Pier Optics Co., Ltd. Japan) was used as the

optical window to avoid the decrease of incident angle due to refraction, and the Cu electrode at the bottom of the cell was pressed tightly against the prism to form a very thin layer of bulk electrolyte (*ca.* 1-2 μm in thickness) in between them so as to suppress IR beam absorption from bulk electrolyte, ensuring a strong absorption intensity of the surface chemical species.

The FT-IRAS measurements were carried out using the FT-IR system (JASCO FT/IR-6000 series), and the simultaneous electrochemical measurements were carried out by the HAB-151A potentiostat/galvanostat (Hokuto Denko Corporation). The incident angle of IR beam was set at *ca.* 60° from the surface normal. The reflected IR beam from the electrode surface was detected by the highly sensitive HgCdTe (MCT) amplified photodetectors which were cooled down by liquid N_2 prior to experiment. The IRAS cell was fixed onto the stage in the chamber filled with dry N_2 gas and was held for 15 mins before starting the measurement to minimize the influence of environmental moisture and CO_2 .

In Chapter 3, the infrared spectra were captured continuously with an acquisition time of approximately 30 seconds while performing CV tests of the first cycle behavior at 1 mV/s. All spectra were taken with the p-polarization. The spectral range was set from 1000 to 4000 cm^{-1} because the strong absorption by the CaF_2 prism prevented the extraction of spectral information below 1000 cm^{-1} . During the IRAS measurements in Chapter 5, the potential was shifted from OCP to a negative potential step (-50, -100, -120, -140, -160, -180, -200 mV) and a subsequent positive potential step (-180, -160, -140, -120, -100, -50, 50, 100, 200 mV). The single beam spectra were successively recorded at each potential. Totally 256 cycles of taking each single beam spectrum at a resolution of 4 cm^{-1} were averaged (*ca.* 3 minutes of data acquisition time) to ensure high signal-to-noise ratios.

It should be noted that the main challenge with infrared spectra analysis is the overlap of peaks from the electrolyte and the degraded electrolyte products that form the SEI, as they share similar functional groups. This overlap complicates both the identification and quantification of the chemical species involved. To secure a more accurate analysis, the normalized intensity was used to highlight subtle differences in the spectra between consecutive conditions. Instead of displaying a single beam spectrum, the normalized absorbance is plotted to make these variations more visible. Consequently, the experiment results were presented by absorbance (A), which was calculated by the following equation (**Equation 2-8**):⁴⁶

$$A = -\log\left(\frac{R}{R_0}\right) \quad (2-8)$$

Where R and R_0 are the reflected IR single beam intensities of the sample and the reference, respectively. In this study, the single beam spectrum taken at OCP or at the previous potential of each step of potential was set as the reference.

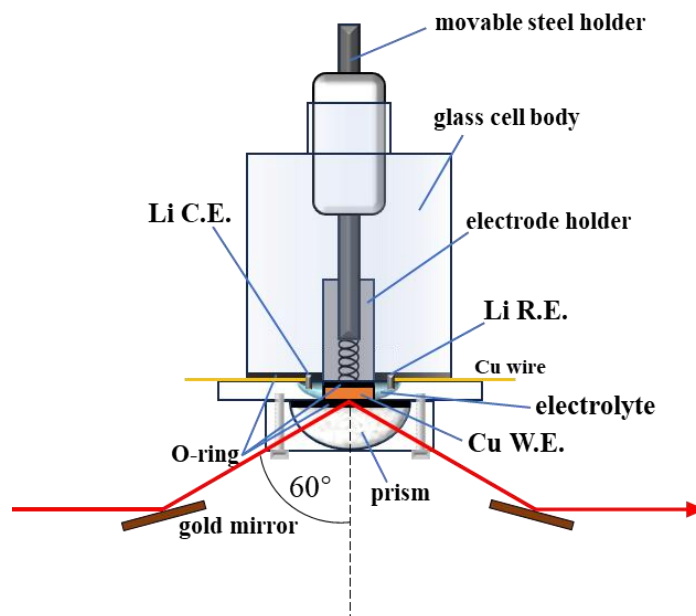


Figure 2-10. Schematic illustration of *in situ* IRAS cell and the experimental setup.

2.7 In-depth X-ray photoelectron spectroscopy (XPS)

2.7.1 Introduction of XPS

XPS provides detailed information on surface chemical bonds at a depth of about 10 nanometers. When studying the surface chemistry of thin SEI layers, *in situ* XPS faces challenges, particularly in the case of liquid electrolytes, which require an ultrahigh vacuum environment.^{47,48} Recently, low-pressure nitrogen environments and liquid electrolytes have been used to address these issues.⁴⁹ In addition, attention should be paid when using XPS in detecting insulating substances within the SEI layer (e.g., LiF, Li₂O), which may cause shifts in energy levels and complicate data interpretation.⁵⁰

2.7.2 Parameters of XPS measurements

XPS depth profile was investigated with the VersaProbe II X-ray Photoelectron Spectrometer (ULVAC-PHI, Inc.) under ultra-high-vacuum condition using monochromatic Al K α (1486.6 eV) as the X-ray source. The samples were prepared by

disassembling Li||Cu half-cells after 50 Li plating/stripping cycles in each electrolyte, taking out the working electrode, rinsing by the TEGDME solvent, and drying the electrode overnight. The sample was loaded in a portable transfer vessel without exposure to air before moving to the XPS spectrometer. The surface of sample was sputtered by Ar⁺ bombardment with a parameter of 2 keV & 20 mA. The F 1s peak at 685.2 eV was used as a reference. A Gaussian-Lorentzian (pseudo-Voigt) function was chosen to deconvolute the XPS peaks, upon which the binding energy in eV and the FWHM (full width at half maximum) of the peaks were determined by referring to literatures and NIST (National Institute of Standards and Technology) database.^{51–60}

2.8 Scanning electron microscope (SEM)

2.8.1 Introduction of SEM

SEM is a very useful technique offering high-resolution imaging of surface morphology. This enables detailed analysis of structures like SEI layers and lithium deposits. With a resolution down to the nanometer scale, SEM is invaluable for visualizing SEI thickness, cracks, and distribution, as well as identifying lithium deposition morphologies such as dendrites or mossy lithium. However, challenges arise when working with highly reactive lithium metal, especially in the vacuum environment required by SEM, where surface oxidation or damage may occur. Recent advancements, such as cryo-SEM and in situ setups, have mitigated these issues, allowing more accurate observations of SEI evolution during cycling.^{61,62} Additionally, while SEM provides excellent surface structural information, care must be taken when interpreting data, especially when correlating morphology with electrochemical performance, as chemical composition and deeper structural changes remain beyond SEM's capabilities.

2.8.2 Parameters of SEM measurements

The scanning electron microscope (SEM) measurement was conducted in the super-dry room using VE-8800 (Keyence) for the observation of the surface morphologies of SEI layers. The samples were prepared by disassembling Li||Cu half-cells after the electrochemical test in each electrolyte, taking out the working electrode, rinsing by the TEGDME solvent, and drying the electrode overnight.

2.9 Electrochemical Impedance Spectroscopy (EIS)

2.9.1 Principle of EIS

EIS is a powerful analytical technique used to study the impedance characteristics of electrochemical systems. By applying a small AC signal and measuring the system's response over a range of frequencies, EIS provides valuable insights into the behavior of different electrochemical processes. In particular, EIS is used to assess electrode interface behavior, characteristics of the SEI layer, and aging processes in lithium batteries.

As shown in **Figure 2-11**, for the electrode-electrolyte interface with SEI layer, the interfacial resistance can be regarded as a combination of the SEI resistance (R_{SEI}) in the high-frequency region of the semicircle and the charge transfer resistance (R_{ct}) in the middle-frequency region of the semicircle. In addition, solution resistance (R_s) represents the resistance of the electrolyte solution, including the ions in the bulk electrolyte. It is typically measured in the high-frequency region and accounts for the ionic conductivity of the electrolyte. This value is generally independent of the SEI layer and charge transfer processes at the electrode interface. The constant phase elements (CPE) represent the capacitive behavior at the electrode-electrolyte interface, often associated with the formation of the electrical double layer. CPE1 (or C_{SEI}) is typically related to the capacitance of the SEI layer, and CPE2 (or C_{dl}) is often associated with the double-layer capacitance directly at the electrode-electrolyte interface. CPE is used instead of a pure capacitor to account for the non-ideal capacitance behavior due to surface roughness or inhomogeneity at the interface. The Warburg element (W_0) accounts for diffusion-controlled processes, particularly the diffusion of ions in the electrolyte. It typically appears in the low-frequency region and reflects the impedance related to the slow diffusion of species like Li^+ through the electrolyte or SEI layer. Together, these elements help to model the overall impedance of an electrochemical system, providing insights into the various resistive and capacitive contributions at different frequencies.

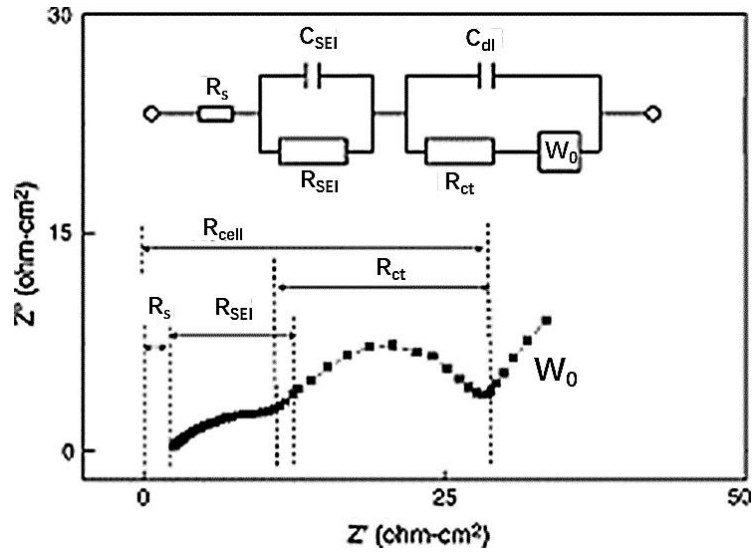


Figure 2-11. Schematic illustration of the typical Nyquist plot for lithium battery's electrode-electrolyte interface with SEI layer, and the corresponding equivalent circuit model.

2.9.2 Parameters of EIS measurements

In this study, the EIS was investigated using Solartron 1255B (Ametek Scientific Instruments) over a frequency range from 100 kHz to 1 Hz with an AC perturbation voltage of 10 mV. A homemade two-electrode cell with Cu as the working electrode and Li foil as the counter electrode ($\phi 16$ mm, Honjo Metal Co., Ltd.) was used for the measurement. The equivalent circuit was determined from the obtained Nyquist plots with referring to literatures.^{51,52,55,57}

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Chapter 3

Chemical and Electrochemical Processes on Copper Electrode prior to Initial Li Plating in TEGDME-based Low-concentration Electrolytes: Effect of the Ratio of LiNO_3

3.1 Introduction

Lithium metal battery (LMBs) have been considered as promising alternative to lithium-ion batteries (LIBs), as the replacement of conventional graphite anode with Li metal anode can greatly enhance the energy density owing to the low redox potential and high theoretical capacity of Li metal.^{1,2} However, the most fundamental obstacle that hinders the practical application of LMBs lies in the highly reactive nature of Li metal, which leads to parasitic reactions and Li dendrites growth during charge-discharge, causing the irreversible loss of both Li metal and electrolyte. To compensate the loss in Li reservoir, LMBs require the usage of excess amount of Li metal in the anode side, which however increases batteries' weight and volume, cost, and risk upon operation.³ Under this circumstance, anode-free lithium metal batteries (AFLMBs) attract growing attentions as an alternative of LMBs.³⁻⁶ In the configuration of AFLMBs, the anode active material is absent in the as-fabricated state, and a bare anode current collector (e.g., Cu) is used as a substrate for Li deposition to create a Li anode after initial charging. In AFLMBs, the negative to positive electrode capacity (N/P) ratio is 0 and 1 after cell assembly and after initial charging, respectively, meaning that all Li resources in the anode come from the cathode during initial charging. Therefore, the use of Li metal can be fully minimized, rendering greatly enhanced energy density and safety compared to LMBs.

A major focus in AFLMBs research is the unstable interface between the electrode and electrolyte, which leads to the formation of the solid electrolyte interphase (SEI) layer. In particular, the first cycle of charge-discharge has garnered significant attention in AFLMBs studies due to its critical role in shaping the n-SEI and pre-SEI, i.e., the two kinds of SEI layers forming before the initial deposition of Li on Cu electrode. Moreover, during the initial stage of charge-discharge, a lot of studies have shown that inorganic species overwhelmingly dominate the composition of the inner SEI layer.⁷⁻⁹ However, it is important to recognize that organic components of the SEI also play a crucial role, particularly in contributing to the flexibility of the SEI layer. Despite their significance, research on organic SEI components in the first-cycle and their influences

in AFLMBs remains limited, especially compared to the extensive studies focusing on inorganic species such as LiF, Li₂O and Li₂CO₃.¹⁰

In recent advancements of AFLMBs, both additives and co-salts have played very similar but significant roles in enhancing battery performance. Additives, such as LiNO₃, are commonly added in small concentrations to improve specific properties like SEI formation. The additive effectively stabilizes the SEI by preventing undesirable side reactions and the growth of Li dendrites, which contributes to improved Coulombic efficiency (CE) and cycle stability.^{11,12} On the other hand, co-salts are added in larger concentrations alongside the main Li salt (e.g., LiTFSI or LiFSI) of the dual-salt system, providing broad benefits such as enhancing ionic conductivity and creating homogeneous and mechanically robust SEI.¹³ The co-salt in the dual-salt system can play a more integral role and generally have a more pronounced impact on the electrolyte's physical properties, leading to synergistic effects that stabilize SEI.¹⁴ In some cases, the dual-salt system bring benefit in terms of cost reduction, particularly when using LiNO₃ as co-salt.¹⁵ Therefore, understanding the similarity and distinction between the roles of additives and co-salts, basically from the aspect of the ratio of the second salt, such as LiNO₃, is crucial for designing more efficient AFLMBs.

Compared with the carbonate solvent, the ether solvent can form a more stable solvation shell owing to its stronger solvating ability.¹⁶ This property is attributed to its longer molecular chain compared to that of the carbonate solvent.¹⁷ Therefore, ether solvents usually have better reduction stability than carbonate solvents. Within the family of ether solvents, tetraethylene glycol dimethyl ether (TEGDME) was found to exhibits less extensive degradation compared with the shorter ethers like 1,2-dimethoxyethane (DME).¹⁸ However, the longer chain and greater molecular weight of TEGDME also results in its complex decomposition mechanism, so the accurate evaluation of SEI components in TEGDME-based electrolyte during cycling is quite challenging.¹⁹ On the other hand, considering that the electrolyte decomposition (E.D.) occurs less thoroughly over Cu electrode surface than over deposited Li surface due to the latter's strong reduction ability, the investigation on the E.D. mechanism over Cu surface in the TEGDME-based electrolyte becomes feasible. As such, a particular focus was put on the region prior to initial Li plating in this study, where the electrochemical processes (including pre-SEI formation) occur on the Cu surface. It is worth noting that, the Cu surface phenomenon before Li plating was previously studied by Gu et al. using depth-sensitive Raman technique, and an improved understanding on the importance of

SEI formation on Cu in affecting the reconstructed SEI upon subsequent Li deposition was proposed, which has been always overlooked in the AFLMBs study.²⁰ However, the pre-SEI formation does not necessarily occur across the whole region, i.e., from open-circuit potential (OCP) to 0 V vs. Li/Li⁺. Especially, species generated at the potentials above *ca.* 1.0 V are believed to have a significant impact on the formation of pre-SEI species below *ca.* 1.0 V, but are rarely studied systematically, prompting more investigations.

In this study, the behaviors of the adsorbed layer (including n-SEI and pre-SEI layer) over Cu electrode surface prior to the initial Li plating was preliminarily investigated in the Li||Cu half-cell. The investigation was conducted at a slow scanning rate of 1 mV/s, allowing for longer reaction time in order to more clearly identify the surface species and investigate their influences. Furthermore, effects of LiNO₃ as additive and as co-salt were preliminarily discussed. Electrolyte solutions were prepared inside a glovebox using TEGDME as solvent, which is commonly used in oxygen battery systems for its excellent cathodic stability. To put a special focus on the solvent-derived adsorbed layer formation, where organic species play an important role, LiTFSI was added as the primary salt at a very-low concentration of 0.4 M (samples were tested without LiNO₃), and for consistency in Li⁺ concentration, LiNO₃ was introduced either as an additive at 0.05 M or as a co-salt at 0.2 M, replacing a portion of LiTFSI. To simplify, the electrolyte solutions containing only LiTFSI is referred to as “LT” while those containing both LiTFSI and LiNO₃ are termed “LN-add” when LiNO₃ is used as an additive and “LN-co” when it acts as a co-salt. All electrolyte solutions were evaluated in a Li||Cu half-cell setup with a Cu working electrode and metallic Li counter and reference electrodes to observe anode behavior.

The primary characterization was done using quartz crystal microbalance (QCM) measurements with the frequency data collected continuously during cyclic voltammetry (CV) tests at a slow rate (1 mV/s), to determine surface mass changes and allow the calculation of MPE (mass change per mole of electrons) values after calibration. Similarly, CV tests with scan rate at 1 mV/s were carried out in conjunction with FT-IRAS spectroscopy to study the surface species behavior. The data acquisition time was set at approximately 30 seconds. Meanwhile, in order to obtain the derivatives of mass change, Savitzky–Golay (SG) filtering, a common data-smoothing method which utilizes local least-squares polynomial fitting, was applied to smooth the data and calculate derivatives (including the successively change of MPE with respect to

applied potential) from the mass datasets.²¹

3.2 Results and Discussion

3.2.1 Electrochemical Behaviors and Identification of Reactions during Cathodic Process prior to Initial Li Plating

CV measurements were conducted to investigate the first-cycle electrochemical behaviors of electrolytes. **Figure 3-1** depicts the first-cycle CV curves among all tested electrolytes at 1 mV/s. Notably, by introducing LiNO_3 the current density of Li plating decreased fourfold (from -2.0 to -0.5 mA/cm^2), which demonstrates a smoother Li morphology.¹⁰ The calculated first-cycle CE are 16%, 45% and 47% for LT, LN-add and LN-co, respectively. This confirms the role of LiNO_3 as an additive in enhancing CE,^{22,23} while the role as co-salt cannot further enhance the CE since LiTFSI is known to surpass LiNO_3 as an Li^+ conductor to ensure sufficient Li plating. Moreover, it is known that the first-cycle Li plating/stripping efficiency is determined by numerous factors such as the substrate condition for Li nucleation/growth and the degree to which the associated E.D. proceeds, while the electrochemical behaviors prior to the initial Li plating should be taken into consideration as well.

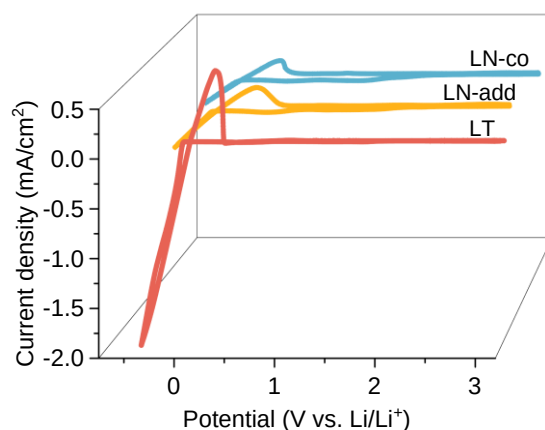


Figure 3-1. First-cycle CV curves measured in LT, LN-add, and LN-co. Potential range: -0.5 to 3.2 V vs. Li/Li^+ . Scan rate: 1 mV/s. W.E.: Pretreated Cu plate, C.E and R.E.: Li.

The electrochemical behaviors during the cathodic scan in the potential range of 0 to 3.2 V were then carefully investigated to clarify possible reactions prior to initial Li plating. The enlarged view of the CV measured in the three electrolytes is shown in **Figure 3-2(a)**. A series of peaks were observed during cathodic scans, and all observed peaks were named by using abbreviated symbols. The cathodic peak with the onset potential and peak potential at around 1.7 and 1.5 V, respectively, was assigned to the

reductive decomposition of electrolyte (which may include both TFSI⁻ anions and TEGDME solvent), which was named as “REL”.^{22,24,25} Gittleson et al. reported the CV curves of pure TEGDME on the glassy carbon working electrode, in which they observed a cathodic peak at around 1.5 V and an anodic peak above 4.0 V.²⁵ The CV of TEGDME solvent was also confirmed in this study, where the peak potential of the broad cathodic peak related to TEGDME reductive decomposition was around 1.5 V (see **Figure 3-2(b)**), same as Gittleson’s result.

Another cathodic peak at 1.1 V, named as “RCO”, could be attributed to the reduction reactions of Cu oxides (Cu_xO).¹⁰ This can be proved by comparing the CV curves between using Cu plate and Au plate as working electrodes, where this peak was not observed in the case of using Au working electrode (**Figure 3-2(c)**). The chemical species on the surface of Cu substrate in this potential range may include Cu_xO, CuF₂, LiF, Li₂O, Li₂O₂, LiOH, etc.¹⁰ The broad cathodic peak “RPS” at around 0.5 V in the first cycle was reported to result from the SEI formation reactions such as the reduction of Li₂CO₃ which was generated from the decomposition of electrolyte.^{10,26}

Regarding the CV curves of the electrolytes with LiNO₃, a weak cathodic peak was observed with onset potential and peak potential of 2.0 and 1.7 V, respectively, indicating the reduction of LiNO₃ (named as “RN”), which occurs prior to the reduction of LiTFSI.^{22,23} Moreover, it was found that the existence of LiNO₃ as an additive shifted the potential of LiTFSI reduction slightly to a more positive potential, which is consistent with the previous report showing the enhanced solvation between Li⁺ and TFSI⁻ by LiNO₃.²² However, this did not occur when LiNO₃ was added as a co-salt.

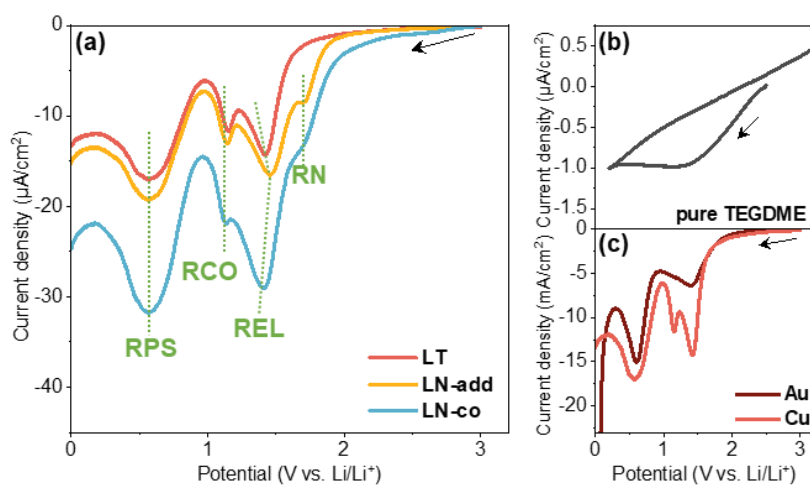


Figure 3-2. (a) Enlarged view of the first-cycle CV curves measured in LT, LN-add and LN-co; (b) The first-cycle CV curves measured in pure TEGDME solvent in the potential range of 0.2 to 3.2 V. W.E.: Pretreated Cu plate, C.E and R.E.: Li; (c) Comparison of the first-cycle CV curves

measured in LT over Cu and Au electrodes. Scan rate: 1 mV/s. The arrows represent the direction of scanning.

3.2.2 *In situ* Adsorbed Layer Mass Change during Cathodic Process prior to Initial Li Plating

As such, the *in situ* mass change during the cathodic process prior to initial Li plating in these electrolytes was examined using QCM coupled with CV. Overall, the current densities present an increasing trend in the order of $LT \approx LN\text{-add} < LN\text{-co}$, indicating that the specific reactions became more pronounced for dual-salt (**Figure 3-3(a)**). Correspondingly, the deposits in LN-co have the largest mass among three electrolytes (**Figure 3-3(b)**). Besides, a different extent of mass increase was found before and after 1.25 V, suggesting that different sets of products can be deposited.

More specifically, the recorded current and mass profiles allow for the cathodic process to be divided into four distinct regions: In Region I (from OCP to 2.0 V), although the current basically remained at baseline levels, the flow was still noticeable for all electrolytes, signifying the initiation of electrochemical reduction (**Figure 3-3(a)**). However, the surface mass decreased initially only for LT and LN-add but not for LN-co (see **Figure 3-3(b)** with respect to left Y-axis). It is possible that the decrease of mass was compensated for by one or more reactions that only occur with relatively high $LiNO_3$ salt concentration, which will be further discussed later. In Region II (from 2.0 to 1.25 V), the largely increased cathodic current indicates the reductions alongside a noticeable mass change. Particularly, the current and mass in the electrolytes with $LiNO_3$ (LN-add and LN-co) increased more rapidly. The increase of mass initiated at 1.7 V for all electrolytes, same as the onset potential of REL peak, whereas the mass increase due to RN peak was not identified. In Region III (from 1.25 to 0.8 V), a narrow current response signifies the reduction of Cu oxides related components (RCO), while in Region IV (from 0.8 to 0 V), the formation of pre-SEI (RPS) became remarkable. Notably, LN-add behaved similarly to LT in Region III and IV, while LN-co continued to increase more rapidly than the other two.

The MPE, calculated from the slope of the plot with Δm as a function of the passed charge, increased from approximately 20 to over 40 during REL upon increasing the ratio of $LiNO_3$ (see **Figure 3-3(b)** with respect to right Y-axis). The MPE reached the maximum at the REL peak top, then dropped from RCO peak for all electrolytes. The

maximum MPE of each electrolyte shows the following sequence of increase: LN-co (MPE = 42) > LN-add (MPE = 26) > LT (MPE = 19). These values are rather close to the formula mass of CH₃OLi (38 g/mol) or Li₂CO₃ (37 g/mol), LiF (26 g/mol), and Li₂O (15 g/mol), respectively. However, these MPE can also be an average of multiple electrochemical reactions over the entire system, which could include:

- (1) Further reduction of N-containing species from LiNO₃ reduction (e.g., LiNO₂ + 6Li⁺ + 6e⁻ → 2Li₂O↓ + Li₃N↓, MPE = 7);²³
- (2) Generation of soluble products or predominant inorganic deposits from TFSI⁻ reduction (MPE unknown);²⁷⁻³⁰
- (3) Reaction with trace oxygen (O₂ + 4Li⁺ + 4e⁻ → 2Li₂O↓, MPE = 15);³¹
- (4) Formation of larger organic compounds;
- (5) Involvement of chemical process rather than a strictly electrochemical one.

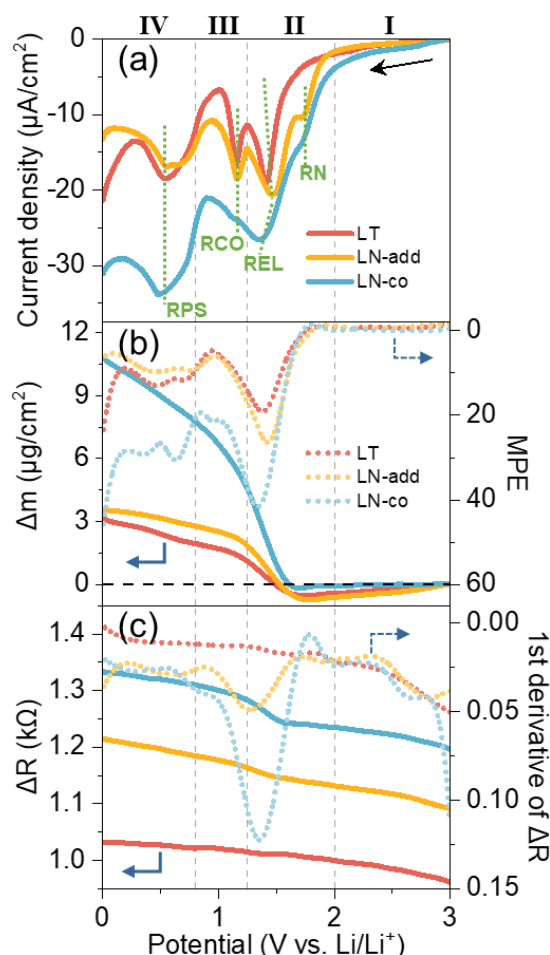


Figure 3-3. The QCM measurement conducted in LT, LN-add, and LN-co: (a) The cathodic process prior to initial Li plating, (b) the simultaneous mass change (left Y-axis, with the dashed line at Y=0 as a reference) and the corresponding MPE change (right Y-axis, data represented by dotted line), and (c) the simultaneous roughness change (left Y-axis) and the corresponding first derivative (right Y-axis, data represented by dotted line). Scan rate: 1 mV/s. The black arrow represents the direction of scanning. The right Y-axes in this figure are inverted for better visualization.

The subsequent decrease in MPE reached the minimum value of 5 ~ 6 for LT and LN-add, and 20 for LN-co in Region III where RCO peak was detected (**Figure 3-3(a)**). The MPE value of 5 ~ 6 is close to 7, implying the net increase of one Li atom during the reaction, which therefore confirms the reduction of Cu oxides on the Cu surface ($\text{Cu}_x\text{O} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{O}\downarrow + x\text{Cu}\downarrow$, $\text{MPE} = 7$).¹⁰ Additionally, it has been previously confirmed that the alloying of Li with a Sn electrode can occur below 0.7 V vs. Li/Li⁺, with an MPE of 7.³² However, as far as we know, no studies have reported the alloying of Li with Cu probably due to the high energy barrier, making it unlikely to consider such a possibility in this study. In terms of LN-co, the MPE value of 20 indicates the concurrence of additional reaction(s) in addition to the reaction related to peak RCO. After entering Region IV where pre-SEI is formed (RPS) based on the products during REL and RCO, MPE increased again for each electrolyte and reached averagely 12, 9 and 30 for LT, LN-add, and LN-co, respectively. These seem to correspond to some inorganic species such as Li₂O, LiF, and Li₂CO₃,^{33,34} and the correspondent reductions among them (e.g., Li₂CO₃ reducing to Li₂O, $\text{MPE} = 7$).³⁵ However, it also suggests that, the ratio of larger MPE species such as organic components in the pre-SEI may gradually increase upon increasing the ratio of LiNO₃ against LiTFSI.

As another physical parameter detected by QCM, the change of resonant resistance ΔR was recorded and used to describe the surface roughness change. The ΔR value at OCP is in direct proportion to the ratio of LiNO₃, while the initial increase in Region I is similar in magnitude. In Region II, it exhibits a turning point around 1.5 V, roughly matching the position of REL peak, in the presence of LiNO₃ (**Figure 3-3(c)** with respect to left Y-axis). This becomes more unambiguous with the increased ratio of LiNO₃, as clearly indicated by the first derivative of ΔR with respect to time (see the data plotted against right Y-axis in **Figure 3-3(c)**). A further negative potential scan into Region III and IV resulted in a near-linear growth of ΔR , but a higher derivative value of ΔR in the existence of LiNO₃ was retained, suggesting that the species initially formed at REL in Region II should continue to form and affect the surface roughness. This agrees with the particularly larger MPE at RCO and RPS for LN-co.

Note that in these regions, i.e., from OCP to 0 V, the increase in roughness cannot be attributed to the Li dendrite growth since no Li plating has occurred. At OCP, it might be due to the trapping of electrolyte with higher viscosity on the electrode surface.³⁶ As indicated by Equation (2-4) and (2-6), the initial $f_{\eta p}$ value can roughly reflect the viscosity of electrolyte, and can be obtained by the difference between the

resonant frequency before and after immersing electrolyte. However, in this study the calculated initial $f_{\eta p}$ values did not show the positive dependence on the LiNO_3 ratio (4338 Hz, 4913 Hz, and 4220 Hz for LT, LN-add, and LN-co, respectively), indicating that another factor except for the viscosity works as the primary cause for roughness increase, which will be discussed later in the IRAS analysis. During cathodic process, it is rather attributed to the formation of more species during REL that can induce a more uneven, roughened surface. These results suggest that LiNO_3 facilitates the roughening of surface at OCP as well as during the electrochemical processes before initial Li plating.

3.2.3 *In situ* Species Change of Adsorbed Layer during Cathodic Process prior to Initial Li Plating

The abovementioned cathodic process was examined in more detail using *in situ* FT-IRAS. **Figure 3-6** shows the *in situ* infrared spectra as a function of applied potential during cathodic scanning in the potential region prior to initial Li plating. Various upward and downward peaks were observed in the wavenumber range of 1300 to 2000 cm^{-1} . The upward peaks indicate the accumulation or formation of related species, while the downward peaks represent the reduction or disappearance of these species. Notably, a downward peak at 1358 cm^{-1} was observed in all electrolytes, corresponding to $\nu_a(\text{SO}_2)$ in TFSI^- anion, which indicates the breaking of $\text{O}=\text{S}=\text{O}$ bond.³⁷ **Figure 3-7(a)** shows the rising of the negative absorbance of this peak started at 1.7 to 2.0 V, near the onset potential of REL peak. This further proves that the decomposition of TFSI^- did occur at REL, and LiNO_3 as additive shifted the decomposition toward a more positive potential while LiNO_3 as co-salt did not.^{22,24}

Another peak at 1505 cm^{-1} can be the sign of Li_2CO_3 , a common SEI species.^{38,39} It could originate from both TFSI^- and TEGDME molecules, or the reaction of organic species with CO_2 .^{40,41} It is clearly observed in LT, starting to increase below 1.0 V as an indicator of pre-SEI formation (see **Figure 3-7(b)**). However, it was nearly absent in LN-add and LN-co, showing the possibility of LiNO_3 suppressing the formation of Li_2CO_3 . The peak at 1465 cm^{-1} is reportedly another major peak from Li_2CO_3 ,³⁹ but the potential-dependent absorbance shift of this peak (**Figure 3-7(c)**) is different from that of the Li_2CO_3 peak. In fact, this peak is most likely attributed to the bending vibration of $-\text{CH}_2-$, with $-\text{CH}_3$ as a secondary possibility, from the cleavage of the TEGDME

chain.³²

In the meantime, three downward and relatively weak peaks at higher wavenumbers, i.e., 1800, 1845 and 1925 cm^{-1} , were assigned to the conjugated or ring-structured C=O stretching, or C=N stretching. The onset potential at which the negative absorbance of these peaks increased is around 2.0 V, close to the onset potential of RN (**Figure 3-7(d)**). Moreover, their absorbance exhibited the dependency on the LiNO_3 ratio. This demonstrates the high possibility of assigning one or more of these peaks to C=N containing species. Besides, these peaks also reflect the underlying chemically proceeded E.D. related to the interaction of LiNO_3 with solvent at OCP, and the produced C=N and/or C=O containing species were further reduced electrochemically by cathodic potential scan.

The peaks at 1405 and 1725 cm^{-1} were both found downward. The former is highly likely to belong to the $-\text{COOH}$ group from carboxylic acid ($\text{R}-\text{COOH}$),⁴² and the latter is usually assigned to the C=O stretching from carbonyl compounds ($\text{R}-\text{CO}-\text{R}'$, such as carboxylic acid, aldehyde, ketone, and ester), or the Li^+ solvation species with C=O bonding ($\text{Li}^+\cdots\text{O}=\text{C}$).^{32,43} Another strong peak was detected at 1630 cm^{-1} for all electrolytes, which was identified as the C=O bond. This peak is upward, and is therefore thought to be Li organic species with C atom in the C=O bond coordinating to Li^+ (i.e., Li carboxylate, i.e., $\text{R}-\text{COOLi}$) as a possible SEI component.^{38,44} By combining the calculated MPE (less than 50 as an average of the entire system) in Section 3.2.2, these species most likely contain:

1. HCOOLi (lithium formate), molecular weight: 52 g/mol
2. CH_3COOLi (lithium acetate), molecular weight: 66 g/mol
3. $\text{CH}_3\text{CH}_2\text{COOLi}$ (lithium propionate), molecular weight: 80 g/mol
4. CH_3OCOOLi (lithium methyl carbonate), molecular weight: 82 g/mol

which could generate from the decomposed TEGDME.

These three peaks exhibited an increase in the positive or negative absorbance at *ca.* 1.7 V (**Figure 3-7(e)**), marking the entrance to the typical E.D. region. Considering that TEGDME molecules do not contain any double bonds, and the absorbance of the peaks at 1405 and 1725 cm^{-1} did not show any positive values before REL, it is clear that the corresponding species of these two peaks were already present at OCP most likely due to the chemical decomposition of TEGDME. This indicates that TEGDME can decompose over Cu electrode before applying potential.

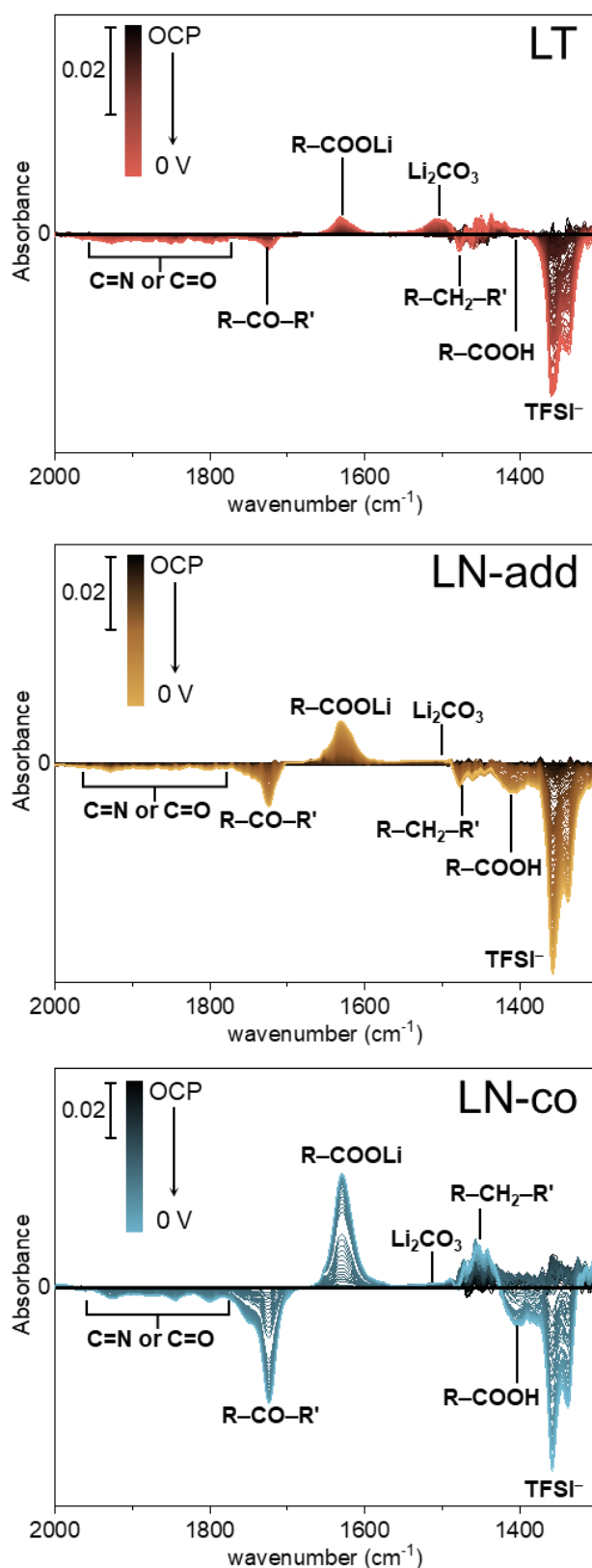


Figure 3-6. FT-IRAS spectra for LT, LN-add and LN-co in the wavenumber range of 1300 to 2000 cm⁻¹ during cathodic scanning prior to initial Li plating. Potential range: 0 to 3.2 V vs. Li/Li⁺. Scan rate: 1 mV/s. The absorbance at each step of potential was obtained by taking the IR intensity at OCP as the reference.

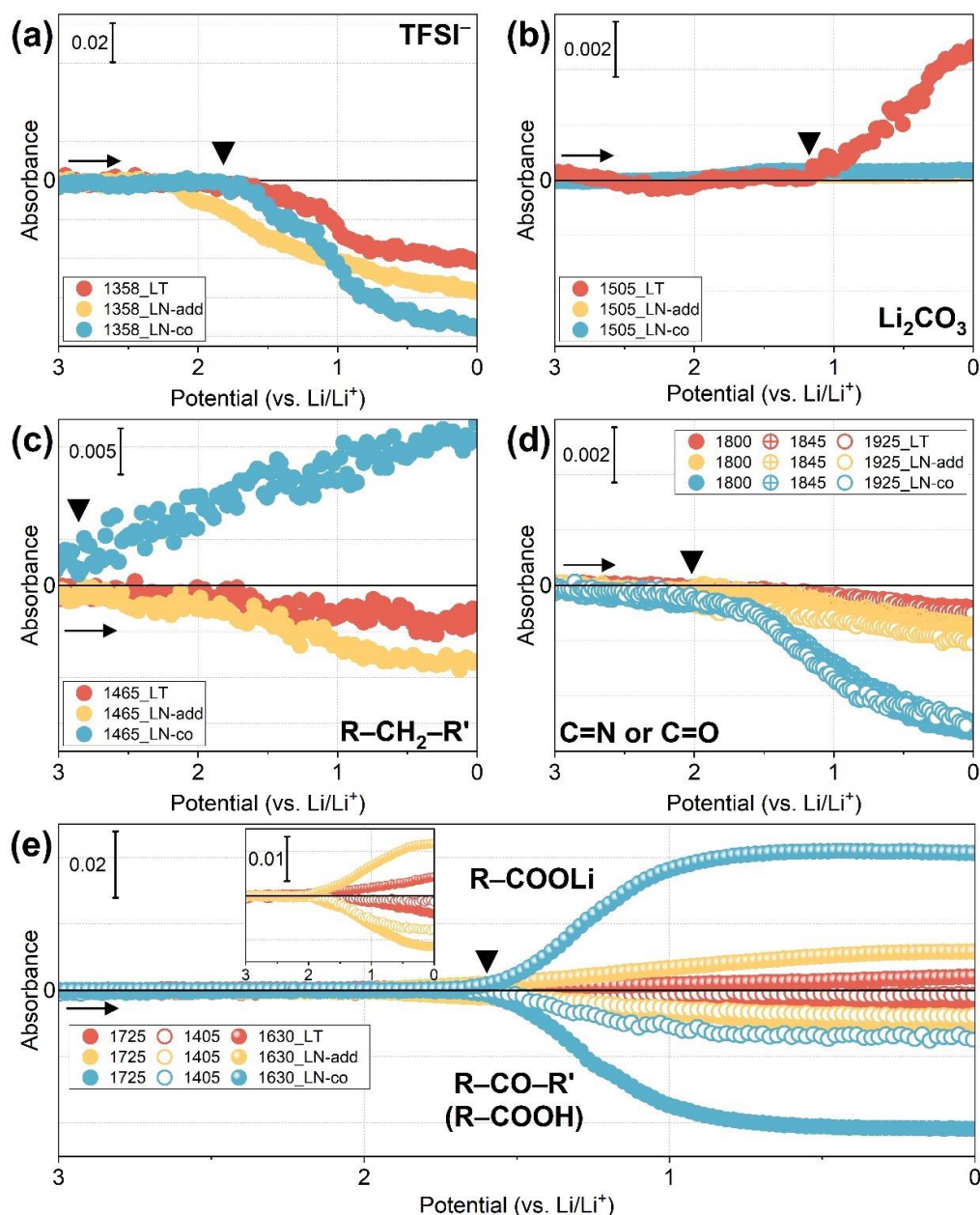


Figure 3-7. Absorbance of IRAS peak at (a) 1358 cm⁻¹, (b) 1505 cm⁻¹, (c) 1465 cm⁻¹, (d) 1800, 1845 and 1925 cm⁻¹, and (e) 1405, 1630 and 1725 cm⁻¹, measured in LT, LN-add and LN-co during cathodic scanning prior to initial Li plating. The arrows indicate the scanning direction. The black triangles mark the starting potential of the (positive or negative) absorbance increase.

The abovementioned chemical decomposition of TEGDME can be verified by the IR spectra measured at OCP after immersing Cu electrode in electrolytes for 30 min (**Figure 3-8(a)**). In the spectra, a series of peaks at 1400 and 1725 cm⁻¹, and the wavenumbers higher than 1800 cm⁻¹, corresponding to the peaks at 1405, 1725, 1800, 1845 and 1925 cm⁻¹ shown in **Figure 3-6**, are all upward in the TEGDME solvent and all three electrolytes. This proves that these peaks belong to the surface species from the chemical decomposition of TEGDME, whose amounts were increased by the

increased LiNO_3 ratio. The time dependences show that the absorbance of these peaks gradually increased as the holding time increased and basically reached the “saturated state” after nearly 10 minutes (the time dependences of the peak at 1725 cm^{-1} is shown in **Figure 3-8(b)** as an example).

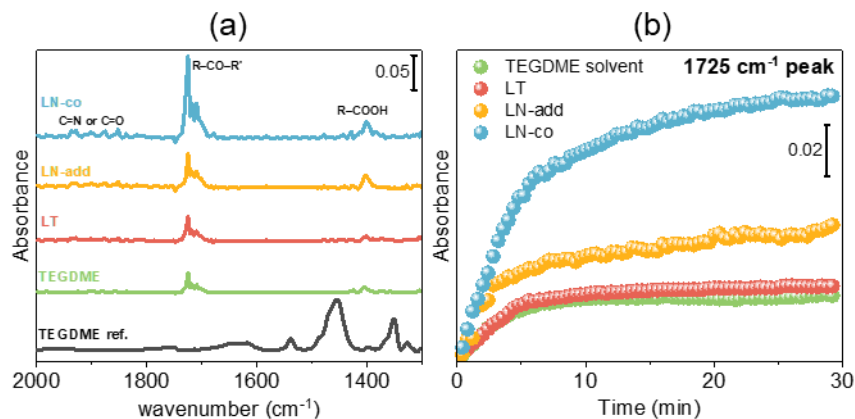


Figure 3-8. (a) FT-IRAS spectra for TEGDME solvent, LT, LN-add, and LN-co in the wavenumber range of 1300 to 2000 cm^{-1} at OCP after 30 min holding of assembled cell. The absorbance was obtained by taking the IR intensity at 0 min (the first take) as the reference. The TEGDME solvent baseline was used for comparison; (b) Time-dependent absorbance of IRAS peak at 1725 cm^{-1} at OCP.

Meanwhile, from SERS spectra it was found that the coordination of TEGDME with Li^+ can be weakened by LiNO_3 at OCP, as indicated by the decreased intensity of Li^+ -solvated C–O–C stretching and CH_2 rocking modes (880 cm^{-1}) from TEGDME with the increased LiNO_3 ratio (**Figure 3-9(a)**).^{45,46} Meanwhile, in the presence of LiNO_3 , Li^+ prefers to coordinate with NO_3^- as indicated by the vibration of solvated NO_3^- (**Figure 3-9(b)**).⁴⁷ This should be due to the higher donor number of NO_3^- (21) than TEGDME (16). Therefore, the effect of LiNO_3 in promoting the chemical decomposition of TEGDME can be explained by the following hypothesis: During the solvation process without LiNO_3 , six O atoms in two TEGDME molecules coordinate with Li^+ to form a stable solvation structure $[\text{Li}(\text{TEGDME})_2]^+$ according to the previous study by DFT.⁴⁵ This causes electron clouds to shift from C atom to O atom. In the presence LiNO_3 , however, Li^+ preferentially coordinates with NO_3^- anions, leaving more O atoms from TEGDME uncoordinated, which leads to unstable Li^+ -TEGDME solvation structure. Under this circumstance, TEGDME could undergo “chain-shortening” via bond cleavage to reach an energetic stable solvation with Li^+ (see **Figure 3-9(c)**). In addition, Li^+ -O coordination from NO_3^- decreases electron cloud density around the two N–O bonds on the other side, making them more prone to breaking, facilitating the formation of C=O containing species. This is evidenced by the IRAS spectra related to LiNO_3 -TEGDME interaction (**Figure 3-7(d)** and **Figure (3-8)**).

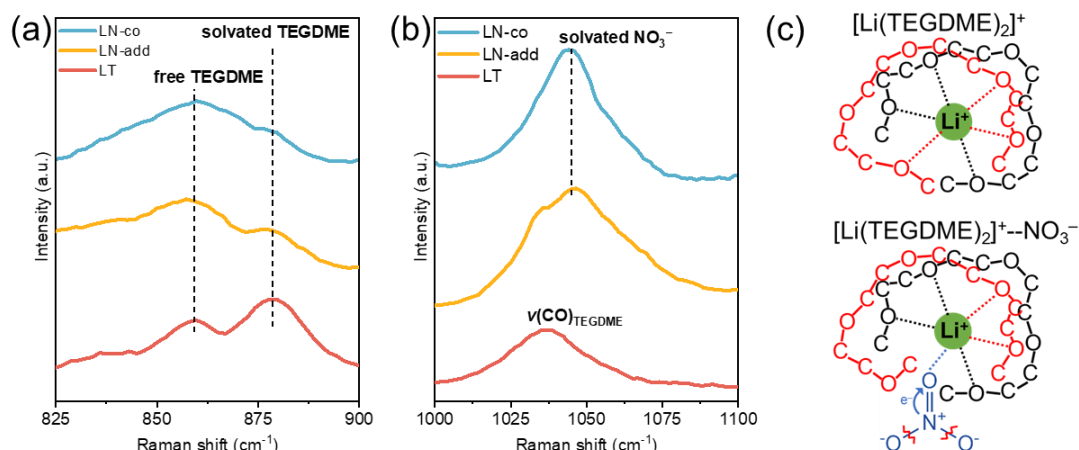


Figure 3-9. SERS spectra of the vibration of (a) C–O–C stretching and CH₂ rocking from free and solvated TEGDME and (b) solvated NO₃⁻ measured in LT, LN-add and LN-co at OCP; (c) Possible solvation structure of Li⁺-TEGDME without and with the competitive solvation of Li⁺-NO₃⁻.⁴⁵

Notably, regarding the peaks at 1405, 1630 and 1725 cm⁻¹, the following can be noticed across all electrolytes (**Figure 3-7(e)**):

1. The increase in the negative absorbance of the peaks at 1405 and 1725 cm⁻¹ correlates with a simultaneous increase in the positive absorbance of the peak at 1630 cm⁻¹, showing very similar trends upon potential scan;
2. The absorbance of the peak at 1725 cm⁻¹ is close to the absorbance of the peak at 1630 cm⁻¹;
3. The peak at 1725 cm⁻¹ is always stronger than the peak at 1405 cm⁻¹.

These suggest that the carbonyl compounds R–CO–R' (including carboxylic acid R–COOH) were originally from the chemical decomposition of TEGDME at OCP, and their coordination with Li⁺ formed R–COOLi as the final product. It should be noted that the latter process particularly shows potential dependency since it initiated with REL around 1.5 V during the cathodic scan, while the coordination process with Li⁺ does not transfer electrons. Therefore, this process is considered to be triggered by other reaction(s) that can produce the dissociated Li⁺ and have the potential dependency. Considering that the reduction of TFSI⁻ occurred at the similar potential (related to REL) as shown in **Figure 3-7(a)**, this suggests that reactions such as the reduction of TFSI⁻ can release Li⁺ ions, which subsequently coordinated with R–CO–R' species to form R–COOLi. As a result, this coordination process did not exhibit any degree of potential dependency after REL, and was irreversible even after the scanning direction was reversed (**Figure 3-10**).

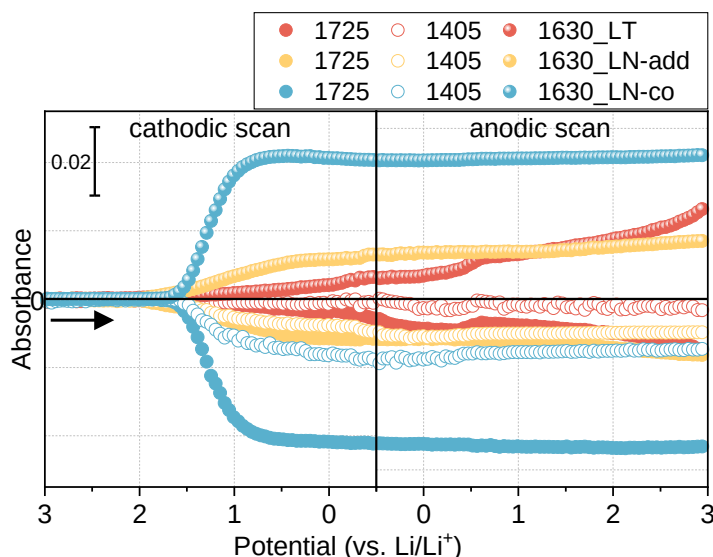


Figure 3-10. Absorbance of IRAS peaks at 1405, 1630 and 1725 cm^{-1} , measured in LT, LN-add and LN-co during cathodic and anodic scanning of the first cycle. The arrows indicate the scanning direction.

Interestingly, these peaks (1405, 1630 and 1725 cm^{-1}) display a clear dependence on LiNO_3 , that is, the amounts of both reactants and products increased as the LiNO_3 ratio increased (**Figure 3-7(e)**). This demonstrates the effect of LiNO_3 to promote TEGDME decomposition. Combined with the QCM results showing that initial roughness and its growth during REL were greater with higher LiNO_3 ratio, it can be consequently deduced that the chemical decomposition products at OCP and the subsequent electrochemically decomposition products have roughened the electrode surface. Moreover, recall from the QCM results that at RCO, only for LN-co there existed additional reaction(s) except for the reduction of Cu oxides. This is clearly demonstrated by the greatest and still-increasing absorbance of the peaks at 1405, 1630 and 1725 cm^{-1} for LN-co, indicating that the aforementioned R-COOLi formation reactions still remained during RCO. However, these reactions did not proceed further at RPS for LN-co, as indicated by the unchanged absorbance of these peaks. In comparison, signs of slowing down and stopping these reactions were observed around 0.5 V for LN-add, while it became progressively more pronounced for LT, as shown in the inset of **Figure 3-7(e)** and **Figure 3-10**. Thus, it can be inferred that the range of potential in which the R-COOLi formation reactions can occur was narrowed down due to the participation of LiNO_3 . By increasing the ratio of LiNO_3 , the ending of these reactions is further brought forward, whereas the stronger absorbance also indicates that increasing the ratio of LiNO_3 correspond to the acceleration of this process. The above phenomenon can be explained by the promoted construction of a relatively stable SEI that can suppress the further decomposition of electrolytes at an earlier stage with the

help of the increased LiNO_3 ratio.

Finally, by reviewing all peaks being discussed above, it can be found that only the peak at 1465 cm^{-1} showed an obvious change in absorbance at the beginning of potential scan, which is in negative value for LT and LN-add but in positive value for LN-co (**Figure 3-7(c)**). This result correlates with the unusual mass change detected by QCM in Region I (**Figure 3-3(b)**). The positive absorbance for LN-co corresponds to the increase the species containing $-\text{CH}_2-$ group, so it might be the formation of more short chain ethers or alkanes due to the electrochemical decomposition of TEGDME that started from the beginning. Regarding the negative absorbance for LT and LN-add, since the oxidation of $-\text{CH}_2-$ to $-\text{C}=\text{O}/-\text{COOH}$ is not possible during cathodic process, it is likely to be a more severe decomposition causing the breaking of $-\text{CH}_2-$ to generate smaller molecules (especially gases like CH_4 or CO_2), which requires further verification. In addition, the further increase in the absorbance of this peak for LN-co in Regions III and IV can also support the observed larger MPE compared to other two electrolytes. In particular, the MPE of approximately 30 in Region IV is attributed to the increased species from the direct decomposition of TEGDME ($\text{MPE} > 30$) rather than Li_2CO_3 or R-COOLi , although the formation MPE for these two species is also above 30. This is because in the case of LN-co, the quantity of Li_2CO_3 is negligible and the formation of R-COOLi has already ceased by Region IV. Correspondingly, the relatively smaller MPE for LN-add than that for LT in Region IV can be explained as the negligible amount of Li_2CO_3 and decreased TEGDME molecules (1465 cm^{-1}) in LN-add, which is only partially offset by the slightly larger amount of generated lithium organic species compared to the case of LT.

3.2.4 Proposed Model of the Behaviors of Adsorbed Layer prior to Initial Li Plating

Based on the overall correlation between the changes in the mass of the adsorbed layer (including n-SEI and pre-SEI) on the electrode and the deposited organic species under the applied potential, it is possible to roughly estimate the extent of influence exerted by the inorganic and organic species. It is evidenced that the ratio and influence of organic species increase as the ratio of LiNO_3 against LiTFSI increases.

Then, a model showing the behaviors of the adsorbed layer on the Cu electrode surface was proposed (**Figure 3-11**). At OCP, n-SEI is mainly composed of R-CO-R' species (including R-COOH) from the chemical decomposition of TEGDME. After

applying voltage, CH₂-containing fragments from the direct bond cleavage of TEGDME are generated, which can proceed a further reduction into smaller gaseous molecules in LT and LN-add but not in LN-co. During REL and RCO, species like R–COOLi from the coordination of the C=O bond of R–CO–R' species with Li⁺ released from reactions like LiTFSI reduction, and products from the reduced Cu oxides, constitute the pre-SEI layer. After RPS, Li₂CO₃ forms probably due to the reduction of LiTFSI and/or TEGDME (and its derivatives), and the further reaction with dissolved CO₂ in the case of LT, which is suppressed in the presence of LiNO₃. Basically, increasing LiNO₃ ratio promotes these reactions to generate more amounts of organic species, so the surface of the adsorbed layer is further roughened. On the other hand, higher LiNO₃ ratio put forward the electrochemical decomposition of TEGDME derivatives (mainly R–CO–R') to reach the equilibrium at an earlier stage prior to initial Li plating, suggesting the faster stabilization of the pre-formed SEI layers (n-SEI and pre-SEI) that can suppress the further progress of E.D.

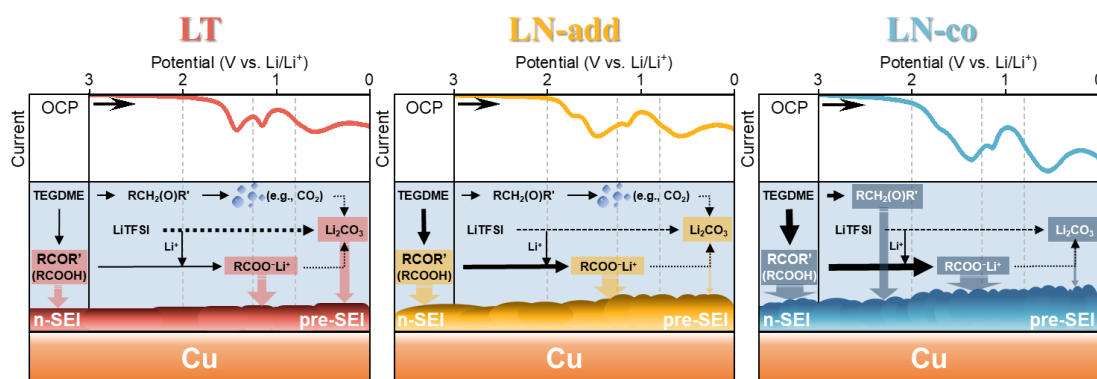


Figure 3-11. Proposed model of the potential-dependent shift of major SEI components during the cathodic process prior to initial Li plating (indicated by the CV curves on the top) in the LiTFSI/TEGDME electrolytes with the increasing LiNO₃ ratio. The bolder arrows indicate stronger reactions that produce a greater quantity of species.

3.3 Conclusion

This study discussed the potential dependent behavior of the adsorbed layer (including n-SEI and pre-SEI) formed on Cu electrode surface in the potential region prior to initial Li plating, ranging from OCP to 0 V vs. Li/Li⁺. This includes the change in mass, roughness, and the adsorbed species that formed due to chemical and electrochemical reduction. It was found that TEGDME is decomposed both at OCP and during cathodic scanning. Meanwhile, a further decomposition of the chemically formed TEGDME derivatives (R–CO–R' species) started at around 1.5 V. The presence of LiNO₃ not only facilitated but also terminated this decomposition at an earlier stage.

Overall, the ability of LiNO_3 to accelerate organic deposition in the SEI layer in TEGDME may help explain its role as a stabilizing agent – as LiNO_3 is known to quicken E.D. process, it may allow the system to reach near-equilibrium before plating and stripping. Alternatively, these results might indicate potential issues with the stability of TEGDME on the anode side. The organic deposition observed may be undesirable and has not been the focus of previous studies with the solvent, which generally emphasize cathode interactions in Li-O_2 systems.

It should be noted that, the total Li^+ concentration in this study was kept constant across the three electrolytes, while the concentration of LiTFSI decreased in the order of $\text{LT} > \text{LN-add} > \text{LN-co}$, remaining the optimal $\text{LiTFSI}:\text{LiNO}_3$ ratio to be further investigated. Moreover, the effects of these chemically and electrochemically formed species over Cu electrode on the further evolution of SEI layers in prolonged cycles could be checked to obtain a more complete understanding of the system. Such an understanding aids in developing the stable SEI layers required for the success of AFLMBs. This work may also motivate study into n-SEI formation and chemical degradation of ether solvents. Such understanding could improve the precision of work throughout the field.

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Chapter 4

Enhancement of Li Plating/Stripping Cycling Efficiency in TEGDME-based Low-concentration Electrolytes: Effect of Potential Range, Concentration, and LiNO₃ Additive

4.1 Introduction

Commercial lithium-ion batteries (LIBs) are the foundation of modern rechargeable energy storage, powering everything from electric vehicles to cell phones. Although ongoing improvements are being made in storage capacity, they are inherently limited by the graphite anode used in current systems — a limitation that becomes more apparent with growing energy storage demands for sustainable infrastructure. Li metal anodes offer a theoretical improvement in specific capacity by an order of magnitude compared to graphite. However, significant challenges remain in making lithium metal battery (LMB) technology commercially viable, such as limited cycle life and safety concerns due to issues like Li dendrite growth and parasitic reactions. Anode-free lithium metal batteries (AFLMBs), where Li is plated directly onto a current collector during the first charge cycle, aim to enhance capacity and simplify manufacturing.¹

Despite the above advantages, the research bottleneck in AFLMBs mainly originates from the immense volume expansion and quick capacity drop during initial state.² In particular, due to the limited Li inventory (low N/P) in AFLMBs, Li plating on the anode usually takes place less evenly,³ hence the mechanical breakage of SEI in the stripping and further plating, which often occurs in LMBs, can be more easily found in AFLMBs. Depending on different electrochemical stages, the SEI can be classified into the “native-SEI (n-SEI)” prior to applying bias voltage,⁴ the “pre-SEI” prior to initial Li plating, and the “subsequent-SEI (s-SEI)” constructing after the breakage of pre-SEI.⁵ An ideal SEI layer should facilitate rapid Li⁺ conduction while electrically insulated to suppress electrolyte decomposition, and currently the most important effort in designing the SEI layer should be the modification of electrolytes.

There are diverse strategies for modifying electrolytes applied in AFLMBs. In general, the selection of solvent is confined to carbonate-based or ether-based solvents, or the “co-solvent”. Compared with carbonate-based electrolytes, ether-based electrolytes have better Li metal compatibility (i.e. less dendrite formation), which ensures a higher Li plating and stripping efficiency. However, the oxidation stability (>

4 V) of ether-based electrolytes usually cannot surpass carbonate-electrolytes.⁶ Meanwhile, the modification of Li salts in the electrolyte involves several technique routes, such as dual-salt electrolytes⁷ and high-concentration electrolytes (HCEs, usually over 4 M).^{8,9} However, high concentration condition will increase the viscosity and decreases the ionic conductivity of electrolytes, and is not a cost-effective route.¹⁰ Although the idea of using localized high-concentration electrolytes (LHCEs) was proposed to solve such problems,¹¹ it is always attractive and challenging to achieve decent performance under lean electrolyte condition (under 3 M).¹² Another common technique in the electrolyte modification is using electrolyte additives, among which LiNO_3 has been studied by many groups as a powerful additive applied in LMBs.^{13–16} It can generate the N-rich components in the inner SEI layer including Li_3N , LiN_xO_y , LiNO_2 , R-NO_2 , most of which are known as good Li^+ conductors that can promote efficient cycling of Li plating/stripping.^{13,14,16}

Operating potential range, an important but often overlooked factor, influences SEI layer structures as well, and ultimately, Li plating/stripping efficiency. Either too wide or too narrow potential range can have a negative impact on sustaining a stable SEI layer structure. It is widely accepted that the SEI usually forms in the potential range of 0.2 to 1.0 V vs. Li/Li^+ , while studies mainly focused on the electrolyte reductive processes via electron-transfer from the anode,¹⁷ with less concerns on the subsequent oxidation processes at a relatively higher potential regime since such kinds of processes would be complicated depending on actual electrolyte conditions such as adding additives. Meanwhile, in the charging-discharging protocol in AFLMBs, adjusting the potential limit to achieve optimal performance is a common strategy.¹⁸ Usually, the charge-discharge at an anode is confined to low potential range to achieve high energy density of the full-cell. However, in a real situation, when the battery is working at high current density or is over-charged or over-discharged, the potential may fluctuate greatly and exceed the normal operating range, which can lead to the destruction of the SEI layer and the degradation of the battery performance. Moreover, the “cross-talk effect” (the crossover of side reaction products from cathode to anode) can change Li plating/stripping and SEI formation mechanism. Therefore, it is necessary to study the properties and stability of SEI over a wider potential range by considering factors like the cross-talk effect, especially at a more positive potential, for the purpose of fully understanding the effect of electrolyte on the SEI layer structure at

the anode side. To address this problem, a more careful investigation by the cyclic voltammetry (CV) method is necessary.

Tetraethylene glycol dimethyl ether (TEGDME) is an ether-based solvent with low volatility and a high degree of oxidation tolerance to ensure a wide operating window, and is commonly used in Li-oxygen batteries (LOBs).¹⁹ A previous study showed that TEGDME slightly decomposes at potentials above 3.8 V vs. Li/Li⁺ in the absence of oxygen and Li⁺ source.²⁰ However, a stable SEI layer cannot be realized in TEGDME solvent-based electrolyte due to the continuous reaction with Li metal, resulting in the formation of a thick SEI layer, leading to low CE.^{13,21} But on the other hand, considering the unstable nature of TEGDME solvent-based electrolyte in the existence of Li metal, it may be a good candidate in regard to the mechanistic study of performance degradation and enhancement in a broad potential range for AFLMBs since the difference in performance should be more evident when different conditions are applied. Furthermore, it is known that the combination of TEGDME solvent with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) as the Li salt is universally used in LOBs research. However, to the best of my knowledge, there is still no report on their application to AFLMBs studies.

In the present study, the effects of operating potential range, electrolyte concentration and LiNO₃ additive on SEI layer structure and Li plating/stripping efficiency were investigated using the Li||Cu half-cell in the TEGDME-based low-concentration electrolytes (0.4 M and 2.0 M, dissolving the LiTFSI salt). TEGDME was used as the solvent due to its oxidation tolerance and good Li competitiveness ensuring a wide operating window, in order to study the potential- and cycle-dependent SEI formation in more detail. Totally four kinds of electrolytes were prepared prior to measurements. For convenience, these electrolytes are hereafter abbreviated as 0.4LT, 0.4LTLN, 2.0LT, and 2.0LTLN, where LT means LiTFSI and LN means 0.1 M LiNO₃ as an additive. The properties of formed SEI layers during electrochemical cycling were elucidated particularly via their abilities in Li⁺/electron conduction, chemical compositions, and surface morphology.

4.2 Results and Discussion

4.2.1 Identification of Electrochemical Reactions during First Cycle

Figure 4-1(a) shows the enlarged view of the CV curves measured in 0.4LT electrolytes under a variety of potential ranges. Recall that in Chapter 3, three typical reduction peaks were identified and named (i.e., REL for the reductive electrolyte decomposition, RCO for the reduction of Cu_xO , and RPS for the reductive pre-SEI formation) during the initial CV cycle with cathodic scan, where 0.4LT was also used as one of the electrolytes. In this study, these peaks were detected as well at an increased scan rate of 10 mV/s. Meanwhile, the corresponding oxidation peaks of these reduction peaks were confirmed during the initial CV cycle with anodic scan: when CV was performed in the potential ranges of 1.0 to 3.2 V and 1.3 to 3.2 V, two peaks at 2.4 and 2.7 V (named as “OCO” and “OEL”, respectively) indicating the correspondent oxidation processes of RCO and REL, respectively, were observed. As soon as the pre-SEI layer was formed by scanning in the range of 0.2 to 3.2 V, two additional oxidation peaks at 0.8 V and 1.9 V (OPS and OPS') during the anodic scan could be assigned to the oxidation reactions of pre-SEI components from RPS. In summary, during the first cycle without (hereafter, w/o) Li plating/stripping, three redox couples were observed, corresponding to the reduction and oxidation of electrolyte (REL/OEL), the reduction and oxidation of Cu_xO remaining on the Cu substrate (RCO/OCO), and the reduction and oxidation reactions related to pre-SEI formation (RPS/(OPS+OPS')).

However, when Li plating/stripping was involved, a strong oxidative current started to flow from 2.2 V and reached a maximum at 2.6 V. This is related to the oxidation of some pre-SEI components to construct an s-SEI layer over the surface of unstripped Li metal, which occurred at a relatively higher potential. This process was hereafter denoted as “OSS” which paired with the correspondent reduction process “RSS” of the next cycle. Because OSS peak appeared only when the Li plating/stripping process was involved, it can be speculated that OSS originated not only from pre-SEI components (which were generated from electrolyte decomposition and Cu substrate reduction) but also from the Li plating/stripping process.

From the second cycle, one can observe another redox couple relevant to s-SEI construction. It was named as RSS'/(OSS'+OSS''), which originally belonged to RPS/(OPS+OPS') related to pre-SEI construction when no Li plating/stripping occurred (see the bottom of **Figure 4-1(a)**), because both redox are involved in the commonly

accepted potential area where the SEI layer usually forms.¹⁷ Notably, these redox couples were observed in all tested electrolytes in this study (**Figure 4-1(b)**).

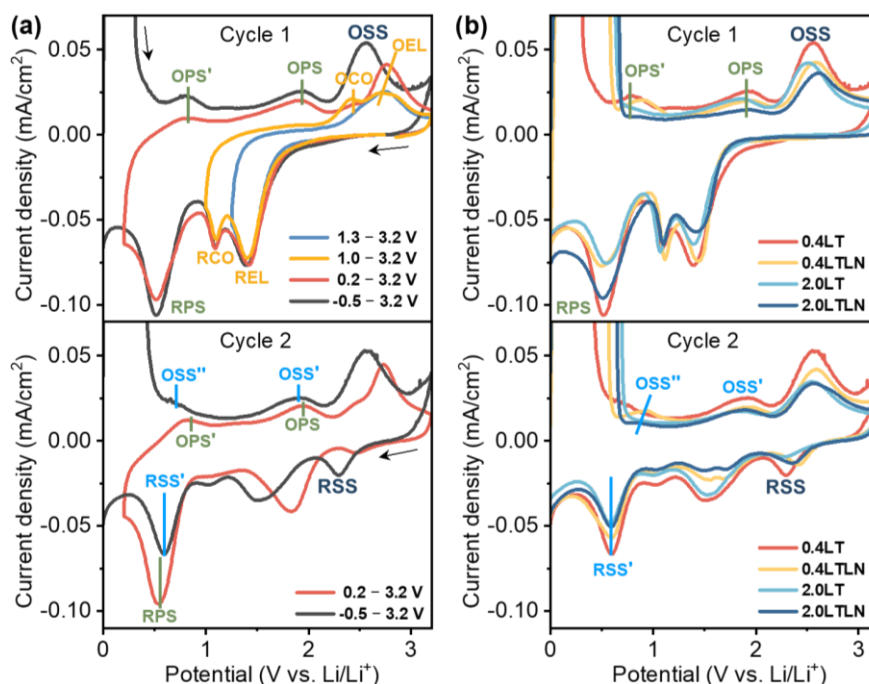


Figure 4-1. Enlarged view of the CV curves: (a) The first- and second-cycle CV curves measured in 0.4LT under different potential ranges; (b) The first- and second-cycle CV curves measured in 0.4LT, 0.4LTLN, 2.0LT and 2.0LTLN. The prime symbols ' and '' on the capitals indicate that the corresponding peaks locate at a more negative potential than those without the prime symbol. W.E.: Pretreated Cu plate, C.E and R.E.: Li. Scan rate was set as 10 mV/s for all measurements. The arrows represent the direction of scanning.

4.2.2 Comparison of Coulombic Efficiency (CE) Performances

Figure 4-2(a) shows the calculated CE values up to 50 cycles in different electrolytes based on their CV curves shown in **Figure 4-3** by taking the influence of concentration, LiNO₃ additive and OSS process into consideration.

Regarding 0.4 LT with r OSS, the overall CE was less than 20% and exhibited a non-stop degradation onward. To understand the function of OSS, its occurrence was blocked by scanning positively to 2.2 V without changing other conditions. As a result, a greatly stabilized CE was found in the prolonged 50 cycles (**Figure 4-2(a)**) with a relatively stabilized Li stripping capacity retention after 50 cycles (90%) compared with that in the case of not blocking OSS (23%) (**Figure 4-2(b)**). Furthermore, the Li plating/stripping proceed more stably with smaller Li plating current densities (**Figure 4-3**), which could result in a smoother and denser Li morphology.⁴ Meanwhile, it is notable that similar CE was achieved in the initial 10 cycles regarding the two potential

ranges, suggesting that OSS did not contribute to enhancing CE, instead it is highly likely to facilitate the construction of unstable SEI. Therefore, it can be concluded that OSS must be one of the major causes for the CE degradation.

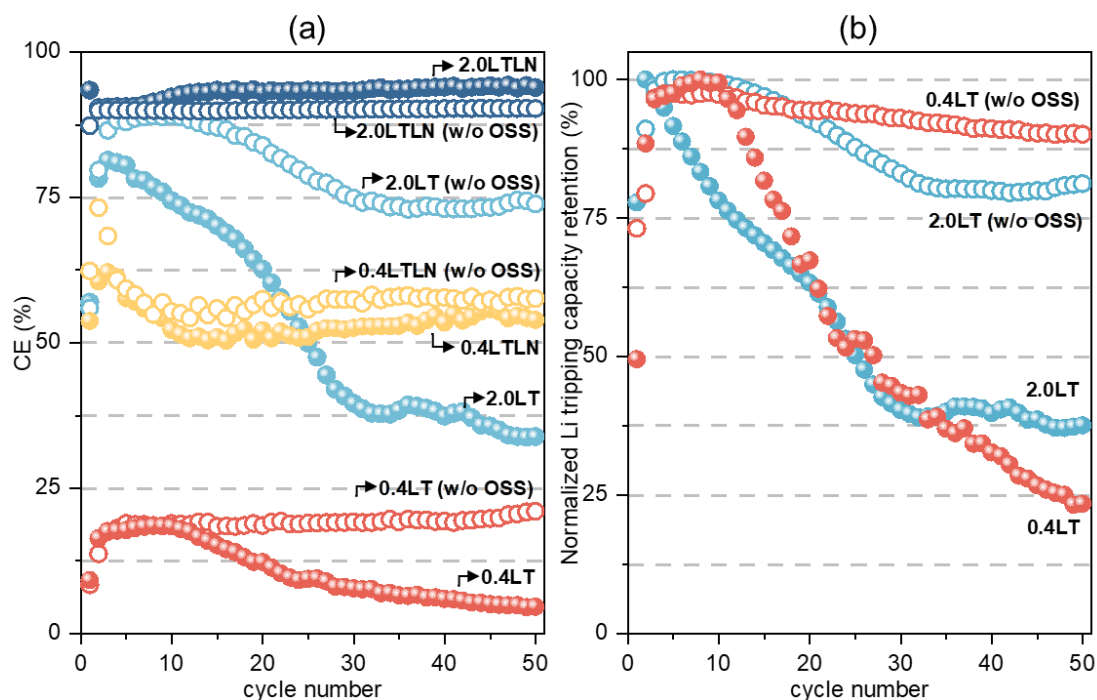


Figure 4-2. (a) The 50-cycle CE measured in 0.4LT, 0.4LTN, 2.0LT and 2.0LTN (with and w/o OSS); (b) The 50-cycle Li stripping capacity retention for 0.4 LT, 0.4LT w/o OSS, 2.0LT, and 2.0LT w/o OSS.

Upon increasing concentration to 2.0 M in the case of OSS occurrence, CE was enhanced as expected. The CE in 2.0LT initially displayed a 4-fold increase compared to 0.4LT. However, both of them showed a gradual decrease afterwards, revealing a very unstable Li plating/stripping process during cycling. Notably, blocking OSS can also relatively stabilize both CE and Li stripping capacity retention in prolonged cycles for 2.0LT. Furthermore, adding 0.1 M LiNO_3 as an additive in either 0.4LT or 2.0LT can not only enhance but also stabilize the CE performance. Interestingly, this remains true when adding LiNO_3 based on blocking OSS, while the opposite operation (blocking OSS based on adding LiNO_3) did not show any remarkable positive effect. Therefore, it is concluded that adding LiNO_3 could significantly compensate for CE degradation caused by OSS, apart from its effect on enhancing the CE values. Besides, the current densities of Li plating/stripping in 0.4LTN and 2.0LTN were smaller than those in 0.4LT and 2.0LT (**Figure 4-3**). This, as mentioned above, is related to a smoother and denser Li morphology.⁴

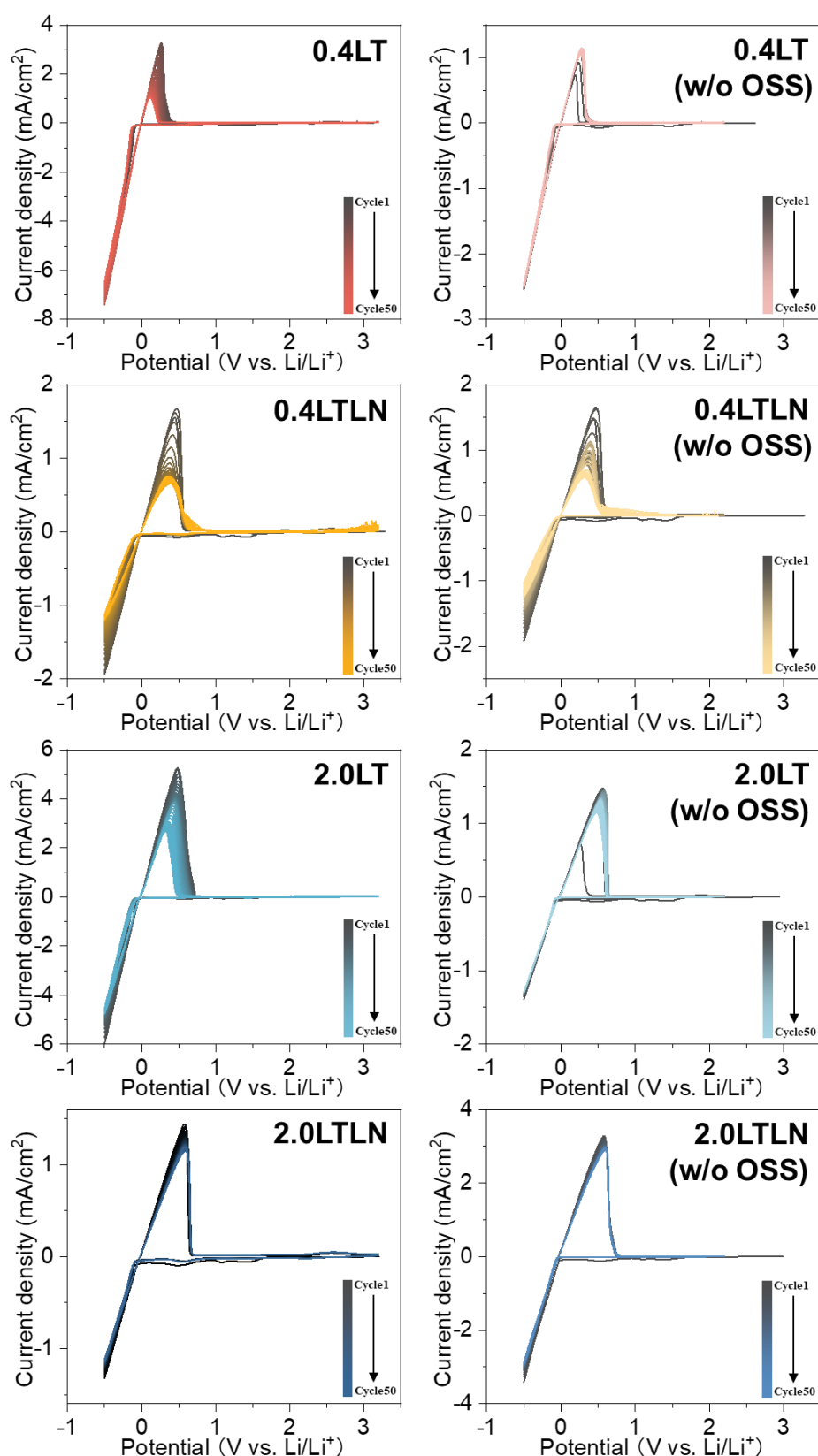


Figure 4-3. 50-cycle CV curves measured in 0.4LT, 0.4LTNL, 2.0LT and 2.0LTNL, as well as the corresponding electrolytes while blocking OSS. Potential range: -0.5 to 3.2 V vs. Li/Li⁺. Scan rate: 10 mV/s.

4.2.3 Li^+ / Electronic Conductivity of the SEI Layer

Since the CE performances should be deeply affected by the stability of electrolytes which can induce corresponding electrochemical reactions as cycling proceeds, a detailed analysis of the CV peaks was further conducted within the range of 0 to 3.2 V throughout the cycling process. **Figure 4-4** shows the enlarged view of 50-cycle CV curves measured in 0.4LT, 0.4LT w/o OSS, 0.4LTLN, 2.0LT and 2.0LTLN. In this figure, except for the labeled peaks (i.e., REL, RSS', and OSS) and the other peaks mentioned in Section 4.2.1 (i.e., RCO, RPS, and RSS), one can observe two more cathodic peaks: the one at 1.7 V (marked by the triangle symbol) existed in the electrolytes with LiNO_3 additive (0.4LTLN and 2.0LTLN). This peak belongs to the reduction of NO_3^- , while it was not observed in the first cycle probably due to the overlap from REL peak at a faster scan rate compared to Chapter 3 (1 mV/s). The other one locating around 1.1 V newly appeared in the prolonged cycles (marked by the circle symbol) in the 0.4 M electrolytes (except for 0.4LT with OSS), which is not found in the 2.0 M electrolytes, suggesting that this peak is presumably related to the solvent reduction that contributed to s-SEI layer formation as well.

Figure 4-5 exhibits the potential and current variations of the OSS, RSS' and REL peaks during cycling obtained from **Figure 4-4**. OSS and RSS' peaks, belonging to the two aforementioned s-SEI related redox reactions, were selected for discussions together with REL peak. In addition, it was reported that larger or smaller currents can indicate the conductive or resistive nature of SEI, respectively.⁹ The OSS/RSS redox couple represents the redox process involving Li^+ to create an s-SEI, whereas the currents of OSS/RSS can be regarded as an indicator of the Li^+ conduction ability of the s-SEI formed in the previous cycle(s) that can facilitate or suppress the redox process, i.e., the larger or smaller currents represent the higher or lower efficiency of Li^+ transport through the s-SEI layer. Meanwhile, the REL currents correlate with the decomposition of electrolyte that occurs due to the enhanced electronic conduction of SEI to facilitate the reaction between Li metal and electrolyte across SEI. Therefore, REL currents can reflect the electronic conductivity of s-SEI which influences the reaction kinetics between electrolyte and plated Li.

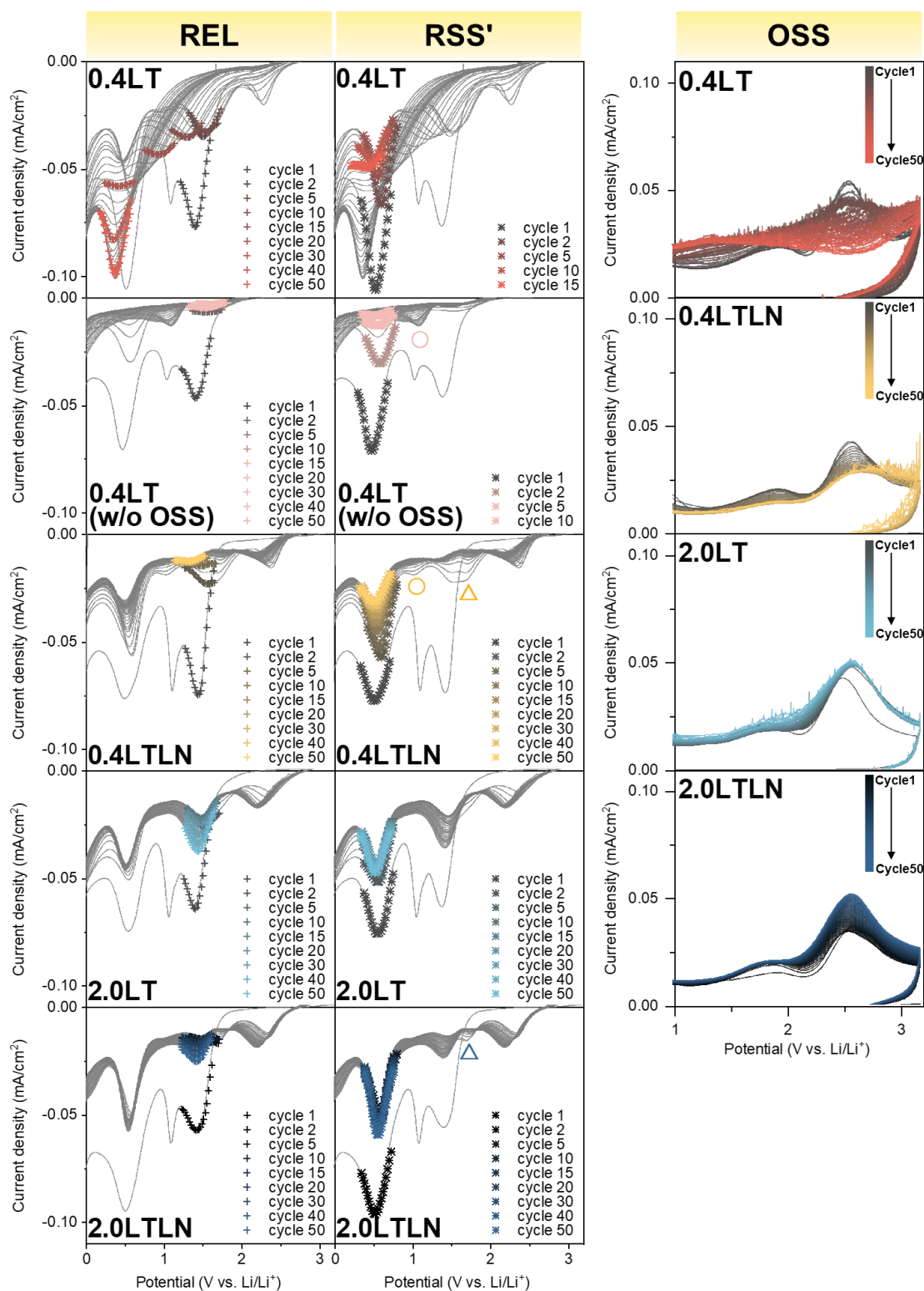


Figure 4-4. Cycling-dependent variation of REL, RSS' and OSS peaks measured in 0.4LT, 0.4LT w/o OSS, 0.4LTNLN, 2.0LT and 2.0LTNLN. Scan rate: 10 mV/s. REL and RSS' at selected cycles were marked by cross and asterisk symbols, respectively, for a better understanding of peak variation.

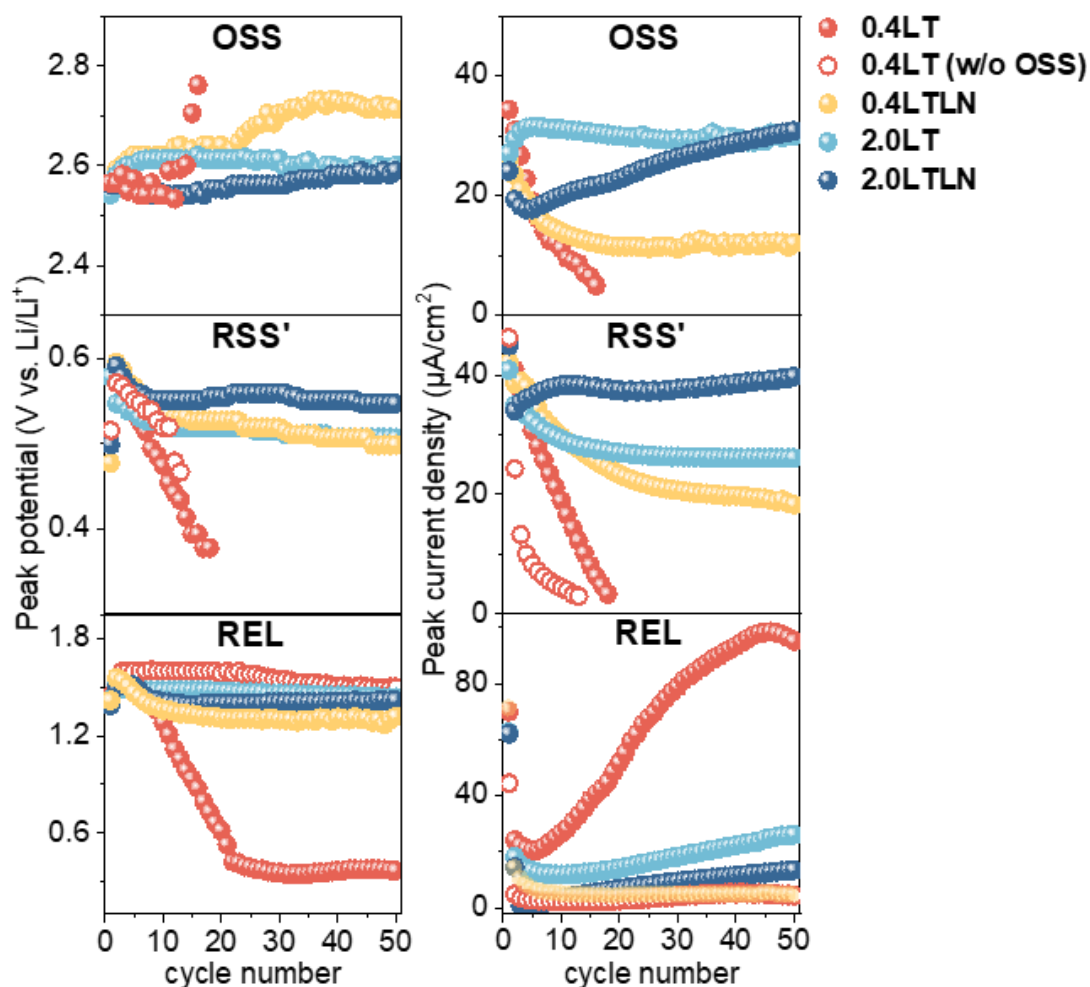


Figure 4-5. Cycling dependence on the peak potential and peak current density of OSS, RSS' and REL obtained from CV measured in 0.4LT, 0.4LT w/o OSS, 0.4LTLN, 2.0LT and 2.0LTLN.

As shown in **Figure 4-5**, for 0.4LT with OSS, peak potential and current variation upon cycling were observed, suggesting the reconstruction of the s-SEI layer. As cycling proceeded, the drastic increase of peak current of REL indicates a faster reaction kinetics.^{7,9} Together with the decreased OSS and RSS' currents, it was thereby inferred that this behavior should be induced by further decomposition of electrolyte due to the formation of the s-SEI layers with decreased Li^+ conduction and rapid electronic tunneling. Furthermore, the peak potential of REL negatively shifted within the initial 20 cycles, indicating an increased potential polarization for electrolyte decomposition induced by the thickening s-SEI layers as a result of electrolyte and Li consumption.⁹ This can be further supported by the increased interfacial resistance in the 10th and 20th cycle by the EIS analysis (**Figure 4-6(a)**), which suggests that more and more dendritic Li gradually increased the active surface area in contact with the electrolyte, facilitating undesirable reactions and generating electrochemically inactive “dead Li” in the subsequent cycling. The SEM image confirmed the growth and accumulation of

whisker-like Li after 50 cycles (**Figure 4-7(a)**). This process consumed more Li-metal and electrolyte and ultimately led to a drop in CE.

On the other hand, the Li^+ conductivity still decreased even blocking OSS for 0.4LT, as the RSS' current decreased even faster than that in 0.4LT with OSS, and almost exhausted within 10 cycles. Instead, the slightly larger interfacial resistance of s-SEI layers represented by the larger semicircles was observed in the EIS profile (**Figure 4-6(b)**) when compared with 0.4LT with OSS. Since the SEM image taken after 50 cycles in the case of blocking OSS provided the evidence of the growth of columnar-like Li with a relatively smooth surface morphology (**Figure 4-7(b)**), the possibility of severe dendritic Li growth was excluded. Therefore, this was rather caused by the formation of some inorganic species (LiF , Li_2CO_3 , Li_2O , etc.) with poor ionic and electronic conductivity to passivate the SEI layer surface.¹³ However, such kind of passivated layer can effectively block the electronic tunneling to suppress the decomposition of electrolyte to a certain extent, as indicated by much smaller currents of REL (**Figure 4-5**). These results together could explain why CE became more stable but was not enhanced when blocking OSS in 0.4LT.

By increasing concentration to 2.0LT, the Li^+ conductivity substantially increased as the OSS and RSS' currents were much larger than those in the 0.4LT after several cycles, but the electrolyte decomposition still proceeded as indicated by the increased REL current (**Figure 4-5**). Notably, adding 0.1 M LiNO_3 not only increased Li^+ conductivity but also greatly suppressed the electrolyte decomposition, as supported by the peak current density comparison between the electrolytes with and w/o LiNO_3 additive (**Figure 4-5**). However, it should be mentioned that the REL currents in 2.0LTLN gradually increased during cycling and surpassed the REL currents in 0.4LTLN. This might be due to the decomposition of LiNO_3 causing the weakened ability to suppress further electrolyte decomposition.

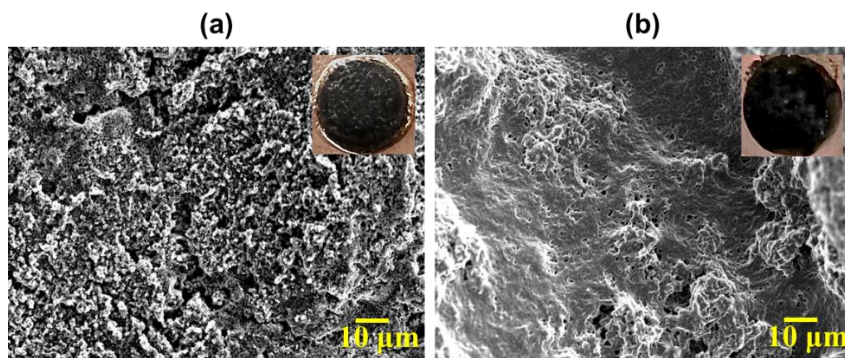
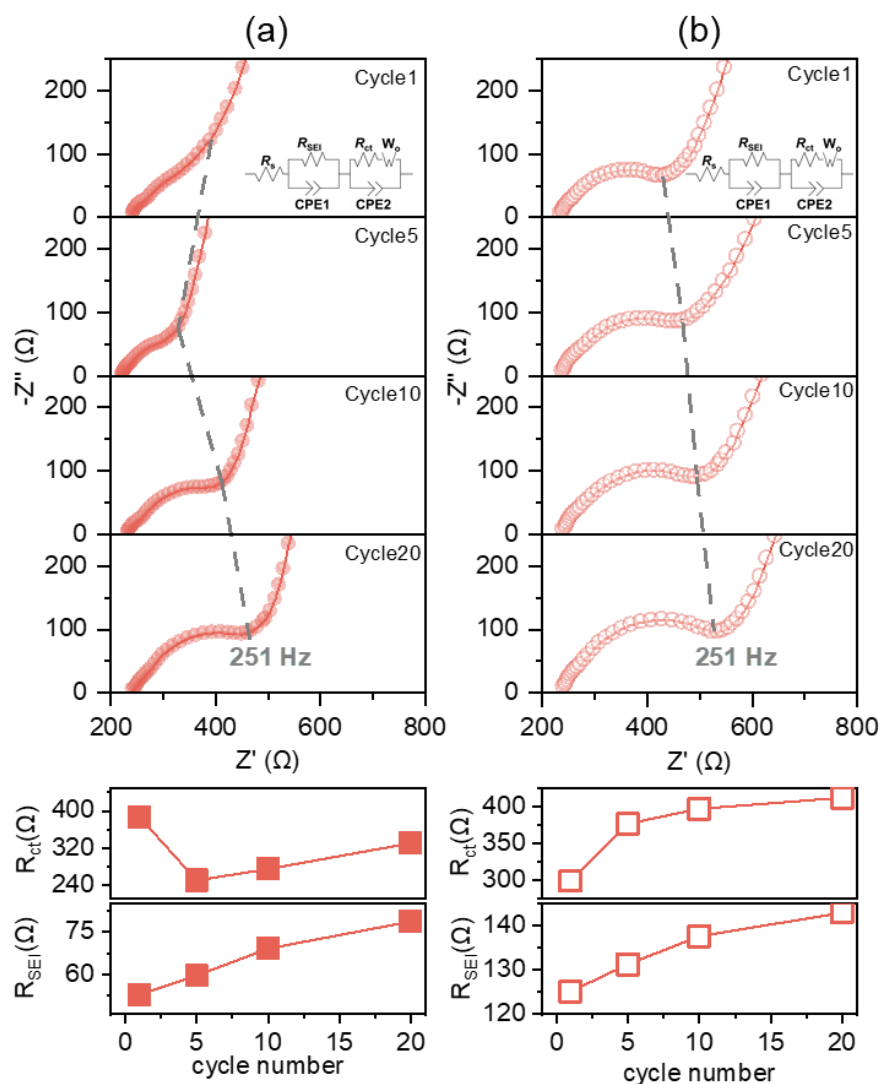


Figure 4-7. SEM morphologies and corresponding optical images of electrode surface in 0.4LT (a) with and (b) w/o OSS after 50 cycles.

4.2.4 Mass and Morphology Variation of the SEI Layer

The first-cycle QCM test was performed in 0.4LT, 0.4LTN, 2.0LT and 2.0LTN, by which the real-time change of mass and surface roughness of the SEI layer were obtained. **Figure 4-8(a)** shows the first-cycle CV curves as well as potential dependent Δm and ΔR measured in the four electrolytes. Markedly, after the initial Li plating/stripping, one can observe an increase in both mass and surface roughness (reflected by increased ΔR) for all electrolytes. Such an increase can be attributed to less than 100% stripping efficiency of Li metal due to inhomogeneous distribution of plated Li metal, and/or the extra deposits from the electrolyte decomposition.²³ Moreover, it can be found that the surface layer in the 2.0 M electrolytes displayed an elevated roughness before measurement compared with 0.4 M electrolytes mainly due to the increased density and viscosity.²⁴ However, it is clearly seen that the overall increase of Δm and ΔR was smaller for the electrolytes with LiNO_3 additive during Li plating/stripping, and the latter can be regarded as a greatly mitigated roughening process.

The MPE values during the initial Li plating/stripping in these electrolytes were also calculated for the prediction of possible dominant SEI components generated in this process, which were exhibited in the Δm vs. charge profile (**Figure 4-8(b)**). Multiple MPE values were confirmed during Li plating reflecting complex electrochemical processes. In particular, the MPE values are much larger than 7 (ideally, it can be regarded as Li plating/stripping exclusively taking place when $\text{MPE} \approx 7$, i.e., 5 to 9),^{25,26} indicating the reaction of plated Li metal with electrolytes, leading to the formation of an additional SEI layer. The major species of the SEI layer at this stage are more likely to be the organic Li salts (MPE around 50 to 80) from decomposed TEGDME since these electrolytes are low-concentrated ($< 3 \text{ M}$) and free-solvent dominated.^{27,28} It should be noted that the total charge consumed during Li plating should include the charge from associated electrolyte reactions in case of the MPE value larger than 7, thus the actual MPE related to electrolyte reactions is normally larger than the observed one which is dependent on the ratio of the charge from electrolyte reactions. Nevertheless, in this study the electrolytes with LiNO_3 additive presented smaller MPE values during Li plating, demonstrating that more inorganic species were generated with the help of LiNO_3 .

During Li stripping, the MPE of -33 and -15 was observed for 0.4LT and 2.0LT, respectively. They are smaller than -7 due to the concurrent oxidation of SEI species

and/or the crack of SEI layer. In contrast, the MPE of -4 and -9 for 0.4LTNLN and 2.0LTNLN, respectively, are close to -7, indicating a relatively protective inorganics-based SEI was formed during Li plating, with which the reaction of Li metal with electrolyte can be efficiently suppressed.

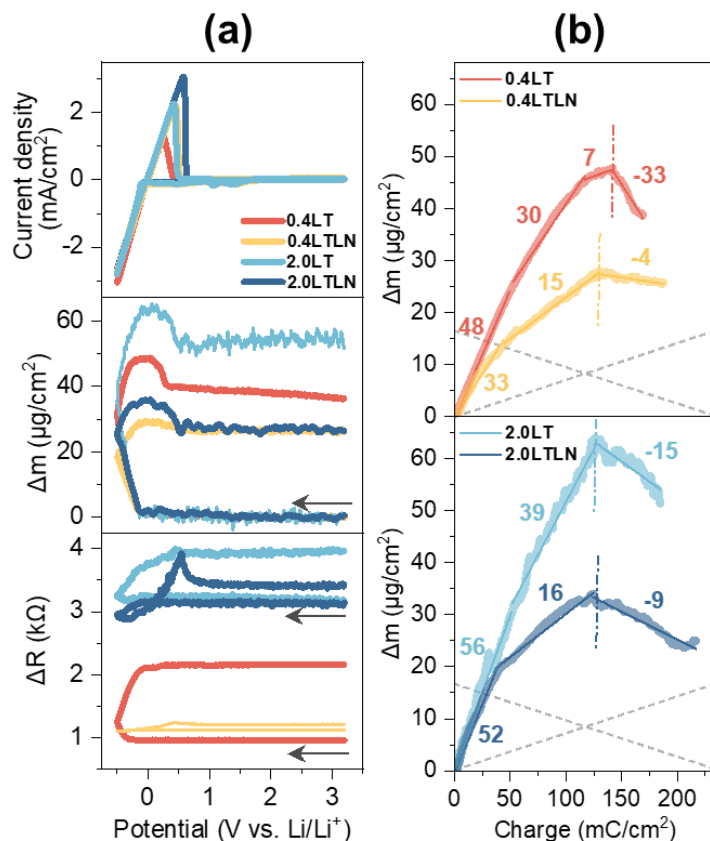


Figure 4-8. (a) First-cycle CV curves as well as the potential dependence of Δm and ΔR measured in 0.4LT, 0.4LTNLN, 2.0LT and 2.0LTNLN. Scan rate: 10 mV/s. The arrows represent the direction of scanning; (b) Calculated MPE values during the initial Li plating/stripping in above four electrolytes. The positive and negative MPE indicate the growth and the loss of mass, respectively. The vertical dash-dotted lines function as borderlines to separate the Li plating region and the Li stripping region; The gray dashed lines were manually added as a reference showing only Li plating and stripping (MPE = 7 and -7, respectively).²⁶

The analyses on the cycling-dependent MPE and ΔR were conducted for the 10th and 20th cycles. As shown in **Figure 4-9(a)**, for 0.4LT with OSS, compared with the MPE in the 10th cycle, the MPE of 7 during Li stripping in the 20th cycle deviated from -7 more markedly, showing that the increase of surface mass originated from more undesired side reactions. Upon increasing the concentration to 2.0LT, the continuously decreasing mass and the negative MPE much smaller than -7 in the 10th and 20th cycle imply the mechanical disconnection of unreactive Li and/or SEI components from the surface. These behaviors also reflect on the prominent rise of surface roughness in 0.4LT and 2.0LT (**Figure 4-9(b)**). In contrast, by either blocking OSS or adding LiNO₃

to 0.4LT, a more stable Li plating/stripping process was achieved as indicated by their MPE close to ± 7 even in the 20th cycle. Moreover, it is obvious for 0.4LT that OSS kept on increasing the surface roughness upon cycling, while blocking OSS did not work as effectively as adding LiNO_3 (0.4LTN) in suppressing the increased roughness. For 2.0LTN cycled to the 10th and 20th cycles, similar results as for 0.4LTN were obtained regarding MPE and the suppression of surface roughness.

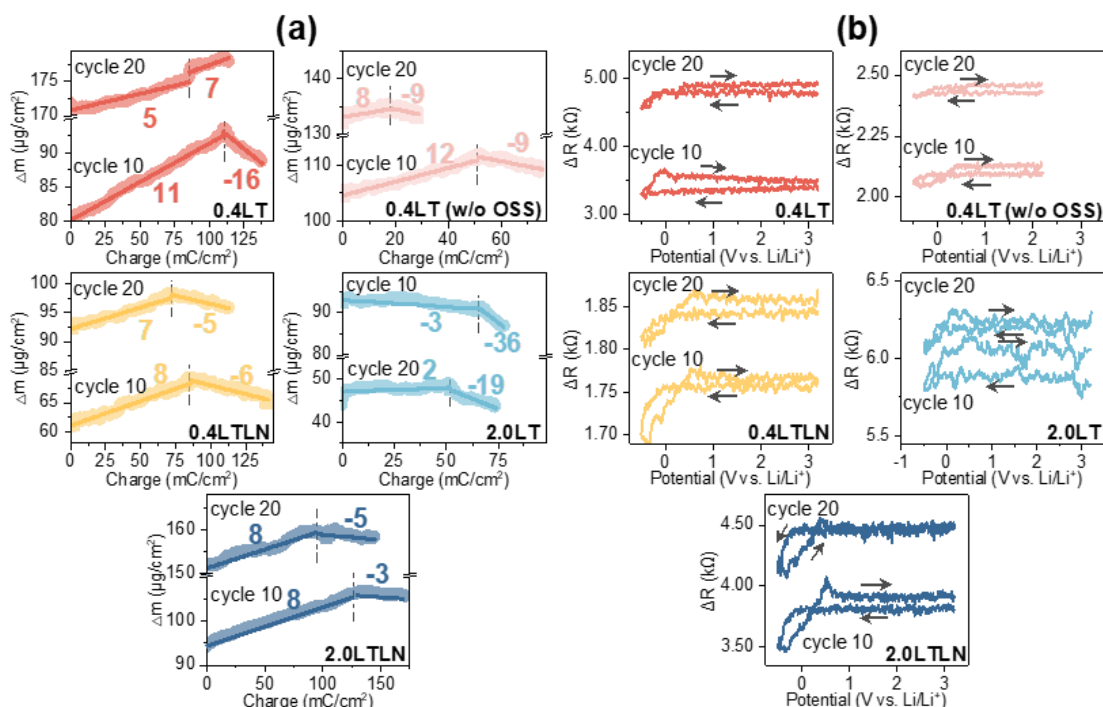


Figure 4-9. (a) Calculated MPE values during Li plating/stripping in the 10th and 20th cycles measured in 0.4LT, 0.4LT w/o OSS, 0.4LTN, 2.0LT and 2.0LTN. The positive and negative MPE indicate the growth and the loss of mass, respectively. The vertical dash-dotted lines function as borderlines to separate Li plating region and Li stripping region; (b) Potential-dependent ΔR in the 10th and 20th cycles measured in 0.4LT, 0.4LT w/o OSS, 0.4LTN, 2.0LT and 2.0LTN.

The above discussions on roughness were evidenced by comparing the surface morphology differences via SEM and optical images of electrode surface after cycling among different electrolytes. Recalling from the discussion of **Figure 4-7**, the whisker-like Li accumulated in 0.4LT, whereas some film-forming products with a relatively smooth surface morphology can be found when blocking OSS. However, a dark grey deposit was visually observed indicating the formed SEI layer on the Cu surface was thick regardless of OSS process.^{29,30} With the help of LiNO_3 additive, smoother morphology and the silver white color of deposits proves the formation of denser and dendrite-free layers (**Figure 4-10(a)**). Meanwhile, the surface for 2.0 LT exhibited irregular protrusions, suggesting uneven Li plating/stripping with the formation and dissolution of dendritic or mossy Li, while the morphology in 2.0LTN appeared much

smoother with minimal observable texture, indicating a remarkably stabilized plating and stripping process (**Figure 4-10(b, c)**).

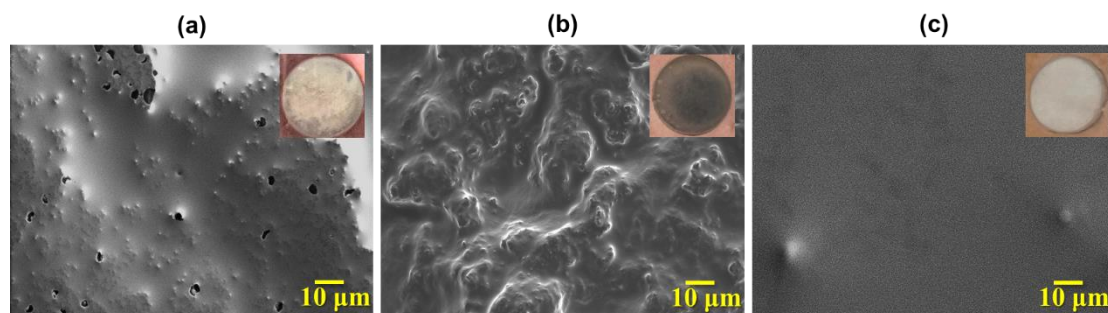


Figure 4-10. SEM morphologies and corresponding optical images of electrode surface in (a) 0.4LTN, (b) 2.0LT, and (c) 2.0LTN after 50 cycles.

4.2.5 Composition Variation of the SEI Layer

To better understand the detailed variation of SEI compositions at different stages of cycling, the SEI layer formed in 0.4LT, 0.4LT w/o OSS, 0.4LTN and 2.0LTN after 50-time cycling were characterized using in-depth XPS analysis by Ar^+ etching for 0, 5, and 10 min. **Figure 4-11(a, b)** shows the Li 1s and N 1s XPS spectra of the s-SEI layers formed at different periods of cycles on the Cu substrate in these electrolytes. Typically, the LiNO_3 decomposition products, such as Li_3N and LiN_xO_y that reportedly enable high Li^+ conductivity,^{13,14} were confirmed for 0.4LTN and 2.0LTN.

In the O 1s spectra (**Figure 4-11(c)**), two peaks were observed in all electrolytes: the one at 531.5 to 533 eV was assigned to $-\text{C}-\text{O}-\text{C}-$ bonding corresponding to poly(ethylene oxide) $((\text{CH}_2-\text{CH}_2-\text{O})_n^-)$ or ROCO_2Li from the decomposition of TEGDME molecules, and the other at 534 ~ 535.5 eV was assigned to Li_2CO_3 .^{13,32} In addition, a down-shift of binding energy was found upon cycling, which was due to the existence of polar decomposed species (such as carbonates, which could involve in further degradation process) on the electrode surface that caused the formation of an electric potential gradient at the interface.³¹ Furthermore, Li_2O at 529 eV was detected for 0.4LT w/o OSS, which as discussed above could generate from the SEI layer related reactions including the reactions between plated Li metal and electrolyte. On the other hand, the existence of Li_2O_2 at 531 eV was observed while no Li_2O was detected regardless of the Ar^+ etching depth in the presence of OSS,³⁵ suggesting that Li_2O could be oxidized to Li_2O_2 during OSS in 0.4LT (the co-existence of Li_2O and Li_2O_2 detected in the Li 1s spectra may indicate that this oxidation is an incomplete process).

Interestingly, Li_2O was detected for 0.4LTLN at the occurrence of OSS but was hardly found for 2.0LTLN. It was previously reported that the decomposition of LiNO_3 could contribute to the formation of Li_2O together with Li_3N .¹⁴ The formed insoluble Li_2O at anode side contributes to construct the SEI layer.³⁶ However, the existence of Li_2O_2 cannot be excluded since it is difficult to unambiguously distinguish Li_2O_2 and Li_2O in the spectra due to their close binding energy.

To this end, *in situ* SERS measurement was conducted at the potential before and after OSS (**Figure 4-12**) to clarify whether the oxidation of Li_2O occurred or not via OSS in 0.4LTLN and 2.0LTLN. It should be mentioned that the SERS band of Li_2O (near 530 cm^{-1}) cannot be confirmed due to the overlap of the broad peak from Cu substrate at $500 \sim 600\text{ cm}^{-1}$.³⁷ However, in both 0.4LT and 2.0LT, a band near 700 cm^{-1} was observed after OSS, which can be assigned to the O–Li–O stretching vibration of lithium superoxide (LiO_2).³⁸ Another band near 800 cm^{-1} was also confirmed, which was considered to be the O–O stretching of Li_2O_2 .^{39,40} Therefore, one can assure that Li_2O , one of the major SEI components formed prior to OSS, was mostly oxidized during OSS to Li_2O_2 , which was further partially oxidized to LiO_2 on the electrode surface. In the LOB configuration, LiO_2 is known as an intermediate of Li_2O_2 , a final product of the discharging process in the cathode.^{41,42} In general, the formation of Li_2O_2 from LiO_2 occurs either via a solution pathway or a surface pathway, depending on the donor number (DN) of solvent as well as overpotential.⁴³ The use of low-DN TEGDME solvent⁴⁴ will usually give rise to a surface pathway where LiO_2 is poorly dissolved in TEGDME, accumulating on the electrode surface and reducing to film-like Li_2O_2 , which is associated with lower specific capacity.^{45–48} During anodic scanning, soluble LiO_2 was generated by the oxidation of Li_2O_2 in high-DN solvents but not in low-DN solvents such as TEGDME (instead, solid LiO_2 could form),^{49–51} enhancing the cycling stability in low-DN solvents than that in high-DN solvents.⁴⁹ This could explain why LiO_2 was detected by SERS on the surface in this study. However, neither Li_2O_2 nor LiO_2 was confirmed for 0.4LTLN and 2.0LTLN regardless of OSS, which implies that on one hand the LiNO_3 additive strongly suppressed the oxidation of Li_2O via OSS in 0.4LTLN, on the other hand Li_2O was not the major SEI component in 2.0LTLN since Li_2O was not found in XPS, and its oxidation products were also not found in SERS.

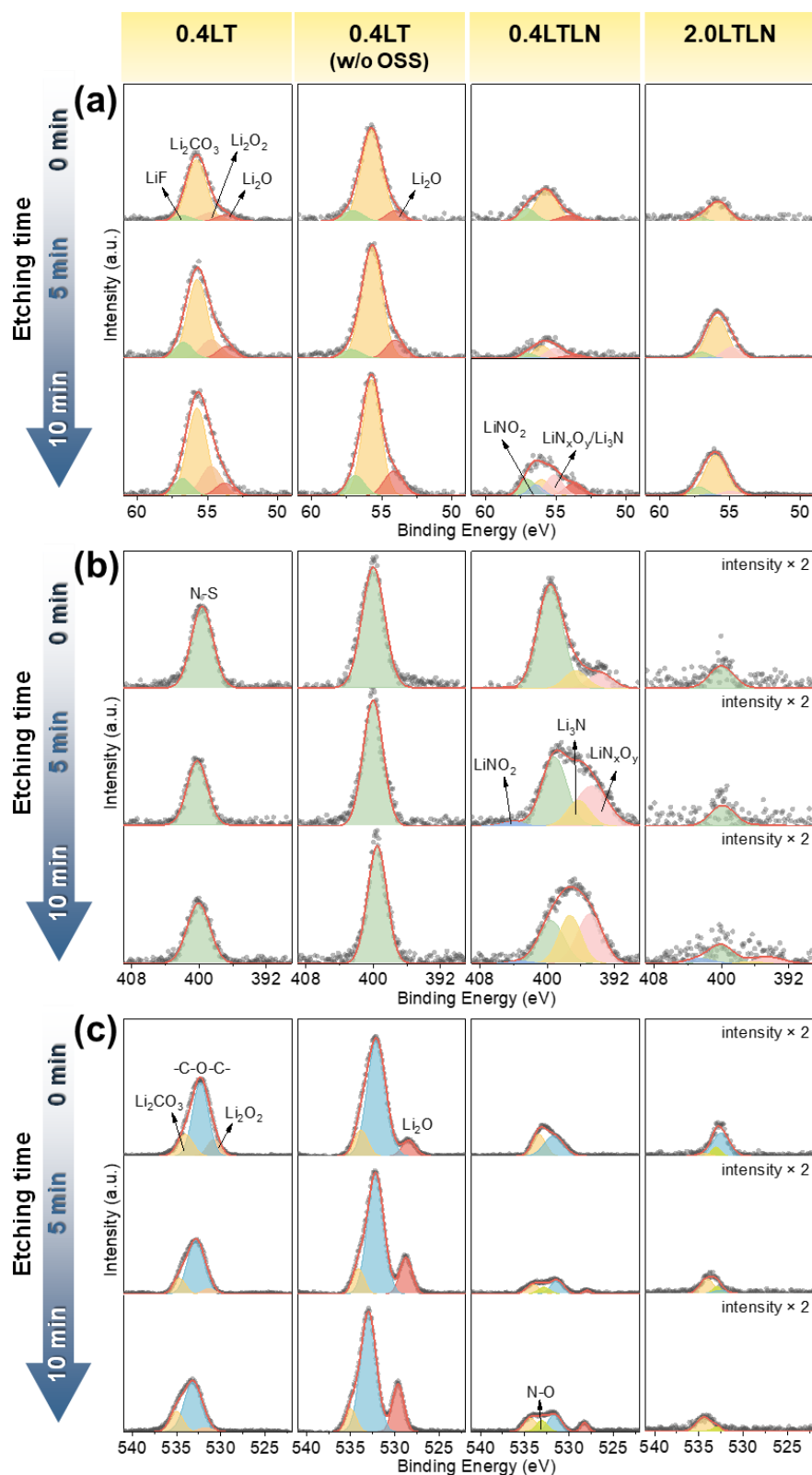


Figure 4-11. (a) Li 1s, (b) N 1s and (c) O 1s depth profiling XPS spectra of the SEI layers for 0.4LT, 0.4LT w/o OSS, 0.4LTLN and 2.0LTLN at different etching times.

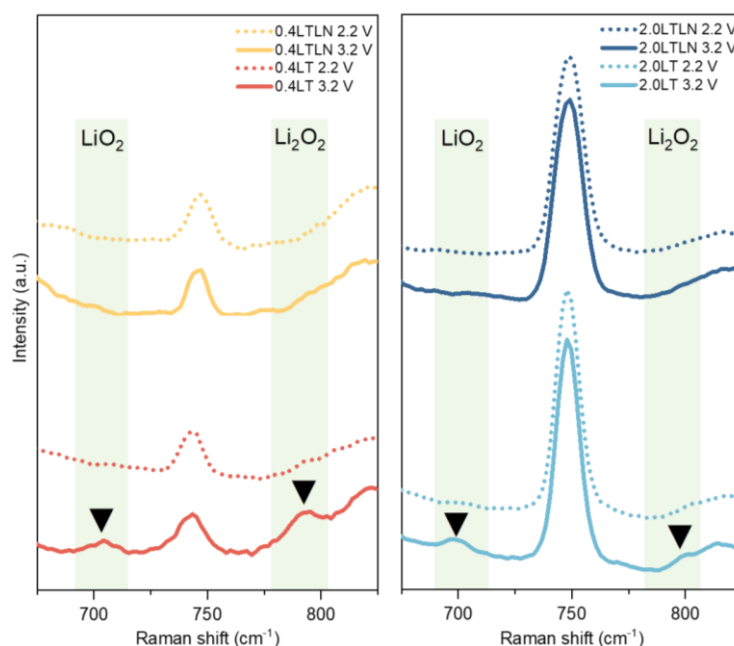
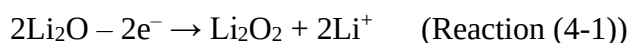


Figure 4-12. *In situ* SERS spectra recorded before (2.2 V) and after (3.2 V) OSS during the first cycle in 0.4LT, 0.4LTNL, 2.0LT and 2.0LTNL.

The function of LiNO_3 additive in suppressing the oxidation of Li_2O was further proved by a more careful analysis (scan rate was reduced to 1 mV/s) of the OSS process in 0.4LT and 0.4LTNL via QCM. When repeating the QCM test with the focus on the OSS process in 0.4LT, a sudden change of MPE around 2.6 V was found in all three tests, which was highly likely to be caused by the oxidation of Li_2O (**Figure 4-13(a)**),^{52,53} irrespective of the distinct MPE values among these tests probably due to the complicated physical and chemical phenomena caused by SEI crack and Li dendrite during OSS. In contrast, the sudden change of MPE was not observed in 0.4LTNL, meaning that the oxidation of Li_2O hardly occurred during OSS (**Figure 4-13(b)**). Sharon et al. reported that Li_2O_2 can be oxidized by the reaction product (NO_2) originated from LiNO_3 which can act as a redox mediator in the Li-oxygen battery.⁵⁴ However, this process was thought to occur at the cathode side above 3.6 V vs. Li/Li^+ . Therefore, the possibility of LiNO_3 further oxidizing Li_2O_2 that generated from Li_2O oxidation during OSS can be excluded in this study. It is worth noting that the possible reaction showing the oxidation of Li_2O to Li_2O_2 is considered as **Reaction (4-1)**:



The correspondent MPE equals -7. Assuming that the change of MPE was mostly due to Li_2O oxidation, then the ratio of the charge released by electrochemical Li_2O oxidation over the total charges during OSS can be calculated. As a result, similar ratios (see **Table 4-1**) were confirmed in all tests using 0.4LT, further proving the above

assumption. This demonstrates that the oxidation of Li_2O was the major OSS reaction that transferred 80 ~ 90% of the total charges, which can be effectively suppressed by LiNO_3 . It should be noted that, since the total mass change during OSS was affected by a series of reactions, the precise identification of all plausible reactions necessitates a combination of QCM with other techniques in the future.

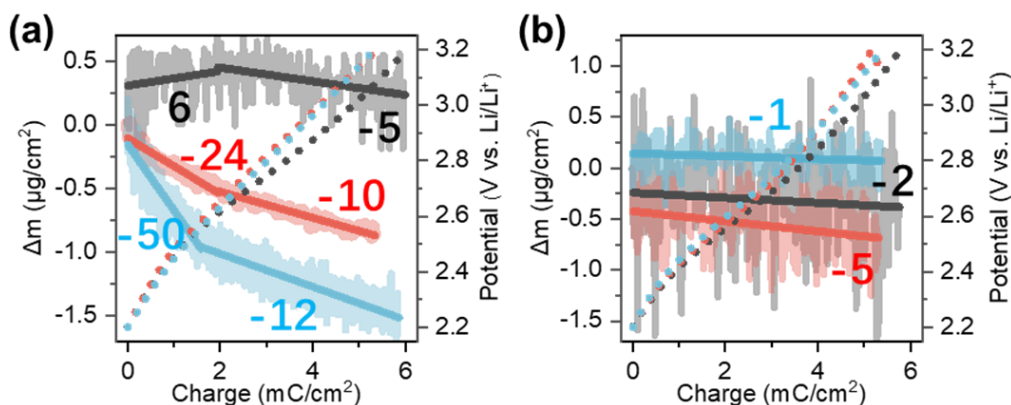


Figure 4-13. The calculated MPE values from the Δm -charge curves (solid bold line, including raw data and linearly fitted data), and the potential-charge curves (dotted line) during OSS in the first cycle measured in (a) 0.4LT and (b) 0.4LTLN. Scan rate: 1 mV/s. Totally 3 samples (represented by 3 different colors) were tested for each electrolyte. The positive and negative MPE indicate the increase and decrease of mass, respectively.

Table 4-1. The ratio of Li_2O oxidation charges over total charges

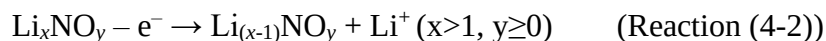
First MPE	Second MPE	Ratio of Li_2O oxidation charges ^a
6	-5	85%
-24	-10	83%
-50	-12	87%

^a Calculation process: The ratio of the charge released by Li_2O oxidation over the total charges can be set as x . Since the MPE of Li_2O oxidation to Li_2O_2 is -7, assuming that the change of MPE was mostly due to Li_2O oxidation, we can obtain the following equation: $A(1-x)-7x=B$, where A and B represent the first MPE and the second MPE, respectively. Finally, the above equation can be changed to: $x=(A-B)/(A+7)$, then x can be obtained.

Since the addition of LiNO_3 can effectively inhibit Li_2O oxidation, it is expected that the total charges transferred during OSS process should be less for the electrolytes with LiNO_3 than for those w/o LiNO_3 . However, as shown **Figure 4-13**, the transferred charges from 2.6 V to 3.2 V for 0.4LT and 0.4LTLN are very close (5 to 6 mC/cm^2), meaning some extra electrochemical oxidations occurred during OSS for 0.4LTLN that compensated for the charges from Li_2O oxidation. Recall that the XPS spectra for 0.4LTLN exhibit two major differences from 0.4LT (**Figure 4-11**):

1. The disappearance of Li_2O_2 ;
2. The generation of nitrogen-containing species (e.g., Li_3N , LiNO_2 , LiN_xO_y)

Therefore, the difference created by LiNO₃ during OSS apart from the suppression of Li₂O oxidation is the electrochemical oxidation of specific nitrogen-containing species (equivalent to peak *a* in **Figure 4-14**, where 0.1 M LiNO₃ was used as the only Li salt). The possible reactions can be expressed as **Reaction (4-2)**:



As an example, the oxidation of Li₃N to LiNO_x (*x* = 2, 3) can possibly occur, whose reverse reaction occurs around 1.7 V during negative scanning (equivalent to peak *a''* in **Figure 4-14**).^{15,55} Considering the fact that the extra reactions instead of Li₂O oxidation occurred in the OSS process for 0.4LTLN, such reactions are therefore highly possible to be related to **Reaction (4-2)**. However, the detailed reaction scheme is still unclear and require a further study.

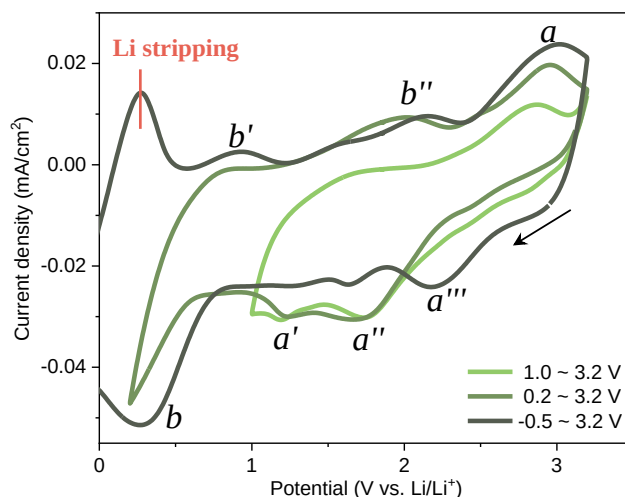
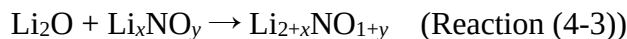


Figure 4-14. Enlarged view of the second-cycle CV curves measured in the 0.1 M LiNO₃-TEGDME electrolyte under 3 different potential ranges. Scan rate: 10 mV/s. The redox *a*/(*a'*, *a''*, *a'''*) indicates the LiNO₃-related reactions, where the oxidative reaction *a* occurs within the OSS region; The redox *b*/(*b'*, *b''*) indicates the SEI-related reactions. The arrows represent the direction of scanning.

Besides, one possible route of LiNO₃ suppressing the oxidation of Li₂O can be speculated by the generation of nitrogen-containing species as well (**Figure 4-11(b)**), which may also come from the reaction of Li₂O with the decomposition products from LiNO₃, as expressed by **Reaction (4-3)**. Through this reaction, the oxidation of Li₂O can be suppressed according to Le Chatelier principle. This can be further supported by the gradual decrease of Li₂O during cycling for 0.4LTLN (**Figure 4-11(c)**). Note that this process did not consume Li₂O as much as its direct oxidation to Li₂O₂ or LiO₂, so that it sustained the amount of Li₂O to a certain extent.



The OSS process was further investigated via S 2p spectra as shown in **Figure 4-15(a)**. In the case of 0.4LT, one can find the weaker and stronger peak intensities of short-chain lithium polysulfides Li_2S_x ($x = 1, 2$) and lithium sulfate (Li_2SO_4), respectively. However, blocking OSS reversed this trend, indicating that the oxidation of Li_2S_x towards Li_2SO_4 occurred via OSS. The existence of Li_2S_x was due to the decomposition of LiTFSI salt, while these short-chain lithium polysulfides were reported to be capable of suppressing Li dendrites growth. This oxidation could also be related to the degraded CE performance in 0.4LT.⁵⁶ On the other hand, it can be found that LiNO_3 additive cannot prevent the oxidation of Li_2S_x since they were nearly absent in both 0.4LTLN and 2.0LTLN, whereas the lack of these species did not degrade the CE performance in the existence of LiNO_3 additive, showing the importance of the presence of Li_2O rather than Li_2S_x .

Furthermore, as shown in the F 1s spectra (**Figure 4-15(b)**), the intensity of LiF is almost the same in 0.4LT regardless of OSS. Although the LiF-rich SEI is commonly considered to be an effective SEI in protecting Li metal, this finding suggests that the existence of Li_2O was rather regarded as the major contributor to the improved Li plating/stripping stability in terms of dilute (0.4 M) electrolyte.⁵⁶⁻⁵⁹ On the contrary, the atomic concentration percentage of the s-SEI composition demonstrates a higher F ratio for 2.0LTLN compared with others (**Figure 4-16**). This also demonstrates that LiF is the major SEI component for 2.0LTLN which played a decisive role in enhancing and stabilizing the CE performance. A similar result was previously reported, showing that LiNO_3 additive can facilitate LiTFSI decomposition to generate more LiF in concentrated electrolyte (3.25 M),¹⁵ though in the present study the concentrations are not over 2.0 M. In summary, for the more dilute (0.4 M) electrolytes, Li_2O (and Li_2S_x when blocking OSS) contributed to enhance the efficiency, while for the 2.0LTLN electrolyte, LiF took over the lead role in affecting the efficiency.

Figure 4-15(c) depicts the depth-dependent C 1s spectra, in which the decrease of inorganic constituent and the increase of organic constituent was clearly seen in the electrolytes with LiNO_3 but was not in the ones w/o LiNO_3 additive. In fact, the inorganic to organic species ratios in the case of with and w/o additives can be roughly determined by the integrated peak intensity ratio based on the result of peak deconvolution, which are listed in **Table 4-2**. It is evidenced that by adding LiNO_3 , the

increase of organic SEI species ratio during cycling is more remarkable, further proving a more heterogeneous SEI layer structure.^{32,33}

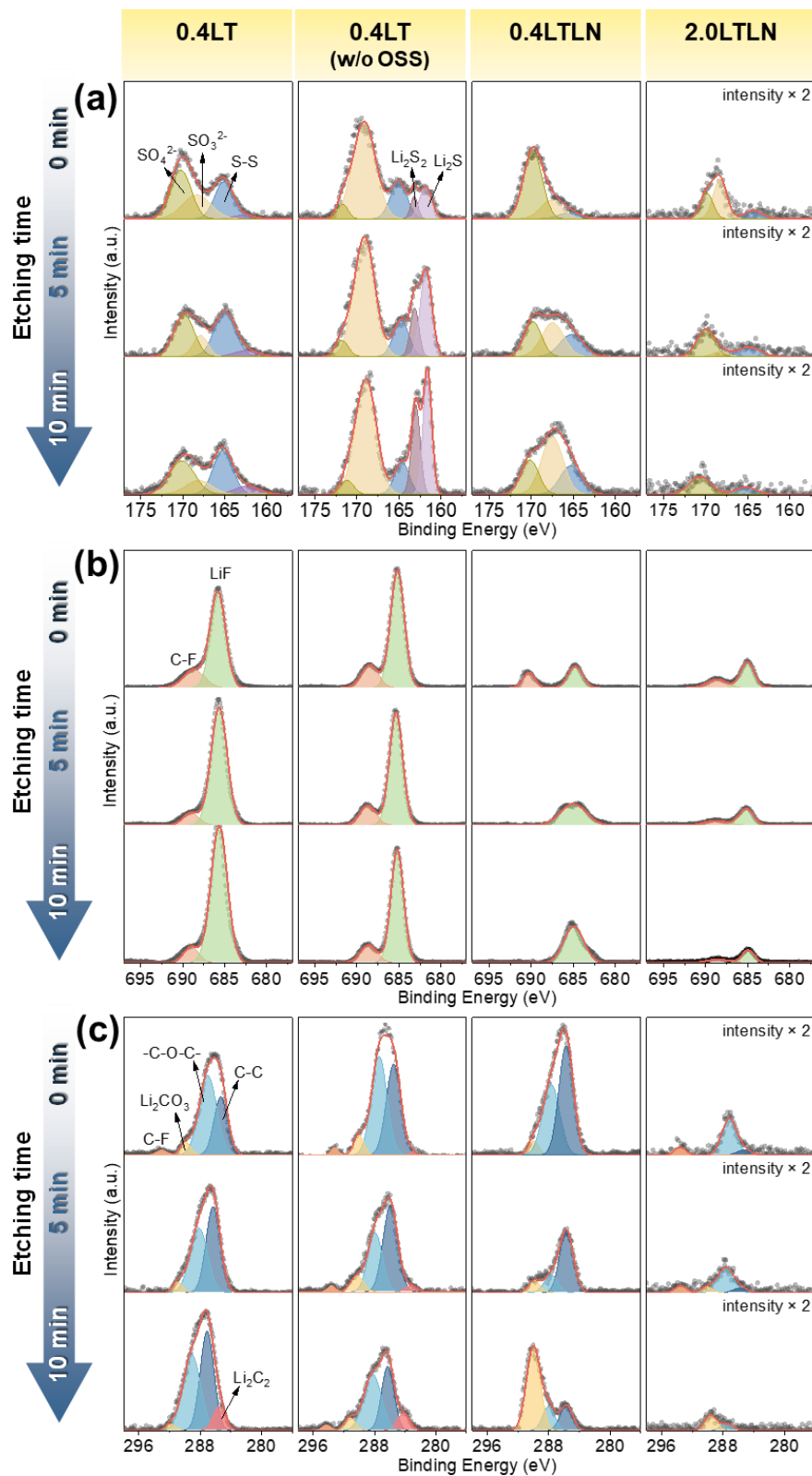


Figure 4-15. (a) S 2p, (b) F 1s and (c) C 1s depth profiling XPS spectra of the SEI layers for 0.4LT, 0.4LT w/o OSS, 0.4LTLN and 2.0LTLN at different etching times.

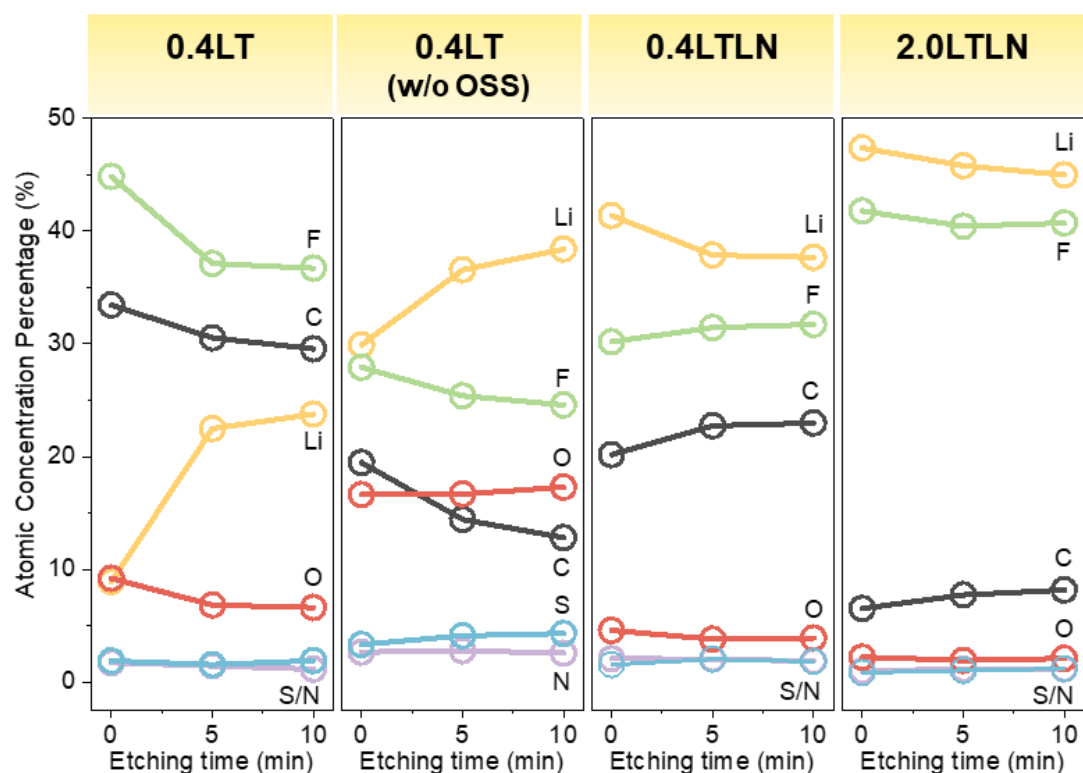


Figure 4-16. Atomic concentration percentage of the s-SEI composition after different etching times cycled in 0.4LT, 0.4LT w/o OSS, 0.4LTLN and 2.0LTLN.

Table 4-2. The etching time-dependent organic to inorganic species ratios of s-SEI layers in 0.4LT and 0.4LTLN. The peak intensities of different elemental spectra were normalized by considering the atomic sensitivity factor (ASF) before the calculation of ratios.³⁴

Electrolyte Etching time	0.4LT	0.4LTLN
0 min (outer SEI)	49%	59%
5 min (middle SEI)	43%	23%
10 min (inner SEI)	33%	12%

4.2.6 Studies of Li Inventory Loss

The existence of the electronically poorly-conductive Li_2C_2 ⁶⁰ was confirmed on the inner s-SEI layer measured in both the electrolytes with and w/o OSS occurring, with a peak at 283 eV in the C 1s spectra shown in **Figure 4-15(c)**. The difference between them is that when OSS was blocked, the amount of Li_2C_2 gradually decreased but was still observed on the outermost s-SEI layer, while Li_2C_2 can only be detected on the inner SEI layer with the occurrence of OSS. On the other hand, it was not detected at any depth of the s-SEI layers formed in 0.4LTLN and 2.0LTLN. It was reported that the formation of Li_2C_2 is prone to occur on the massively plated Li metal

surface.⁶¹ These differences therefore indicate that with OSS, a poor reversibility of Li plating/stripping will lead to the accumulation of Li_2C_2 , and ultimately a severe loss of Li inventory fundamentally prohibit the further formation of Li_2C_2 . In sharp contrast, a greatly improved reversibility of the dissolution of formed Li_2C_2 together with an enhanced Li stripping efficiency can be achieved by the LiNO_3 additive.

In situ SERS measurement also proves that Li_2C_2 is the major component of the formed s-SEI layers, which was detected via the $\text{C}\equiv\text{C}$ stretching vibration mode around 1853 cm^{-1} on the plated Li metal surface (**Figure 4-17**), similar as Schmitz et al.'s report.⁶¹ The normalized integrated intensity of the Li_2C_2 peak at the measured cycles for all electrolytes are also summarized in **Figure 4-18**, through which the change of the relative amount of Li_2C_2 on Li surface during cycling can be estimated. During the initial 10 cycles for 0.4LT, the amount of deposited Li_2C_2 drastically decreased during cycling even at the stage where Li was deeply plated at -0.5 V vs. Li/Li^+ , indicating the severe loss of Li inventory. A similar tendency was also observed in 2.0LT, while for 0.4LT w/o OSS, 0.4LTLN and 2.0LTLN, the intensity of Li_2C_2 band almost did not change during cycling, meaning that a more stable SEI layer was formed to suppress Li loss via reacting with electrolyte and reconstructing s-SEI layers. These results were well in accordance with the observed C 1s spectral behaviors. Additionally, it is worth stating that the aforementioned larger interfacial resistance of s-SEI layers when blocking OSS (**Figure 4-6(b)**) could therefore majorly originate from the continuous existence of Li_2C_2 .

Meanwhile, the atomic concentration percentage of the s-SEI composition at different depths of the s-SEI layer also demonstrates the Li inventory change during cycling, as shown in **Figure 4-16**. In the case of 0.4LT with OSS, the apparent increase of C, O, F content and drop of Li content in the outer SEI layer (corresponding to the etching time of 0 min) proves the severe decomposition of electrolyte associated by the exhaustion of Li inventory. By contrast, Li deposits were more evenly distributed across the s-SEI layers during cycling by blocking OSS, and a homogeneous distribution of Li was almost achieved by the help of LiNO_3 additive.

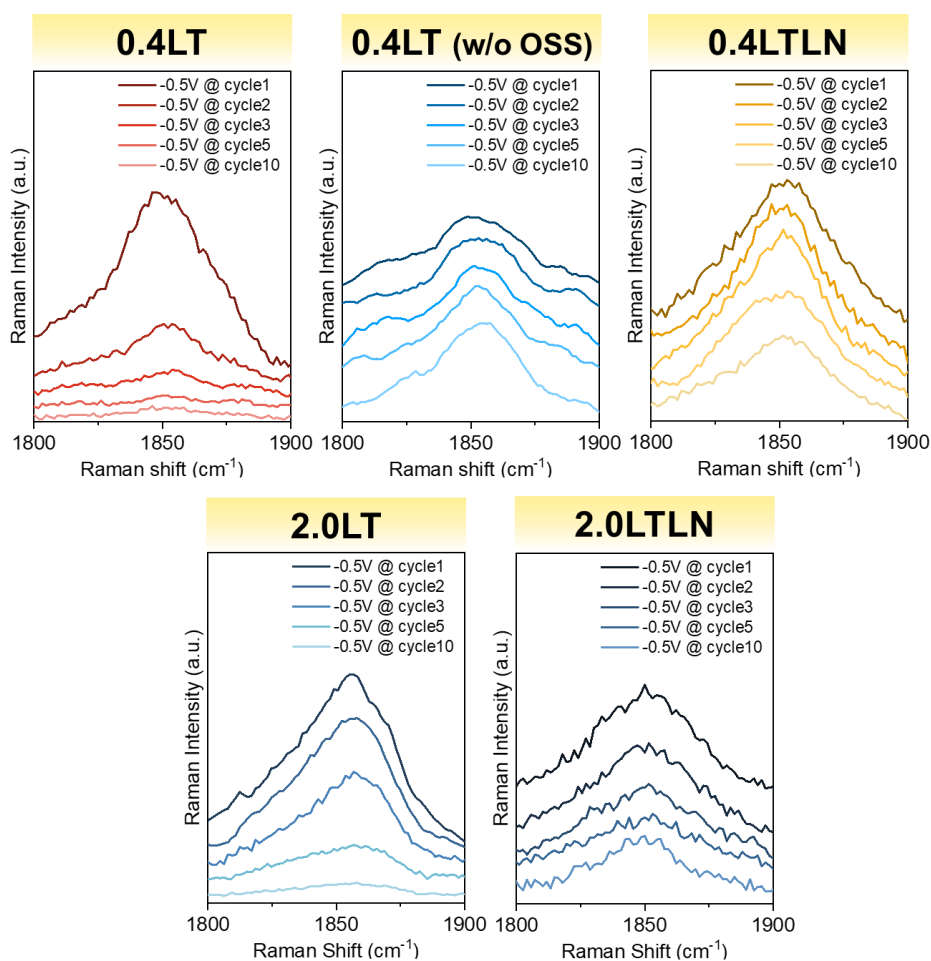


Figure 4-17. Cycle-dependent SERS intensity of $\nu(\text{C}\equiv\text{C})$ band in 0.4LT, 0.4LT w/o OSS, 0.4LTNLN, 2.0LT and 2.0LTNLN. The SERS spectra were recorded at -0.5 V vs. Li/Li^+ during cycle 1, 2, 3, 5 and 10.

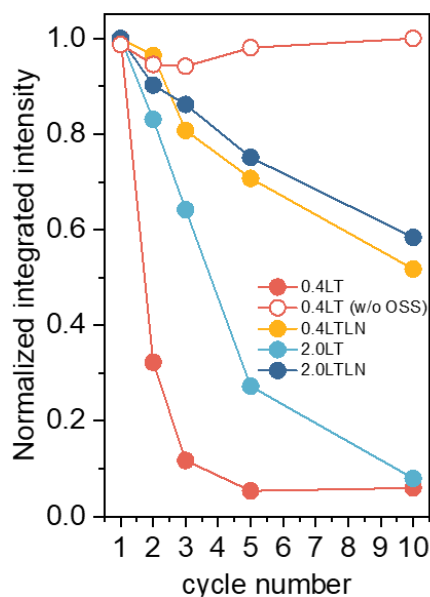


Figure 4-18. Summary of the normalized integrated intensity of all electrolytes.

4.2.7 Proposed Model of Major SEI Components and Morphology Variation via OSS

Based on the above discussions, a model was proposed to show the variation of major species via OSS in more detail (**Figure 4-19**). The major s-SEI components in the 0.4LT electrolyte prior to OSS include Li_2O and Li_2S_x . When adding LiNO_3 , nitrogen-containing species appear to be another major species. Further increasing the concentration to 2.0 M, LiF replaces Li_2O_x and becomes the major species.

In the case of w/o LiNO_3 additive, a series of oxidative reactions occur during OSS, where the oxidized species are generated to construct the s-SEI layer. Upon the occurrence of OSS, Li dendrite can grow more heavily during subsequent plating/stripping due to the influence of renewed major s-SEI species ($\text{Li}_2\text{O} \rightarrow \text{Li}_2\text{O}_2$, $\text{Li}_2\text{S}_x \rightarrow \text{Li}_2\text{SO}_4$), resulting in the severe roughening of electrode surface and the degradation of CE performance. By adding LiNO_3 , the problem can be solved through the prevention of Li_2O oxidation, and the resultant electrode surface after OSS will retain rather lower roughness.

These results suggest that adding LiNO_3 as an additive could be of great help in sustaining the SEI layer stability when the operating potential range of AFLMBs is considered to be broadened. In addition, this study provides a promising strategy to optimize the compositional and morphological conditions that could be degraded by OSS and similar reactions occurring in a higher potential region.

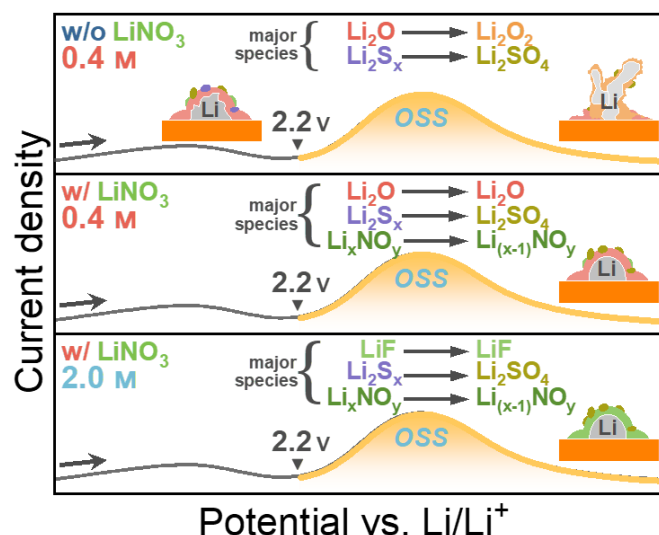


Figure 4-19. Proposed model of the change of major SEI components via OSS under the influence of electrolyte concentration and LiNO_3 additive in the LiTFSI/TEGDME electrolytes.

4.3 Conclusion

In this study, LiTFSI in TEGDME as the dilute electrolyte applied in an AFLMB anode half-cell (Li||Cu) configuration was investigated by a series of electrochemical tests and compositional characterizations. This study provided a viewpoint in evaluating the impacts of the electrochemical reactions in the potential range of 0 to 3.2 V vs. Li/Li⁺, with an emphasis on the effect of “s-SEI” layer. The effect of SEI layer structure and composition on the performance of Li plating/stripping under different modification conditions were discussed in detail. It was found that blocking OSS by applying a narrower potential range (up to 2.2 V vs. Li/Li⁺) resulted in the formation of Li₂O- and Li₂S_x-based s-SEI layers with smaller surface roughness (i.e., less amount of dendritic and dead Li), enabling a more stable Li plating/stripping process. It also demonstrates the possibility of effectively stabilizing Li plating/stripping efficiency even under lean electrolyte conditions. Moreover, purely increasing salt concentration from 0.4 M to 2.0 M is not beneficial to improve the stability of s-SEI layers on the surface under a low-concentration condition due to the unavoidable electrolyte decomposition, while adding 0.1 M LiNO₃ as an additive could result in the formation of Li₂O-based SEI layers - similar as blocking OSS – by blocking the oxidation of Li₂O, to suppress the decomposition of electrolyte as well as ensure an efficient Li plating/stripping. Meanwhile, the effect of increasing to 2.0 M in the existence of 0.1 M LiNO₃ additive shifted the decisive SEI species from Li₂O to LiF, further assuring the enhanced Li plating/stripping performance.

However, in consideration of the gradual consumption of LiNO₃ additive during cycling, the optimization of the LiNO₃:LiTFSI ratio should be further considered to achieve better performances based on the concept of low concentration. Moreover, other countermeasures targeted on up-regulating the composition and morphology caused by s-SEI layer formation process (i.e., OSS), such as additives⁶² and dissolved gases⁵⁹, should also be discussed in the future.

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Chapter 5

Degradation of DME-based Low-concentration Electrolytes during Initial Li Plating/Stripping: Effect of LiNO₃ Co-salt

5.1 Introduction

As a next-generation rechargeable battery, anode-free lithium-metal batteries (AFLMBs) are considered as a potential candidate of lithium-metal batteries (LMBs). The most attractive feature of AFLMBs is the hugely reduced battery's weight and volume to further enhance the energy density.¹ In addition, there is no excess Li and the battery performance is completely dependent on Li plating/stripping efficiency, which will enable a more realistic evaluation of degradation mechanisms. However, the first charging in AFLMBs usually causes large volume expansion. This is because the initial plating of Li produces a "Li-metal anode" on the current collector, which requires an extra space for the battery to accommodate the automatically generated anode. Also, due to this process, the first cycle's behavior is totally different from the follow-up cycles' behaviors. Especially, the higher possibility of inhomogeneous Li plating and dendrite formation, which is greatly dependent on surface morphology of current collector,^{2,3} will decrease the first-cycle Coulombic efficiency (CE) and the realizable energy density, even if the following cycle's efficiency is high.^{4,5} Consequently, the first cycle behavior is very important in AFLMBs studies.

Li nucleation and growth is gradually becoming an important issue in both conventional battery research and in AFLMB research, because the behavior of Li metal during its nucleation and growth will lead to dendrite growth and SEI instability.^{6,7} Meanwhile, electrolyte decomposition (E.D.) process, including the degradation of solvents, lithium salts and additives, is another critical factor that limits the development of AFLMBs. The SEI layer is known to originate from the E.D. products at anode, while the cracking of SEI layer will expose Li metal to electrolyte, in turn facilitating E.D. reactions. In this regard, E.D. is considered highly related to the nucleation and growth behavior of Li metal as well.³ Wu et al. studied the E.D. process on the Li electrode by *in situ* Fourier-transformed IR (FTIR) spectroscopy and *ab initio* molecular dynamics (AIMD).⁸ They investigated the spectra at both OCP and various potentials during Li plating/stripping. Olana et al. reported the SEI species originated from E.D. on both Li and Cu metal surface at the potential ranging from OCP to -0.1 V vs. Li/Li⁺ by using *in situ* DRIFTS (diffuse reflectance infrared Fourier-transformed

spectroscopy).⁹ Both studies adopted LiTFSI salt in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) as the electrolyte with or without LiNO₃ additive. In spite of all the great efforts made, the exact mechanisms in this process have yet to be fully clarified. Moreover, as far as we know there are few studies exclusively focusing on the real-time E.D. process during initial Li plating/stripping (i.e., E.D. over Li plated on Cu).

As a practical countermeasure in electrolyte engineering to address the challenges in E.D., the dual Li-salt electrolytes have been widely used, especially the inorganic-organic Li-salt electrolytes which have shown remarkable enhancements in the SEI properties to suppress further E.D. reactions when compared with single-salt electrolytes.^{10–12} However, the differences upon E.D. process between single and dual Li-salt electrolytes have not yet been sufficiently understood. As one of the candidate salts for the dual-salt electrolyte, LiNO₃ is more commonly used as an inorganic additive in the electrolytes. However, it was found that LiNO₃ suffers from progressive consumption on the Li anode, so the SEI could grow continuously to develop extra thickness after the depletion of LiNO₃. Therefore, it will be of great interest to adopt LiNO₃ as a co-salt in dual-salt electrolytes instead of an additive.¹³ Another significant issue of dual-salt electrolytes is that, they could be surpassed by additives from the aspect of economic feasibility, due to the larger amount required for the second Li salt as a co-salt than as an additive. For this reason, recent studies are inclined to replace the expensive Li salts with inexpensive LiNO₃.¹⁴ The gradual consumption of LiNO₃ in the electrolyte during cycling is mainly due to its low solubility in organic solvent and ease of agglomeration. In fact, the maximum concentration of LiNO₃ single salt dissolved in 1,2-dimethoxyethane (DME) was tested to be *ca.* 0.2 M. Previously, Kang et al. reported the addition of LiFSI to increase the solubility of LiNO₃ in DME solvent, and the LiFSI-LiNO₃ dual-salt electrolyte was successfully prepared with the concentration of LiNO₃ up to 2 M.¹⁵ In contrast, to the best of my knowledge there have been no reports for the LiTFSI-LiNO₃ dual-salt in DME probably due to the difficulty of realizing relatively high concentration like LiFSI-LiNO₃ in DME.

In addition, the separation of E.D. process from pure Li plating/stripping is another challenge but is of great significance in unraveling not only the reaction schemes of electrolyte degradation but also the true CE of Li plating/stripping. According to the “Li-SEI model” proposed by Thirumalraj et al. via the chronoamperometry (CA) method,¹⁶ which is expressed by **Equation 1-4** in Chapter 1, it was noticed that the current of E.D. can be distinguished from the current of Li plating, although physically

these two processes strongly collaborate with each other as also can be found in the sharing of several parameters for $j_{\text{Li}}(t)$ and $j_{\text{E.D.}}(t)$. This indicates that the charge of E.D. can be extracted from the total charge at any step of potential during Li plating or stripping, as long as the time of the step in potential is determined.

Meanwhile, it has been found that comparing with the commonly adopted CV method, the CA method with a short period is more explicit for evaluating complicated electrochemical environment involving E.D. and SEI layer growth, particularly regarding the accuracy of MPE (mass change per mole of e^-) calculation.¹⁷ The purpose of using CA method is to eliminate the influence of scan rate and the ohmic drop in the case of CV method,^{17,18} though it is unlikely that totally different species will be formed on the electrode for different scan rates. Furthermore, the CA method is more compatible with *in situ* techniques which require a long data acquisition time at each step of potential. This kind of CA method is named as “multiple potential step chronoamperometry” (MUSCA) method,¹⁸ and can be coupled with *in situ* spectroscopy like SERS and FT-IRAS. Particularly, by linking MUSCA method with surface mass change recorded by QCM, where the total charges consumed is involved, the E.D.-derived charges and MPE can be isolated, enabling an objective analysis of E.D. process without the averaging by Li plating/stripping (MPE = 7).

In the present study, the two typical organic Li salts, i.e. LiFSI and LiTFSI, were selected as the constituent of the inorganic-organic Li-salt electrolytes, coupled with LiNO₃ co-salt which functioned as the inorganic portion. DME was selected as the solvent, for the purpose of reducing the mechanistic complexity of the target model since DME possesses simpler structure than other commonly used linear ether solvents with longer chain such as diglyme and TEGDME, or the fluorinated ether solvents. Two types of DME-based dual-salt electrolytes with practically low concentration, namely 0.6 M LiFSI + 0.6 M LiNO₃, and 0.6 M LiTFSI + 0.6 M LiNO₃ (total concentration = 1.2 M for a purpose of emphasizing the decomposition from both Li salts and solvent) were used for the investigation on the mechanism of E.D. simultaneously occurring with Li plating/stripping using the Li||Cu half-cell (a model cell to study the anode side of AFLMBs). All salts were confirmed to be completely dissolved without any agglomeration. Two single-salt (1.2 M LiFSI, 1.2 M LiTFSI) electrolytes were also prepared in order to investigate the function of LiNO₃ as the co-salt. For convenience, these electrolytes are hereafter named as “LF”, “LT”, “LFLN” and “LTLN”, where LF, LT and LN are the abbreviation of LiFSI, LiTFSI and LiNO₃, respectively. Cu was used

as the electrode for Li plating/stripping.

First of all, E.D. charge was extracted from total charge at each designated potential during initial Li plating/stripping via MUSCA method and data fitting by the modified “Li-SEI model”. By further cooperating with QCM, the E.D.-derived mass change and $\text{MPE}(E.D.)$ (i.e., an average MPE contributed by all E.D. reactions) was separated. Then, the potential-dependent variation of surface dominant chemical species originating from E.D. was investigated via *in situ* SERS measurements. After that, several possible E.D. reactions were proposed via *in situ* FT-IRAS measurements, and the corresponding E.D. reaction mechanisms were discussed. Finally, based on the potential-dependent change of $\text{MPE}(E.D.)$, the relative amount of dominant chemical species, and the proposed E.D. reaction equations, an “average MPE” (abbreviated as $\alpha\text{-MPE}$), which is related to all possible E.D. reactions generating each surface dominant chemical species, was calculated. Then, according to the MPE of each E.D. reaction and the corresponding $\alpha\text{-MPE}$, the ratio change of each E.D. reaction during initial Li plating was calculated. Overall, the differences between single-salt electrolyte and dual-salt electrolytes with the emphasis on the effect of LiNO_3 were discussed.

5.2 Results and Discussion

5.2.1 Electrochemical Reduction Stability of DME-based Electrolytes

First of all, the first-cycle CV curves of the four DME-based electrolytes in this study are shown in **Figure 5-1(a)**. As can be found, the current density of both the plating and the stripping of Li decreased upon adding LiNO_3 as the co-salt. Meanwhile, the calculated first-cycle CE values for the dual-salt electrolytes (< 50%) were lower than the single-salt electrolytes (> 50%). This is mainly due to the poor solubility of LiNO_3 in DME causing its inferior Li^+ conductivity compared with LiFSI and LiTFSI. **Figure 5-1(b)** shows the CV curves of these electrolytes during the cathodic scanning (negative scanning) prior to initial Li plating/stripping. Totally three reduction peaks were found for each electrolyte. The two peaks at around 1.5 and 1.1 V correspond to the reduction of LiFSI and LiTFSI (REL) and the reduction of copper oxide on the Cu surface (RCO), respectively.¹⁹ The former shows that LiFSI was reduced at more positive potential than LiTFSI. In addition, the formation of “pre-SEI” is identified by the broad reduction peak from 1.0 to 0.2 V (RPS).²⁰

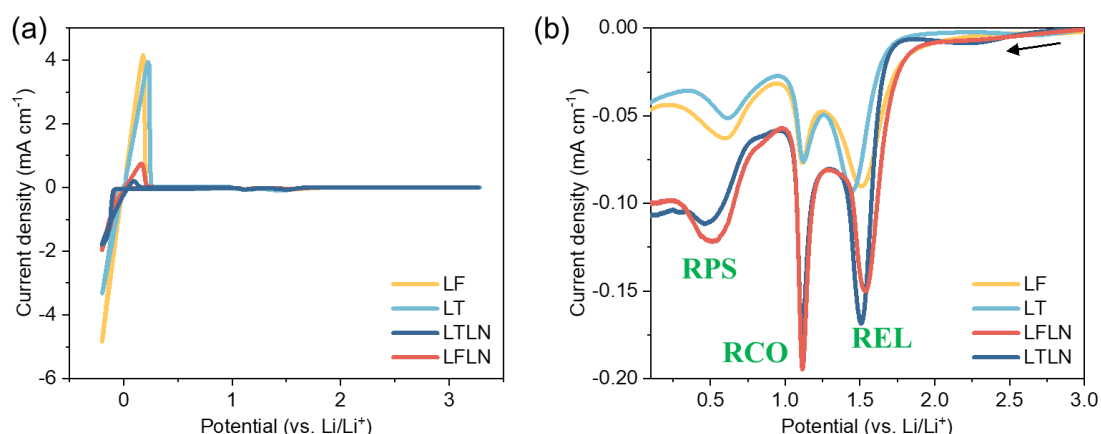


Figure 5-1. Comparison of the first-cycle CV curves among LF, LT, LFLN and LTLN electrolytes: (a) the full-cycle curves; (b) the enlarged view showing the potential range (0 to 3.0 V) prior to Li plating/stripping. Scan rate: 10 mV/s. The arrows indicate the direction of scanning.

Then, the stability of these electrolytes against plated Li metal was confirmed. **Figure 5-2** shows the CV curves of all tested electrolytes during initial Li plating with cathodic scanning. For all electrolytes, the onset potential of Li plating was found to be nearly -70 mV, demonstrating an overpotential of 70 mV to initiate the massive Li plating (i.e., higher number density of Li nuclei) due to a relatively poor lithiophilic property and high energy barrier of pure Cu.^{21,22} A reduction peak (represented by ▲) was found with the peak potential locating at -200 to -300 mV, suggesting an extra reaction along with Li plating. Interestingly, there was a small “shoulder peak” (represented by △) on the positive potential side of the reduction peak, which might indicate another extra reaction taking place. These could correspond to another E.D. reaction and will be further investigated in the following sections. As a comparison, when using TEGDME as the solvent associated with the LiTFSI-LiNO₃ dual salt of the same total Li⁺ concentration (1.2 M), the CV curve did not exhibit any reduction peak by scanning negatively to -500 mV. This result further suggests the existence of reactions related to E.D. during Li plating when using DME as the solvent. These reactions occurred and then reached a steady-state, where the reductive currents were still detected representing the still-going-on Li plating process.

Therefore, in order to discuss the E.D. individually without the influence of Li plating/stripping, QCM tests coupled with MUSCA method were conducted during initial Li plating/stripping (see Chapter 2 for the details in measurement program). In addition, the lower limit of applied potential was set as -200 mV in order to exclusively focus on the E.D.-related reactions parallel by Li plating/stripping.

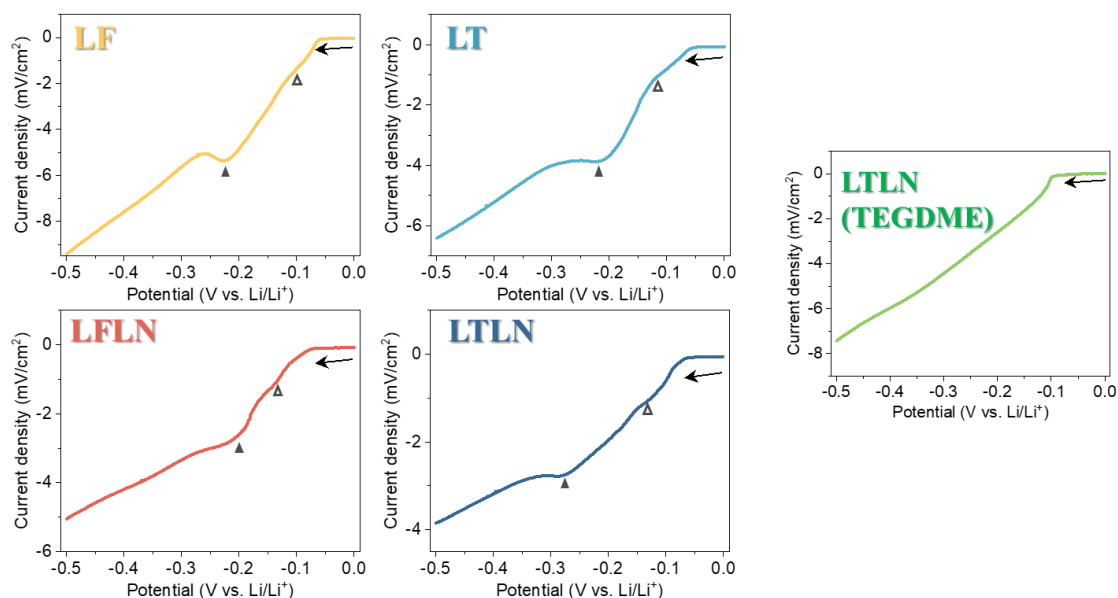


Figure 5-2. Comparison of CV curves during initial Li plating (lower limit of potential: -0.5 V vs. Li/Li⁺) for LF, LT, LFLN and LTLN electrolytes. Scan rate: 10 mV/s. The LTLN dual-salt dissolved in TEGDME solvent was used for comparison. The arrows indicate the direction of scanning. The symbol ▲ and △ indicate the two reduction peaks.

5.2.2 Separation of E.D. Derived Current and Charge during Initial Li Plating/Stripping

Figure 5-3 shows the QCM results in four electrolytes obtained via the MUSCA method. The scanning potential range was set from -10 mV to -200 mV and reversely to 200 mV, with 10 mV as an interval. The holding time was set as 5 seconds for each potential. It should be mentioned that although the simultaneous response of current and mass as a function of potential was recorded, this section only focused on analyzing the behaviors of current, and the behaviors of deposit mass will be discussed in the next section.

From the figure it is clearly seen that the current at each potential exhibited a transient response for all electrolytes, forming a stepwise pattern across the whole plating and stripping process. Then, the current-time (j - t) responses at different applied potentials were analyzed separately.

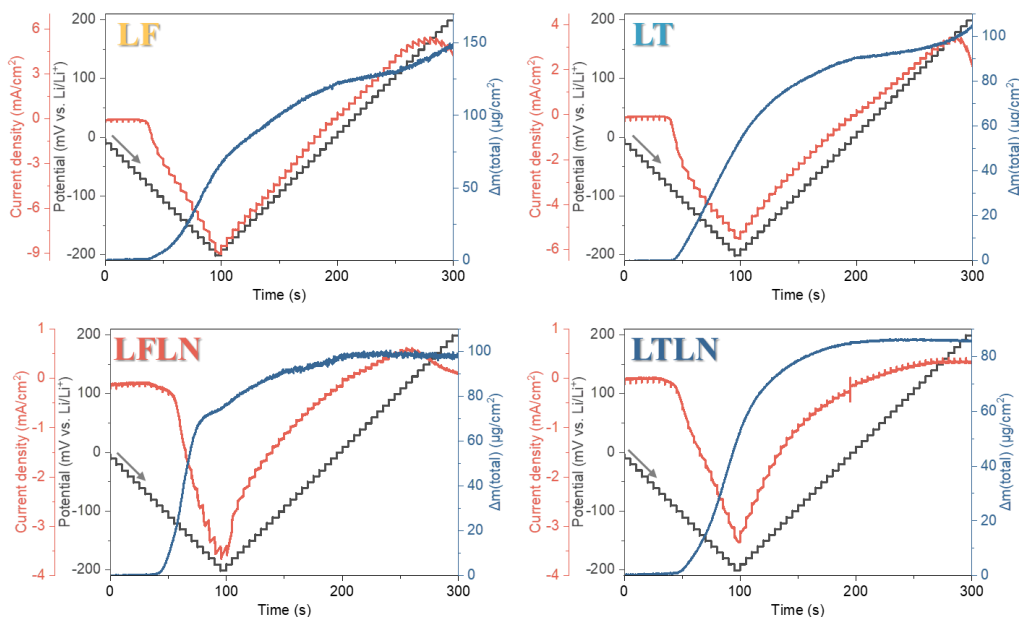


Figure 5-3. The current response and the potential dependence of mass change measured in LF, LT, LFLN and LTLN via the MUSCA method during the initial Li plating/stripping. Totally 60 potentials were stepped, varying from -10 to -200 mV and reversed to 200 mV. The holding time for each potential is 5 seconds. The arrows represent the direction of scanning.

Figure 5-4 shows the j - t curves at several representative potentials isolated from the curves in **Figure 5-3**. These curves were normalized with their starting time set to $t = 0$ to enable a clearer comparison and evaluation of the transient current behaviors at each potential. The current transients increased immediately after the electrode potential was stepped to the next potential, and the spike currents (i.e. the first maximum value of cathodic currents) could be found at all potentials, which is due to the simultaneous occurrence of Li nucleation and the additional SEI (i.e., the SEI layer over deposited Li metal) formation at the electrode-electrolyte interface. It was found that the value of spike currents increased when the applied potential became more negative, and vice versa. The subsequently decrease of currents observed at the potential stepped negatively to -60 mV could be a sign of the evolution of diffusion layers of Li^+ near the surface.^{16,23} As the potential reached more negative than -60 mV, the currents increased again. This could reflect the process of Li growth associated with E.D. in the formed additional SEI.²³ However, a peak of current (i.e. the second maximum value of cathodic currents, marked by ▼) gradually appeared as the potential was applied negatively towards -200 mV in the case of dual-salt electrolytes. In fact, a lot of studies on metal electrodeposition with concurrent reactions (e.g. water reduction) have found the tendency showing that the time of reaching maximum current would be shortened as the metal deposition proceeds more deeply.^{24–27} This study presents a

similar tendency, showing the existence of diffusion limit of DME or anions, although the peak of current can be observed after the potential was more negative than -150 mV under current experimental condition (5 seconds).

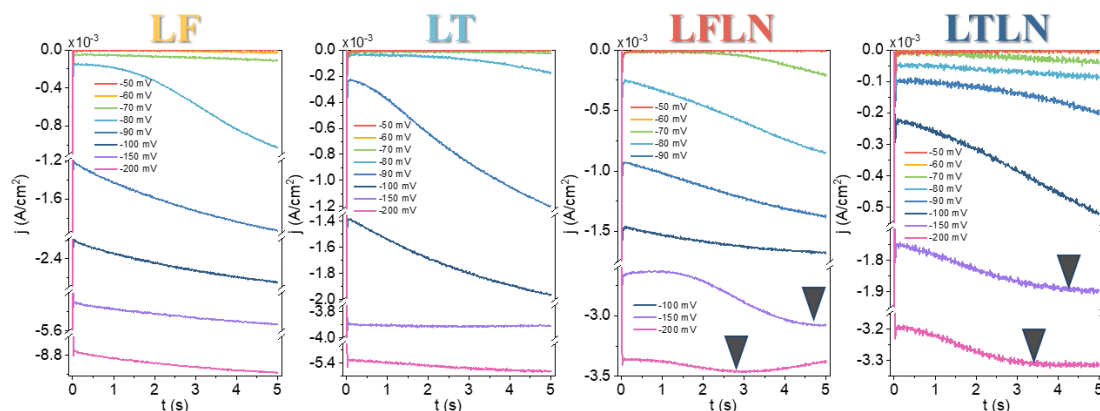


Figure 5-4. Chronoamperometric current-time (j - t) curves over 5 seconds for Li plating at -50 to -100 mV, -150 mV, and -200 mV during cathodic scanning for LF, LT, LFLN and LTLN.

In addition, the Scharifker and Hills (SH) model introduced in Chapter 1 was used to fit the j - t curves. However, a huge upward deviation in the dimensionless plot of experimental current transients from the SH model (either the 3D instantaneous or the 3D progressive nucleation model) was found at all potentials in this study (see **Figure 5-5** for the example potentials in LTLN), which further proves that the severe E.D. has occurred simultaneously with Li plating/stripping. Hence, the “Li-SEI model” was considered for the data fitting in order to separate the current of E.D. from the observed Li plating/stripping process for each j - t curve.

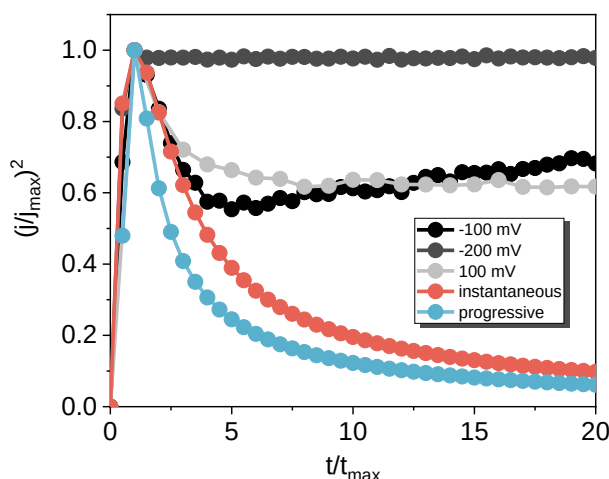


Figure 5-5. Comparison of the dimensionless plot of experimental current transients with the theoretical model of instantaneous nucleation and progressive nucleation at -100 mV, -200 mV, and 100 mV for LTLN. $j_{\max}$ corresponds to the maximum current during Li nucleation.

It should be mentioned beforehand that in the study by Thirumalraj et al.,¹⁶ each target potential was stepped from the same initial potential, ensuring identical initial

conditions (i.e., the Cu electrode covered with pre-SEI layer at 200 mV), and the current response was entirely driven by the overpotential of the target potential. However, for the MUSCA method, each potential was tested based on the changes induced by the previous potential (e.g., SEI formation, lithium deposition, electrode polarization). Since the transient current at previous potential may not have reached a steady state, the transient current at subsequent potential can incorporate the residual process from the previous potential. This means that the current reflects not only the direct response to the target potential but also the “residual effects” of the previous potential.

To include the influence of “residual effect” during data fitting, a modified approach of the “Li-SEI model” was proposed in this study, where the residual currents (defined as the final currents observed at the end of the 5-second step at each previous potential), were incorporated into the “Li-SEI model” as constants. This modification assumes that the residual currents do not follow time-dependent behaviors such as those described by the Cottrell equation. Note that according to **Equation 1-4**, the calculated $j_{total}(t)$ must be positive, so the absolute values of experimentally obtained currents should be taken for the fitting. The modified equation is shown by **Equation 5-1** and **5-2**:

$$j_{total}(t) = j_{Li}(t) + j_{E.D.}(t) = (j_{Li,rel}(t) + j_{Li,res}) + (j_{E.D.,rel}(t) + j_{E.D.,res}) \quad (5-1)$$

$$j_{total}(t) = j_{Li}(t) + j_{E.D.}(t) = (j_{Li,res} - j_{Li,rel}(t)) + (j_{E.D.,res} - j_{E.D.,rel}(t)) \quad (5-2)$$

Where $j_{Li,res}$ and $j_{E.D.,res}$ indicate the residual currents of previous potential, $j_{Li,rel}(t)$ and $j_{E.D.,rel}(t)$ indicate the currents relative to $j_{Li,res}$ and $j_{E.D.,res}$, respectively. **Equation 5-1** or **Equation 5-2** are applied when the absolute current at present potential is larger or smaller than that at previous potential, respectively.

Figure 5-6 shows the examples of the nonlinear curve fitting results with the modified “Li-SEI model” at several potentials using LTLN as an example electrolyte. The accuracy of fitting results reached over 90% at all potentials, showing the rationality of the modified equation. From the best fitting of experimental data, $j_{Li}(t)$ and $j_{E.D.}(t)$ were obtained and plotted. Based on these simulated current transient, the corresponding charges transferred over the 5 seconds potential holding at each potential were calculated as a result of current integration (as illustrated in **Figure 5-6**). Consequently, the E.D. charge within 5 seconds ($Q_{5s}(E.D.)$) can be obtained as the function of potential during initial Li plating/stripping, which was subsequently used to extract the E.D.-derived mass change in the next section.

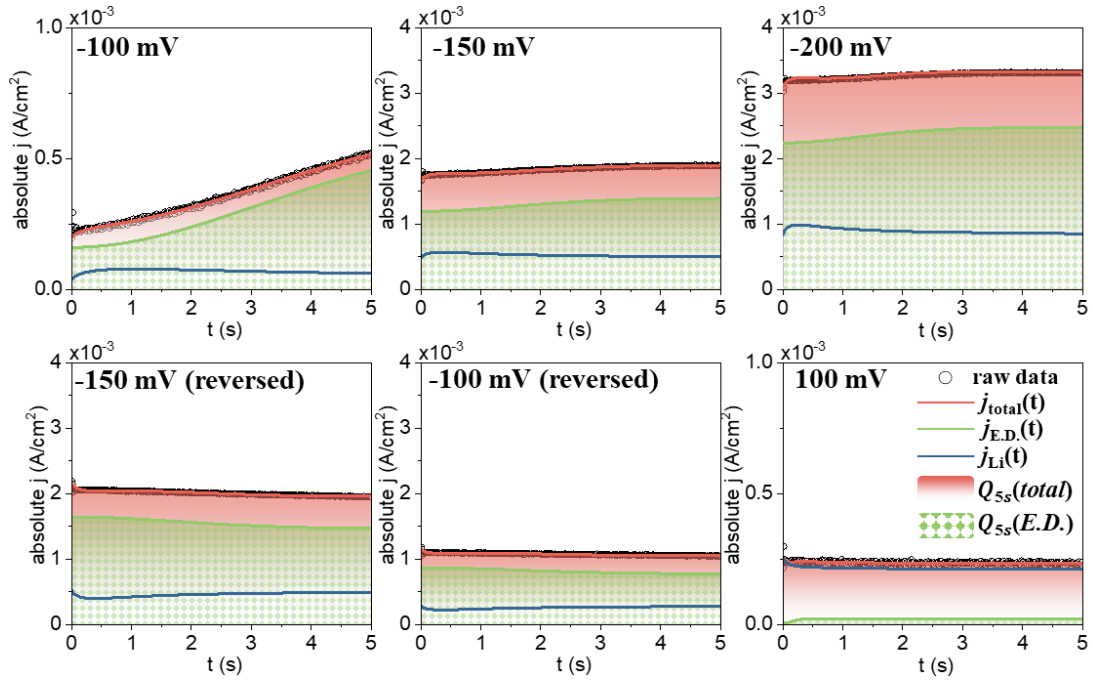


Figure 5-6. Nonlinear curve fitting results of experimental current transients during Li plating at -100, -150, -200, -150 (reversed), -100 (reversed) and Li stripping at 100 mV for LTLN. The corresponding theoretical current transients $j_{Li}(t)$ and $j_{E.D.}(t)$ obtained from the fitting were also plotted for comparative analyses. The total charge and the charge of E.D. over 5 seconds were illustrated as the filled area under the curves.

5.2.3 Separation of E.D. Derived Mass Change and MPE during Initial Li Plating/Stripping

As **Figure 5-3** in Section 5.2.2 shows, the change of mass by applying step potential was successfully obtained by QCM. It was found that the surface mass increased smoothly regardless of the step potential. Moreover, a massive growth of mass was in step with the increase of current density at overpotential of -70 mV. From Li stripping, mass kept increasing for the single-salt electrolytes due to the E.D. process that produced additional deposition. On the contrary, a subtle decrease of mass was noticed regarding the dual-salt electrolytes. In terms of the underlying reason, although the low stripping current accounts for the limited amount of Li that was stripped away, the simultaneous E.D. process may have also contributed to additional deposits that offset the decreased Li mass.

In order to obtain $MPE(E.D.)$, mass change from E.D. ($\Delta m(E.D.)$) was calculated based on the overall mass change ($\Delta m(total)$), and the calculated $Q_{5s}(total)$ and $Q_{5s}(E.D.)$. To be more specific, the following **Equation 5-3** can be used:

$$\Delta m(E.D.) = \Delta m(total) - \Delta m(Li) = \Delta m(total) - \frac{MPE(Li) * [Q(total) - Q(E.D.)]}{F} \quad (5-3)$$

Where $MPE(Li)$ equals to 7 during Li plating and -7 during Li stripping. The calculated $\Delta m(E.D.)$ can be either positive or negative, indicating an increase or decrease in mass due to the E.D. process, respectively.

Upon obtaining $\Delta m(E.D.)$, the Δm -charge curves of E.D. were plotted for all electrolytes and were compared with the Δm -charge curves of the overall process that were obtained experimentally (**Figure 5-7**). The $MPE(E.D.)$ and $MPE(total)$ (i.e., an average MPE of the overall process, which contains the information about $MPE(E.D.)$ and $MPE(Li)$) were obtained by taking the first-order derivative of the Δm -charge curves from the overall process and from E.D., respectively. All curves were divided into three regions, namely Li plating (cathodic scanning), Li plating (anodic scanning), and Li stripping, for explicitly distinguishing $MPE(E.D.)$ from $MPE(total)$. As shown in **Figure 5-7**, for all electrolytes, both $MPE(total)$ and $MPE(E.D.)$ during the initial Li plating continuously decreased with cathodic scanning, which became nearly constant from anodic scanning. From Li stripping, the nearly constant MPE values were also confirmed.

Moreover, by comparing dual-salt electrolytes (LFLN and LTLN) with single-salt electrolytes (LF and LT) more carefully, the following differences can be found:

1. A significantly larger MPE for the whole Li plating process can be observed in the dual-salt electrolytes;
2. An obvious difference lay in the Li stripping process, in which the $MPE(total)$ for the single-salt electrolytes kept increasing, whereas the $MPE(total)$ decreased for the dual-salt electrolytes;
3. Regarding the $MPE(E.D.)$ values between Li plating (anodic scanning) and Li stripping, the same values were found for single-salt electrolytes, while large differences were found for dual-salt electrolytes.

The above results indicate that more than one reductive E.D. reactions occurred during Li plating with cathodic scanning, and the addition of $LiNO_3$ (i.e., dual-salt electrolytes) resulted in the generation of some components that largely enhanced the $MPE(E.D.)$ as an apparent average value. However, several reductive E.D. reactions gradually stopped, then from anodic scanning there should be only one reductive E.D. reaction. From Li stripping, for single-salt electrolytes the same reductive E.D. reaction continued, while for dual-salt electrolytes, the remaining reductive E.D. reaction should

be accompanied by at least one oxidative E.D. reaction, which was apparently due to the addition of LiNO_3 as a co-salt. For convenience, the above statements are summarized in **Table 5-1**.

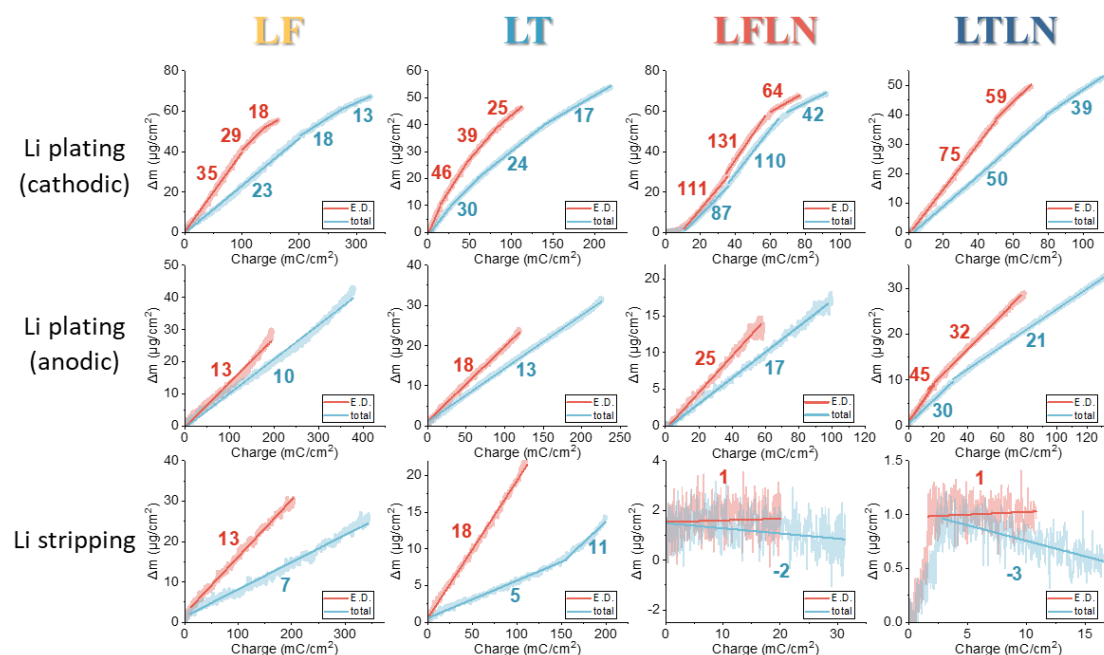


Figure 5-7. Summary of MPE(*total*) and MPE(*E.D.*) from the Δm -charge curves in the three regions during initial Li plating/stripping for LF, LT, LFLN and LTLN electrolytes. The positive and negative MPE indicate the growth and the loss of mass, respectively. The selected MPE values are marked besides the curves.

Table 5-1. Summary of the number and type of E.D. reactions involved in the initial Li plating/stripping process.

Process	E.D. reactions	
	Single-salt electrolytes (LF, LT)	Dual-salt electrolytes (LFLN, LTLN)
Li plating (cathodic)	> one <i>Re.</i>	> one <i>Re.</i>
Li plating (anodic)	one <i>Re.</i>	one <i>Re.</i>
Li stripping	one <i>Re.</i>	one <i>Re.</i> , $\geq$ one <i>Ox.</i>

Re. and *Ox.* represent reductive reaction(s) and oxidative reaction(s), respectively.

5.2.4 Detection of E.D. Species Deposited on Electrode Surface

It should be noted that the MPE(*E.D.*) values shown in **Figure 5-7** are all average values without considering the individual contribution of all possible reactions at each step of potential. To conduct the analysis of potential-dependent E.D. reaction mechanisms in more detail, including the influence of LiNO_3 in the change of MPE(*E.D.*), *in situ* spectroscopic analysis should be conducted. In this section, the potential-dependent compositional changes were investigated by *in situ* SERS.

As shown in **Figure 5-8**, in total 16 potentials during initial Li plating/stripping process were selected for taking the spectra. In regard to the single-salt electrolytes, except for the peaks being confirmed as the vibrations of chemisorbed electrolyte molecules, Li_2O , Li_2CO_3 and Li_2C_2 (lithium carbide), as newly generated chemical species, were detected on the surface,^{28–30} while the variation of their intensities were dependent on the applied potential. This indicates that reactions involving Li_2O , Li_2CO_3 and Li_2C_2 should be the major constituent of E.D. during the initial Li plating/stripping.

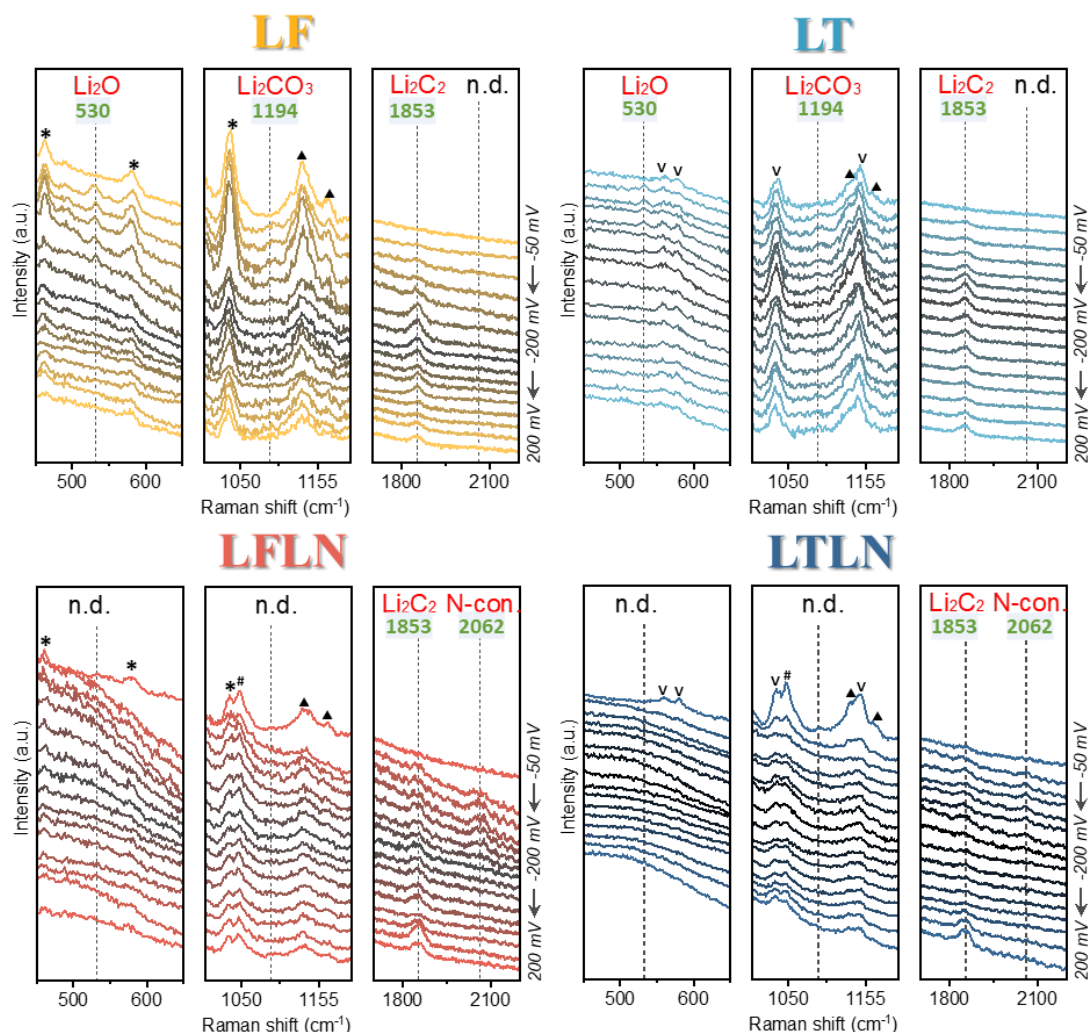


Figure 5-8. Potential-dependent SERS peak variation during initial Li plating/stripping for LF, LT, LFLN and LTLN electrolytes in 450 to 650 cm^{-1} , 1000 to 1200 cm^{-1} , and 1700 to 2200 cm^{-1} regions. The numbers correspond to the Raman shift of the detected chemical species, and “n.d.” is the abbreviation of “not detected”. The symbols *, V, ▲, and # represent vibrational mode from FSI^- , TFSI^- , DME and LiNO_3 , respectively. “N-con.” represents N-containing species.

In the case of dual-salt electrolytes, only two peaks assigned to Li_2C_2 and the species containing nitrogen element (the “N-containing” species) were detected, demonstrating different dominant species during E.D. process for the dual-salt electrolytes compared with single-salt electrolytes. The N-containing species with the

SERS band around 2062 cm^{-1} are mainly constructed by the chemical bonds formed by N atoms and C/O atoms, which may include $\nu_a(\text{C}\equiv\text{N})$, $\nu_a(\text{C}=\text{C}=\text{N})$, $\nu_s(\text{C}\equiv\text{C}-\text{N})$, $\nu_a(\text{O}-\text{C}\equiv\text{N})$, $\nu_s(\text{N}-\text{O})$, etc.^{31–34} Meanwhile, these two peaks were also detected in the LiNO_3 single-salt electrolyte (**Figure 5-9**), proving that Li_2C_2 was from the reduction of DME solvent molecules,³⁵ and the N-containing species came entirely from the interaction of LiNO_3 decomposition products with DME solvent. These observations suggest that in the existence of LiNO_3 , two sets of reactions generating Li_2C_2 and N-containing species, respectively, predominated the E.D. process.

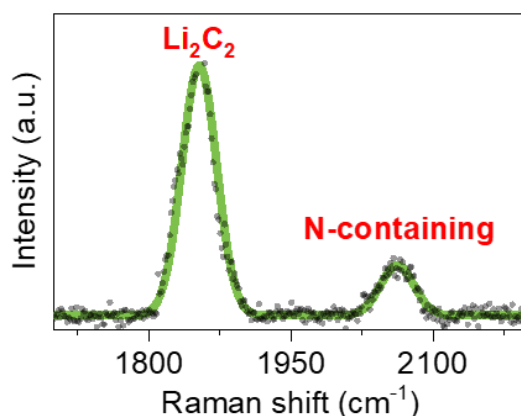


Figure 5-9. SERS of 0.1 M LiNO_3 in DME in the range of 1700 to 2200 cm^{-1} . Potential: -0.1 V vs. Li/Li^+ . The black dots stand for the original spectra data of samples.

If the observed mass change did not originate from factors other than chemical (electrochemical) reactions, then the potential-dependent variation of peak intensity ratio (i.e., relative amounts of chemical species with respect to a selected reference species, which is Li_2C_2 in this study) and $\text{MPE}(E.D.)$ should exhibit similar tendency. Hence, the integrated SERS peak intensities of the chemical species detected using different electrolytes as a function of applied potential were obtained by peak fitting, which will be used to calculate the relative amounts of respective species. Regarding the peak fitting of Li_2O (530 cm^{-1}) and Li_2CO_3 (1194 cm^{-1}), due to the overlap by other peaks with stronger intensity, the full width at half maximum (FWHM) of these peaks investigated in previous works was referred during fitting to ensure the fitting accuracy.^{36,37} The fitted peaks of all electrolytes are shown in **Figure 5-10**. The existence of Li_2C_2 was found at almost all potentials, and basically its peak intensity increased as potential became more negative.²⁸ On the contrary, Li_2O , Li_2CO_3 , and N-containing species only appeared at the initial stage of Li plating. In view of the abovementioned MPE variations for each electrolyte, it can be concluded that the progressive disappearance of Li_2O , Li_2CO_3 , and N-containing species on the surface directly caused the drop of $\text{MPE}(E.D.)$ during Li plating with cathodic scanning.

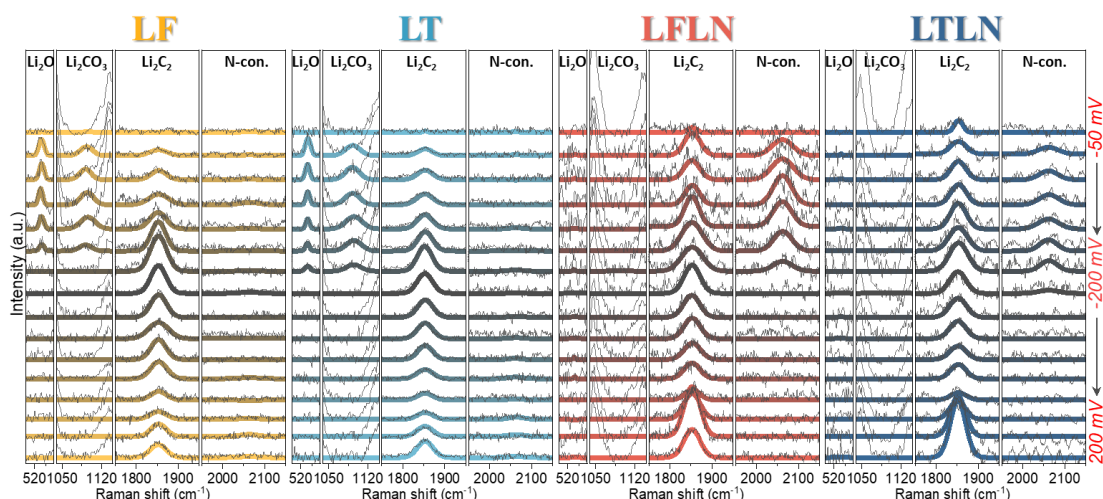


Figure 5-10. Fitting of the peaks of Li_2O , Li_2CO_3 , Li_2C_2 and N-containing species for LF, LT, LFLN and LTLN during initial Li plating/stripping. “N-con.” represents N-containing species. The gray curves stand for the original spectra data of samples.

Next, the integrated SERS peak intensities were plotted as a function of applied potential, as shown in **Figure 5-11**. It can be clearly confirmed that the sum of integrated SERS peak intensities had the same variation tendency as $Q_{5s}(E.D.)$ (obtained in Section 5.2.2) did as a function of potential. This further proves that the reactions producing the above species (Li_2O , Li_2CO_3 , Li_2C_2 , N-containing) are the dominant E.D. reactions.

Furthermore, now it becomes clear that the aforementioned reductive E.D. reaction that existed during the entire Li plating/stripping process (**Table 5-1**) is related to the formation of Li_2C_2 . That is to say, the α -MPE values of the reaction(s) generating Li_2C_2 , named as “MPE(Li_2C_2)”, are therefore directly reflected by the MPE(E.D.) during Li plating with anodic scanning (**Figure 5-7**), which turns out to be 13, 18, 25 and 32 for LF, LT, LFLN and LTLN, respectively. Moreover, it is noticeable that the MPE(Li_2C_2) values among four electrolytes are all different, which indicates that in the reaction(s) producing Li_2C_2 , there must be other reactants and/or products with different molecular weights among four electrolytes. Specifically, the MPE(Li_2C_2) values demonstrated two tendencies:

1. They are larger in electrolytes containing LiTFSI, i.e., LTLN(=32) > LFLN(=25), LT(=18) > LF(=13). This should correlate with the difference in their final products;
 2. They are larger in dual-salt electrolytes, i.e., LFLN(=25) > LF(=13), LTLN(=32) > LT(=18). This suggests that LiNO_3 can affect Li_2C_2 formation process.
- More details of these will be revealed by FT-IRAS studies in the next section.

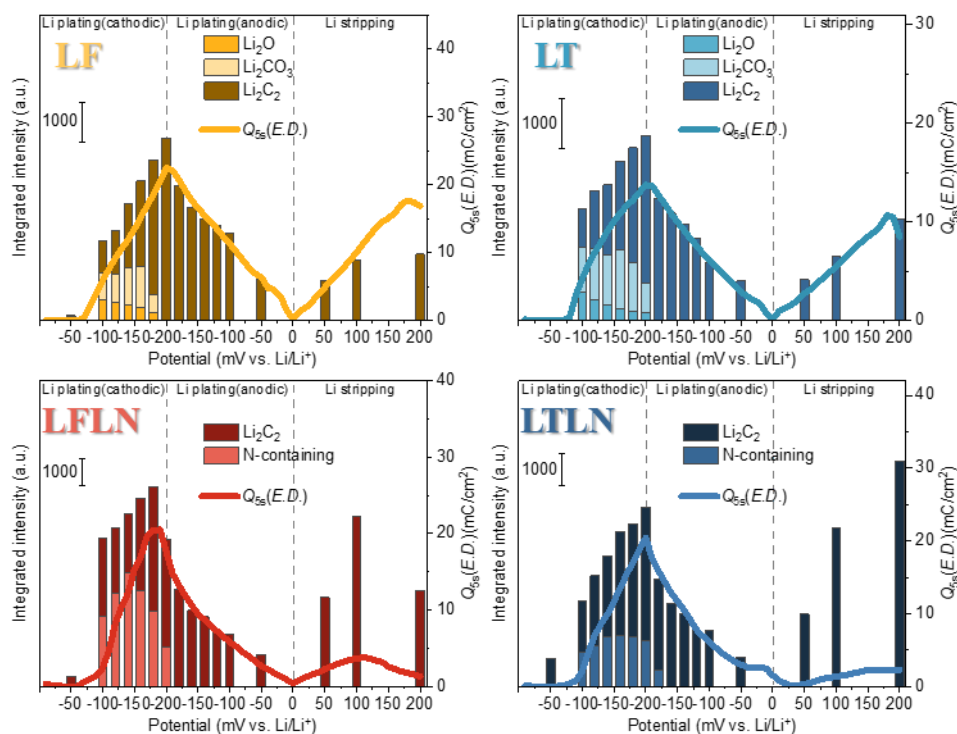


Figure 5-11. Integrated SERS peak intensities and $Q_{55}(E.D.)$ as the function of applied potential for LF, LT, LFLN and LTLN electrolytes. The histogram corresponds to the integrated intensity, and the curve corresponds to $Q_{55}(E.D.)$.

5.2.5 Prediction of Possible E.D. Reactions

In order to support the findings of *in situ* SERS and to further clarify the E.D. mechanisms during initial Li plating/stripping, *in situ* FT-IRAS measurements were carried out.

5.2.5.1 DME decomposition

First of all, recall that the existence of Li_2C_2 was confirmed by SERS. In this section, Li_2C_2 was also found by FT-IRAS in all electrolytes, as indicated by the upward peak of $\text{C}\equiv\text{C}$ bond vibration at 2170 cm^{-1} (**Figure 5-12(a)**). Besides, several downward peaks were found, including the peaks at 1270 to 1290 cm^{-1} (CH_2 twist) and the peaks at 1450 to 1470 cm^{-1} (CH_3 asymmetric deformation, CH_2 scissor) (**Figure 5-12(b)**). Most of them are known to come from the characteristic vibration modes of DME molecules, showing the decrease of DME molecules on the surface.^{38–40}

Additionally, two upward peaks at 2730 and 2710 cm^{-1} were found and assigned to $\nu_a(\text{C-H})$ and $\nu_s(\text{C-H})$ of ROLi (R is the alkyl group with low molecular weight), respectively (**Figure 5-12(c)**).^{9,41,42} In fact, ROLi is most commonly found in the SEI formed in ether electrolytes, and has been proved to be the major degradation product

of DME as well.^{43–45} In general, ROLi is soluble when R is a bulkier group than CH₃,^{46,47} and CH₃OLi is thought to be less soluble. Therefore, these two peaks were attributed to the formation of CH₃OLi. By taking the absorbance of the vibrations from DME, Li₂C₂ and CH₃OLi, it can be found that they showed same potential-dependence for all electrolytes (**Figure 5-12(d)**). This shows that they are from the same reaction, that is, Li₂C₂ and CH₃OLi were produced from DME decomposition.

It has been reported that one pathway of DME decomposition can proceed by consuming 4e[−] to generate two CH₃OLi and one Li₂C₂H₄.⁴⁴ Based on this, Li₂C₂ could come from the further reduction of Li₂C₂H₄ which requires extra 4e[−]. Hence, a two-step 8e[−]-transferred reaction can be proposed (**Reaction (5-1)**, where and hereafter the wavy lines indicate the cleavage of chemical bond) by considering the favorable decomposition pathway of DME, i.e. the C–O bond cleavage under Li attack, where C is from the ethane group in the middle of DME structure.⁴⁴ Note that H₂ gas might be generated during the reduction of DME, while it will readily react with deposited Li metal to produce LiH, which was dissolved in polar organic solvents including DME.^{48,49}

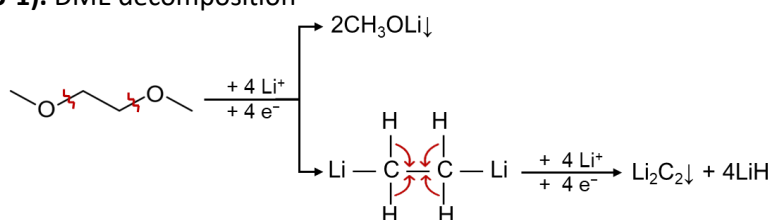
The MPE of **Reaction (5-1)** was calculated to be 14. However, given that the MPE(Li₂C₂) values for the four electrolytes (13 for LF, 18 for LT, 25 for LFLN, and 32 for LTLN) were all different from 14, there should be at least one additional reaction that meets all the following conditions:

1. Parallel with **Reaction (5-1)**;
2. Involving DME as reactant and generating Li₂C₂ as the major product;
3. Possessing MPE different from the MPE(Li₂C₂) of the four electrolytes:
 - for LF, it is not larger than 13;
 - for LT, LFLN and LTLN, it is not smaller than 18, 25 and 32, respectively.

Such kind of additional reaction could be the interaction between the fragments from the LiFSI/LiTFSI decomposition and the DME molecule,^{44,50–52} which will be discussed in more details below. In addition, this also strongly suggests that, during Li plating with anodic scanning, the “only one reductive E.D. reaction” (as described in **Table 5-1**) should be regarded as “a set of parallel reductive E.D. reactions”. This ultimately results in a consistent observed MPE(E.D.) (practically, MPE(Li₂C₂) under this circumstance) value as well.

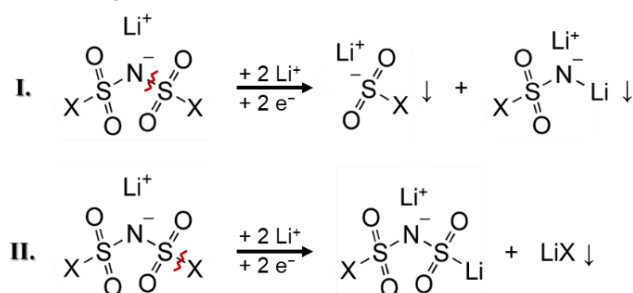
Reaction (5-1). DME decomposition

(MPE = 14)

**5.2.5.2 LiFSI/LiTFSI decomposition, and the interaction with DME**

As discussed above, LiFSI/LiTFSI may also participate in the generation of Li_2C_2 . This can be strongly associated with the decomposition behavior of LiFSI and LiTFSI. In fact, the decomposition steps of LiFSI and LiTFSI have been studied by several researchers.^{44,50,53,54} Ideally, FSI^- and TFSI^- have two possible first-step reductive decomposition routes, as illustrated in **Scheme 5-1**. Note that the species formed via either route I or route II are all insoluble, and can undergo further reduction to more inorganic compounds (except for LiX , where X represents F or CF_3 as used hereafter).⁴¹

Scheme 5-1. Two possible first-step reduction routes of FSI^- and TFSI^- anions: **I.** N-S bond cleavage to form LiSO_2X and $\text{Li}_2\text{NSO}_2\text{X}$; **II.** S-F/S-C bond cleavage to form $\text{Li}_2\text{SO}_2\text{NSO}_2\text{X}$ and LiX . Here, -X stands for -F or $-\text{CF}_3$.



In this section, FT-IRAS spectra related to LiFSI/LiTFSI decomposition were carefully examined. This process is first demonstrated by the downward peak between 1320 and 1440 cm^{-1} relative to OCP (**Figure 5-12(b)**) was confirmed as $\nu_a(\text{SO}_2)$. This corresponds to the cleavage of $\text{O}=\text{S}=\text{O}$ in bond FSI^- and TFSI^- anions, which is a typical step during LiFSI/LiTFSI decomposition.^{55,56} This observation also indicates that FSI^- and TFSI^- at OCP have formed a certain aggregation near electrode surface or an adsorption layer on the electrode, and the changes in their chemical state, such as $\text{O}=\text{S}=\text{O}$ bond cleavage, will lead to the downward peaks. Note that although the vibrations of S-N-S, S-F and S-C bonds (all under 1000 cm^{-1}) were unable to be identified by IRAS due to the limitation of CaF_2 prism adopted in this study, their cleavage during scanning can be confirmed by the gradual decreasing SERS intensity

of the S–N–S and S–F bonds in LF and LFLN, as well as the S–N–S and S–C bonds in LT and LTLN (**Figure 5-13**). Combining the observed O=S=O bond cleavage, this indicates that the decomposition of LiFSI/LiTFSI proceeded thoroughly over Li metal, which is in consistent with the previous report.⁴³

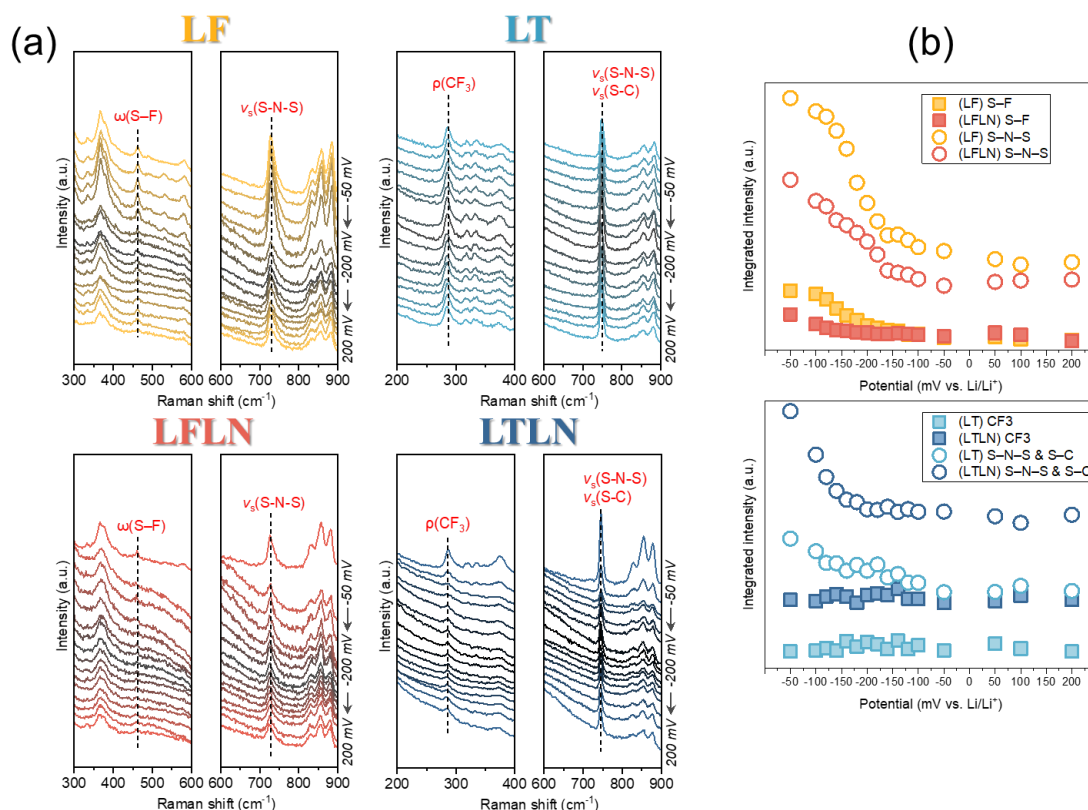


Figure 5-13. (a) Potential-dependent SERS peak variation during initial Li plating/stripping for the S–N–S and S–F bonds in LF and LFLN, as well as the S–N–S and S–C bonds in LT and LTLN. ω : wagging, ρ : rocking; (b) The summary of the potential-dependent integrated peak intensity of each bond.

To more intuitively elaborate the mechanism, the potential-dependent absorbance variation of $\nu_a(\text{SO}_2)$ based on the spectra relative to the spectra at “every previous potential” (instead of OCP) was examined, and the results are shown in **Figure 5-14**. For all electrolytes, the amounts of SO_2 -containing species on the surface decreased as the Li plating started, which can be attributed to either or both of the following reasons:

1. The massive reduction of SO_2 -containing species into smaller inorganics like Li_2S via O=S=O bond cleavage;
2. The coordination of SO_2 -containing species with the fragments of decomposed DME that generated soluble SO_2 -containing species and diffused away from surface.⁵⁰

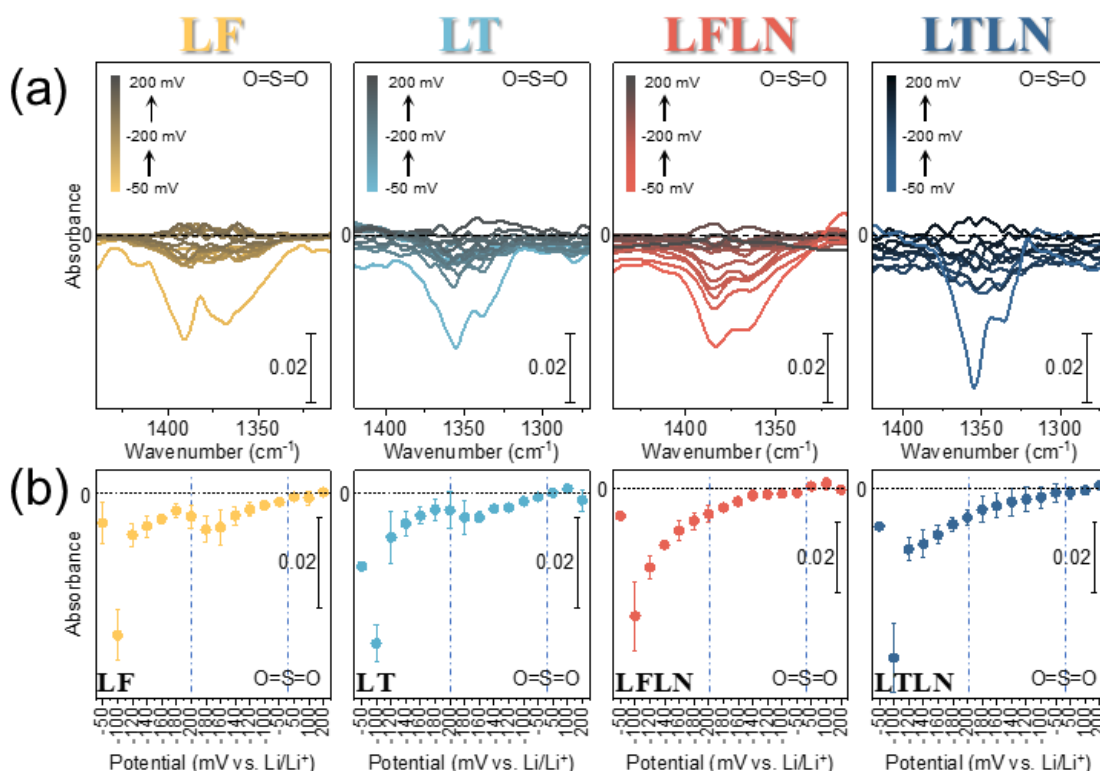
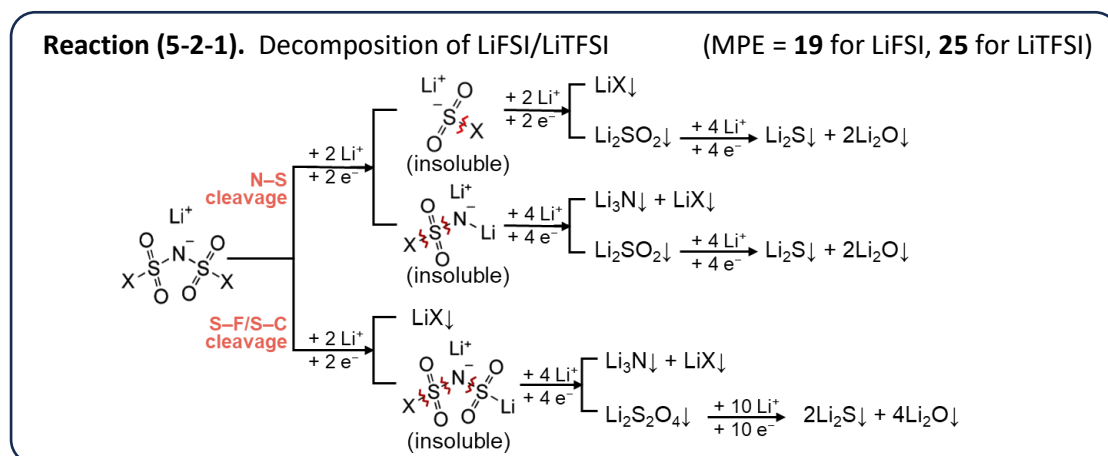


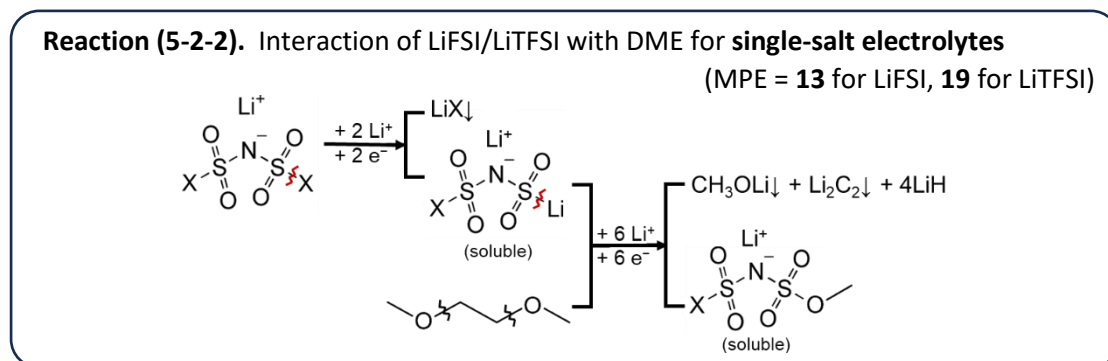
Figure 5-14. (a) FT-IRAS spectra of $\nu_a(\text{SO}_2)$ for LF, LT, LFLN and LTLN electrolytes. The absorbance at each step of potential was obtained by taking the IR beam intensity at the previous potential as the reference; (b) The potential-dependent absorbance variation of $\nu_a(\text{SO}_2)$ at 1385 cm^{-1} from FSI^- and at 1358 cm^{-1} from TFSI^- . The vertical dashed-dotted lines divide the potential range into three regions: Li plating (cathodic), Li plating (anodic) and Li stripping. The negative absorbance indicates the decreased SO_2 -containing species compared to the previous potential. The error bar was shown based on replicated experiments.

Furthermore, regarding single-salt electrolytes LF/LT it is noticeable that, the SERS integrated intensity of Li_2O behaves similarly as the absorbance of SO_2 -containing species during Li plating with cathodic scan (see **Figure 5-8** and **Figure 5-14(b)**). It is well known that Li_2O is one of the final products from the decomposition of $\text{LiFSI}/\text{LiTFSI}$ that can occur on the plated Li metal.^{43,56} Based on this, it can be concluded that the insoluble intermediate fragments from route I and II in **Scheme 5-1** can serve as the reactants of the further reduction to generate Li_2O via $\text{O}=\text{S}=\text{O}$ bond cleavage during Li plating. Moreover, although it was previously reported that the CF_3 fragment from TFSI^- could be further reduced,⁴⁴ the unchanged SERS intensity of CF_3 band in **Figure 5-13** demonstrates that CF_3 fragment was not reduced any further. Therefore, **Reaction (5-2-1)** was proposed as a complete process of both route I and II. Either complete process can be expressed by a 16e^- -transferred reaction, where the undissolved portion of $\text{Li}(\text{XSO}_2\text{NSO}_2\text{Li})$ works as an intermediate,⁴³ and the corresponding MPE equals to 19 and 25 for LiFSI and LiTFSI , respectively. Despite complex reaction mechanisms, the major deposited products except for Li_2O have been

confirmed by other researchers as LiF, LiCF₃, Li₃N, Li₂S, Li₂SO₂, Li₂S₂O₄, etc.,^{43,57} although they were not detected by SERS in this study due to the overlapped peaks from chemisorbed electrolyte molecules.



Notably, a “turning point” was found around -200 mV for LF/LT (**Figure 5-14(b)**). This is related to the SERS result that Li₂O only appeared in LF/LT, which disappeared around -200 mV during cathodic scanning (**Figure 5-10**). This result implies that the disappearance of Li₂O is a sign of the cease of **Reaction (5-2-1)**. However, it is noticeable that SO₂-containing species still decreased after the disappearance of Li₂O. This is because that only a fraction of Li(XSO₂NSO₂Li) intermediate is insoluble and continues to reduce to inorganic products including Li₂O, whereas the other fraction is dissolved and reacts with DME solvent (Li atom is replaced by -OCH₃ fragment from DME), as shown in **Reaction (5-2-2)**.⁵⁰ The whole process demonstrates the substitution of one -X by -OCH₃, generating Li(XSO₂NSO₂OCH₃) as a more soluble product, which can diffuse away from surface and reduce the surface concentration of SO₂-containing species. This can be further supported by the diverse MPE(Li₂C₂) in four electrolytes, which cannot be explained only by **Reaction (5-1)**. Hence, **Reaction (5-2-2)** must have occurred to trigger Li₂C₂ formation.



In terms of dual-salt electrolytes LFLN/LTLN, given that the amounts of SO₂-containing species decreased (**Figure 5-14(b)**) but Li₂O was not found as the final product (the SERS results, see **Figure 5-10**), such a decrease was apparently not due to the cleavage of O=S=O. Note that there is another possibility that **Reaction (5-2-1)** eventually produced SO₂-containing intermediates (i.e., Li₂SO₂ or Li₂S₂O₄) instead of Li₂O as the final deposits. However, since SERS analysis (**Figure 5-11**) has pointed out that reactions generating the species detected by SERS are the dominant E.D. reactions, it is believed that **Reaction (5-2-1)** did not produce Li₂SO₂ or Li₂S₂O₄ in the case of LFLN/LTLN, instead, it was suppressed in the presence of LiNO₃. On this occasion, **Reaction (5-2-2)** should apparently occur to reduce the overall SO₂-containing fragments on the surface.

Interestingly, IRAS also confirmed the formation of CH₃OSO₂R-like component (R can be Li or a functional group) through the upward peak near 1200 to 1220 cm⁻¹ (O=S=O vibration from RSO₂R') for LFLN/LTLN (**Figure 5-15(a)**),^{8,58} which is an evidence of the interaction between Li salts and DME. Regarding LF/LT, the fact that the CH₃OSO₂R-like component was not detected further proves the dissolution of SO₂-containing products from **Reaction (5-2-2)**. In the meantime, it can explain the larger MPE(Li₂C₂) for LFLN/LTLN since the CH₃OSO₂R-like deposit may form together with Li₂C₂ and cause a substantial mass growth. Note that the CH₃OSO₂R-like molecule contains O=S=O with the electron-donating –OCH₃ group attaching on the S atom, which can weaken the double-bond strength and therefore reduce the vibration frequency of O=S=O bond. As a result, the absorbance of O=S=O for the dual-salt electrolytes decreased, and the absorbance of CH₃OSO₂R increased accordingly, as indicated in **Figure 5-15(b)**.

On this basis, **Reaction (5-2-2)** was extended for dual-salt electrolytes: Initially, Li(XSO₂NSO₂OCH₃) was formed as an intermediate due to the S–F/S–C cleavage and the subsequent substitution of one –X by –OCH₃, which is same as in the case of LF/LT. In the presence of LiNO₃, however, the other –X could be further substituted by –OCH₃ in the same manner, generating Li(CH₃OSO₂NSO₂OCH₃) as the final deposit.

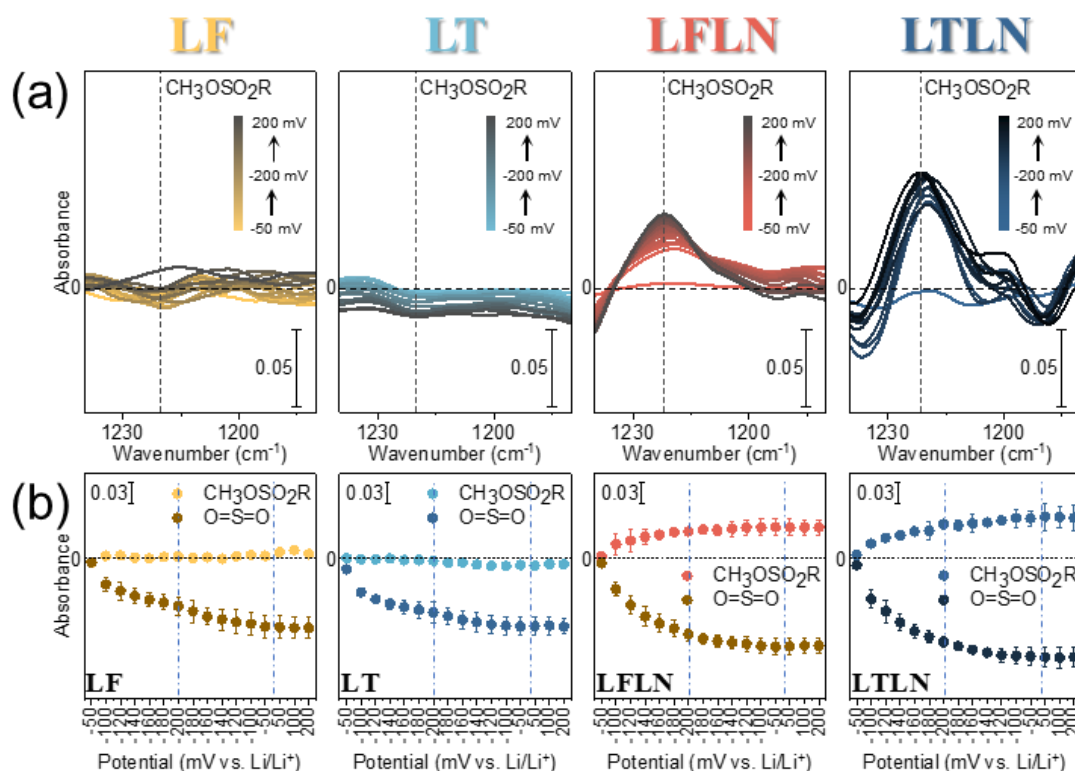
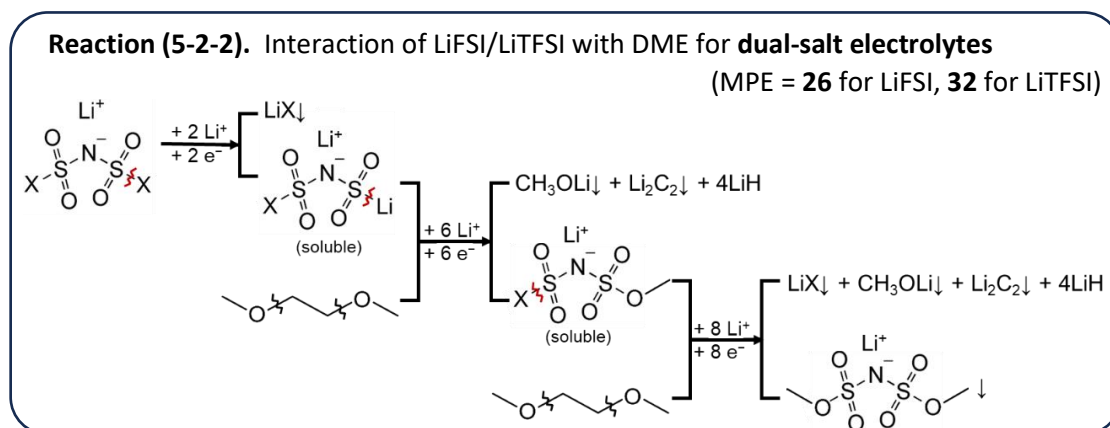


Figure 5-15. (a) FT-IRAS spectra of $\nu(\text{RSO}_2\text{R}')$ from $\text{CH}_3\text{OSO}_2\text{R}$ -like components for LF, LT, LFLN and LTLN electrolytes. The absorbance at each step of potential was obtained by taking the IR beam intensity at OCP as the reference; (b) The potential-dependent absorbance variation of $\nu(\text{RSO}_2\text{R}')$ and $\nu_a(\text{SO}_2)$. The vertical dashed-dotted lines divide the potential range into three regions: Li plating (cathodic), Li plating (anodic) and Li stripping. The negative absorbance indicates the decreased amounts of corresponding species compared to OCP. The error bar was shown based on replicated experiments.



The reliability of **Reaction (5-2-2)** for dual-salt electrolytes can be supported by the red-shift of the SERS bands related to S–F bond from FSI^- , S–C bond from TFSI^- , and C–O–C bond from DME, comparing to single-salt electrolytes (**Figure 5-16**). This shows that these bonds are more easily broken in the presence of LiNO_3 , thereby promoting the interaction between LiFSI/LiTFSI and DME.

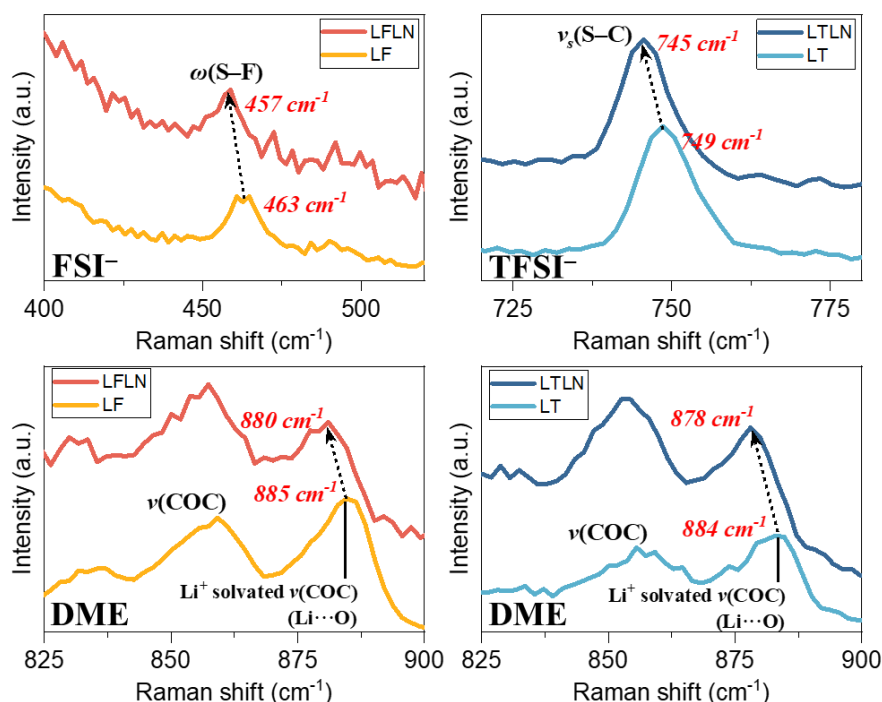
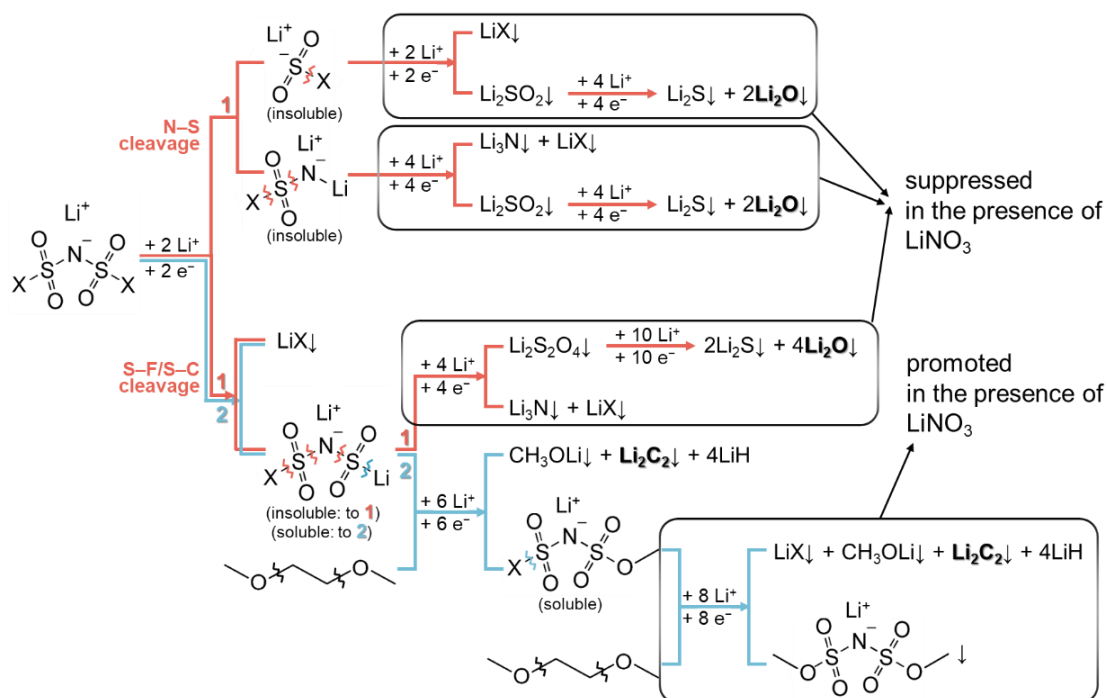


Figure 5-16. SERS bands of the S–F bond from FSI[−], the S–C bond from TFSI[−], and the C–O–C bond from DME at -100 mV. ω : wagging, ν : stretching.

To sum up, **Reaction (5-2-1)** and **(5-2-2)** are integrated into **Reaction (5-2)**. This particularly demonstrates the effect of LiNO₃ in suppressing the individual reduction of LiFSI and LiTFSI into small inorganic deposits, as well as promoting the substitution of –X by the DME fragment during the interaction of LiFSI/LiTFSI with DME solvent.

Reaction (5-2). LiFSI and LiTFSI decomposition and interaction with DME. Number 1 and 2 represent Reaction (5-2-1) and (5-2-2), respectively.



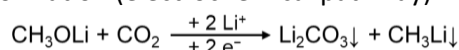
5.2.5.3 Li₂CO₃ formation

As another E.D. component found by SERS for the single-salt electrolytes (**Figure 5-8**), Li₂CO₃ is one of the major SEI components and is commonly detected in organic electrolytes. There are a couple of approaches to form Li₂CO₃ as the SEI component:

1. The direct reduction of CO₂;⁴⁶
2. The reaction of ROCO₂Li and ROLi with CO₂ or even trace water;^{41,57}
3. The chemical reaction of Li₂O₂ with CO₂.⁵⁹

However, approach 1 usually occurs on noble metal surface of graphite electrode in batteries. Regarding approach 2, ROCO₂Li is generally the product from carbonate solvent like PC (propylene carbonate) or EC (ethylene carbonate)), but not DME. Also, since Li₂O₂ was not found in this study, approach 3 was excluded. Therefore, regarding this study, the most possible reaction to produce Li₂CO₃ will be the reaction of ROLi with CO₂. It can be assigned to a 2e⁻-transferred reaction between CH₃OLi and trace CO₂ dissolved in the electrolytes (**Reaction (5-3)**, MPE = 29).^{20,41}

Reaction (5-3). Li₂CO₃ formation (electrochemical pathway) (MPE = 29)



Besides, the reaction between CH₃OLi and CO₂ may also appear as a chemical pathway (MPE = ∞). It is considered feasible because the MPE of the proposed electrochemical reactions related to single-salt electrolytes (i.e., 14, 13 to 25, and 29 for **Reaction (5-1)**, **(5-2)**, and **(5-3)**, respectively) is smaller than MPE(E.D.) at the initial stage of Li plating for single-salt electrolytes (**Figure 5-7**).

These reactions show that the influence of atmospheric and dissolved gases (e.g. CO₂) cannot be ignored when discussing the E.D. mechanisms.⁶⁰ However, such an influence was effectively reduced in the dual-salt electrolytes since Li₂CO₃ did not emerge to be detectable (**Figure 5-8**). As discussed in Chapter 3, the formation of Li₂CO₃ on the surface of Cu metal could possibly be suppressed by LiNO₃. This result demonstrates that the effect of LiNO₃ also extends to the Li metal surface.

5.2.5.4 N-containing species formation

Regarding the E.D. reaction directly related to LiNO₃, it was previously discovered that the intermediates of LiNO₃ decomposition, especially like LiNO₂ that forms prior to initial Li plating and is insoluble, could further react with organic solvent

to generate N-containing species such as NO^- and CN^- .^{9,58,61} In this study, based on the SERS results (**Figure 5-8**), the reactions between LiNO_3 decomposed products and DME fragments is considered to occur, producing N-containing species that deposited on the electrode surface. Notably, in the IRAS result shown in **Figure 5-17(a)**, a $\text{C}\equiv\text{N}$ vibration peak was found near 2240 cm^{-1} in the spectra of LFLN/LTLN. It is known that the vibration of unconjugated $\text{C}\equiv\text{N}$ usually appears near 2250 cm^{-1} ,⁶² which will downshift to 2240 cm^{-1} upon conjugating.⁶³ Therefore, in the present study, the $\text{C}\equiv\text{N}$ was considered to be in a conjugated state due to the formation of $\text{R}-\text{C}\equiv\text{N}$, while R is a function group containing a π -electron system or lone electron pairs capable of conjugation, such as aromatic rings, carbonyl groups ($-\text{C}=\text{O}$), or heteroatoms like oxygen or nitrogen in functional groups (e.g., $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{NO}_2$). Moreover, LiOH was detected at 3675 cm^{-1} only in the case of LFLN/LTLN (**Figure 5-17(b)**).^{64,65} In general, LiOH is considered to mainly come from water contamination in the electrolyte,⁴⁵ but the absence of LiOH in the case of LF/LT demonstrates the origin of LiOH in this study is not necessarily the reaction of Li with trace water.

In addition, it was found that the potential-dependent absorbance change of $\text{R}-\text{C}\equiv\text{N}$ (**Figure 5-17(c)**) is in consistent with the integrated intensity change of N-containing species that was found by SERS (**Figure 5-11**). Hence, the N-containing species can be determined as the $\text{R}-\text{C}\equiv\text{N}$ like species. Interestingly, the absorbance of the $\text{R}-\text{C}\equiv\text{N}$ and LiOH vibration peaks showed a similar potential-dependent behavior with respect to every previous potential, that is, the positive absorbance gradually decreased and reached 0 during Li plating, and decreased to negative from Li stripping. This demonstrates that these two species could be the products of the same reductive E.D. reaction. Hence, **Reaction (5-4)** was proposed based on these findings and the detected $\nu(\text{C}-\text{H})$ band from $-\text{OCH}_3$ as shown in **Figure 5-12**. This reaction indicates the formation of $\text{CH}_3\text{OC}\equiv\text{N}$ together with LiOH via the direct interaction between LiNO_2 and the fragment from DME (MPE = 52). Furthermore, this reaction stopped on the way of Li plating, followed by the oxidative reaction(s) from Li stripping, which is in line with the results of QCM (**Figure 5-7** and **Table 5-1**).

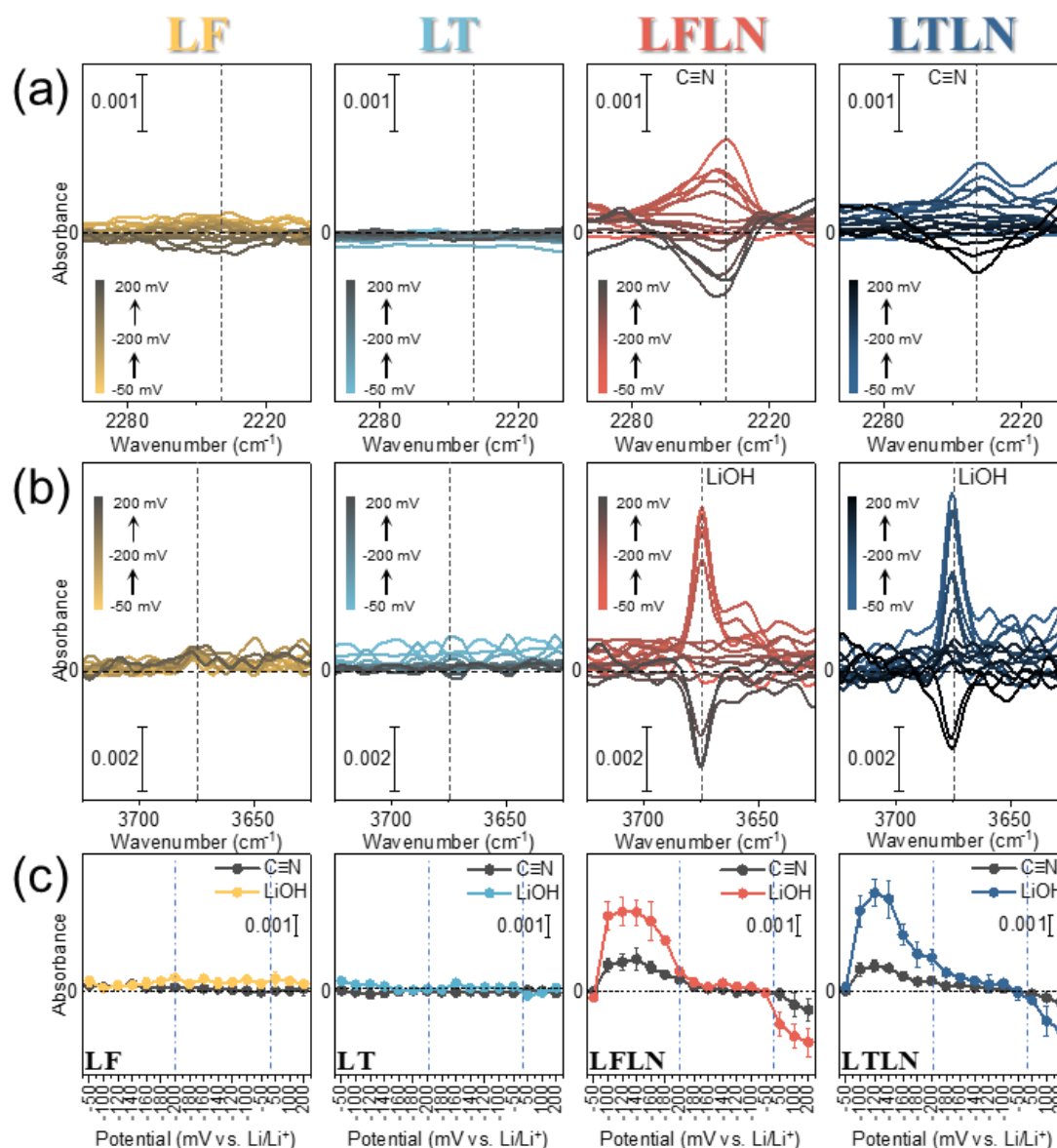
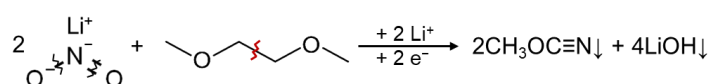


Figure 5-17. FT-IRAS spectra of (a) $\nu(\text{C}\equiv\text{N})$, and (b) $\nu(\text{O}-\text{H})$ from LiOH, for LF, LT, LFLN and LTLN electrolytes. The absorbance at each step of potential was obtained by taking the IR beam intensity at the previous potential as the reference; (c) The potential-dependent absorbance variation of $\text{C}\equiv\text{N}$ at 2240 cm^{-1} and LiOH at 3675 cm^{-1} . The vertical dashed-dotted lines divide the potential range into three regions: Li plating (cathodic), Li plating (anodic) and Li stripping. The negative absorbance indicates the decreased amounts of corresponding species compared to the previous potential. The error bar was shown based on replicated experiments.

Reaction (5-4). LiNO_2 interaction with DME (electrochemical pathway) (MPE = 52)



Additionally, considering that the MPE of the proposed electrochemical reactions related to dual-salt electrolytes (i.e., 14, 26/32, and 52 for **Reaction (5-1)**, **(5-2-2)**, and **(5-4)**, respectively) is smaller than $\text{MPE}(E.D.)$ during Li plating with cathodic scanning

for dual-salt electrolytes (**Figure 5-7**), the existence of non-electrochemical reaction(s) (MPE = ∞) related to N-containing species is also possible. Since the N-containing species have been attributed to the R–C $\equiv$ N like species, such kind of non-electrochemical reaction(s) must produce R–C $\equiv$ N like species as well, together with LiOH since its potential-dependent behavior is similar as R–C $\equiv$ N like species.

5.2.6 Calculation of α -MPE for Reactions Generating E.D. Species, and Charge Ratio Change of E.D. Reaction during Initial Li Plating

In Section 5.2.4, *in situ* SERS measurements only detected Li₂O, Li₂CO₃, and Li₂C₂, or N-containing species on the surface. Then, the calculation of the α -MPE of E.D. reactions generating respective E.D. products (except for Li₂C₂ whose α -MPE was already known) for each electrolyte is performable since the stoichiometric coefficients of transferred electrons “C(e[−])” and product “C(P)” (P can be Li₂O, Li₂CO₃, and Li₂C₂, or N-containing species) can be obtained from the E.D. reactions predicted in Section 5.2.5. **Table 5-2** summarizes the C(e[−])/C(P) ratio and the MPE of all electrochemical reactions based on **Reaction (5-1) to (5-4)** which is related to the formation of Li₂O, Li₂CO₃, Li₂C₂ and N-containing species, which requires an environment of 4e[−], 2e[−], 8e[−], and 1e[−] per molecule, respectively.

Table 5-2. Summary of the C(e[−])/C(P) and MPE of all feasible electrochemical E.D. reactions shown in Reaction (5-1) to (5-4). “N-con.” represents N-containing species.

Species	Reaction number	$\frac{C(e^-)}{C(P)}$	MPE			
			LF	LT	LFLN	LTLN
Li ₂ O	(5-2-1)	4	19	25		
Li ₂ CO ₃	(5-3)	2	29	29		
Li ₂ C ₂	(5-1)	8	14	14	14	14
	(5-2-2)	8	13	19	26	32
N-con.	(5-4)	1			52	52

Next, α , β and γ were used to represent the ratio of the charges in reactions producing Li₂O, Li₂CO₃ and N-containing species to the charges in reactions producing Li₂C₂ (set as reference since it was found in all electrolytes), respectively. They were calculated by multiplying the average ratio of C(e[−])/C(P) with the potential-dependent integrated SERS peak intensity ratio (obtained from **Figure 5-11**) of Li₂O, Li₂CO₃ and N-containing species with respect to Li₂C₂, respectively (see **Equation 5-4 to 5-6**):

$$\alpha = \frac{Q(Li_2O)}{Q(Li_2C_2)} = \frac{n(e_{Li_2O}^-)}{n(e_{Li_2C_2}^-)} = \frac{\frac{c(e_{Li_2O}^-)}{C(Li_2O)} \times n(Li_2O)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times n(Li_2C_2)} = \frac{\frac{c(e_{Li_2O}^-)}{C(Li_2O)} \times I(Li_2O)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times I(Li_2C_2)} = \frac{\frac{c(e_{Li_2O}^-)}{C(Li_2O)}}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)}} \times \frac{I(Li_2O)}{I(Li_2C_2)} \quad (5-4)$$

$$\beta = \frac{Q(Li_2CO_3)}{Q(Li_2C_2)} = \frac{n(e_{Li_2CO_3}^-)}{n(e_{Li_2C_2}^-)} = \frac{\frac{c(e_{Li_2CO_3}^-)}{C(Li_2CO_3)} \times n(Li_2CO_3)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times n(Li_2C_2)} = \frac{\frac{c(e_{Li_2CO_3}^-)}{C(Li_2CO_3)} \times I(Li_2CO_3)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times I(Li_2C_2)} = \frac{\frac{c(e_{Li_2CO_3}^-)}{C(Li_2CO_3)}}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)}} \times \frac{I(Li_2CO_3)}{I(Li_2C_2)} \quad (5-5)$$

$$\gamma = \frac{Q(N-con.)}{Q(Li_2C_2)} = \frac{n(e_{N-con.}^-)}{n(e_{Li_2C_2}^-)} = \frac{\frac{c(e_{N-con.}^-)}{C(N-con.)} \times n(N-con.)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times n(Li_2C_2)} = \frac{\frac{c(e_{N-con.}^-)}{C(N-con.)} \times I(N-con.)}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)} \times I(Li_2C_2)} = \frac{\frac{c(e_{N-con.}^-)}{C(N-con.)}}{\frac{c(e_{Li_2C_2}^-)}{C(Li_2C_2)}} \times \frac{I(N-con.)}{I(Li_2C_2)} \quad (5-6)$$

Where Q is the total charges of reactions generating respective species, n is the total number of moles of electron and respective species, I is the integrated SERS peak intensity of respective species. “N-con.” represents N-containing species.

After obtaining α , β and γ , the α -MPE of all possible E.D. reaction(s) generating respective dominant species on the surface as one of the final products, i.e., MPE(Li_2O), MPE(Li_2CO_3), MPE(Li_2C_2) and MPE(N-con.), were calculated via the non-linear fitting of the data in **Table 5-3**, including the potential-dependent variation of MPE(E.D.) obtained in Section 5.2.3. It should be noted that in this study, although Li stripping was analyzed in the same manner as Li plating, the complexity of Li stripping still remains challenging. This essentially includes the possibility of the dissociation of partial E.D. species from electrode surface together with the physical disconnection of “dead Li”, which can lead to the misjudgment of E.D. species quantitatively. Such an issue will practically make the calculation results not convincing. Therefore, the calculation and discussion of the charge ratio of each E.D. reaction regarding Li stripping are omitted in this section, and only Li plating is considered.

Table 5-3. Summary of the ratio of charges and MPE(E.D.) as the function of applied potential during initial Li plating for data-fitting. Totally 12 potentials during Li plating were selected.

Potential /mV	LF			LT			LFLN		LTLN	
	α	β	MPE (E.D.)	α	β	MPE (E.D.)	γ	MPE (E.D.)	γ	MPE (E.D.)
-100	0.32	0.20	35	0.36	0.29	46	0.23	83	0.17	77
-120	0.21	0.17	33	0.18	0.23	43	0.37	111	0.15	74
-140	0.12	0.15	32	0.11	0.18	40	0.48	131	0.15	75
-160	0.08	0.12	29	0.07	0.17	39	0.26	95	0.12	68
-180	0.03	0.03	18	0.04	0.11	32	0.15	64	0.11	65
-200	0	0	13	0.03	0.05	25	0.09	38	0.09	59
-180	0	0	13	0	0	18	0	25	0.04	48
-160	0	0	13	0	0	18	0	25	0	32
-140	0	0	13	0	0	18	0	25	0	32
-120	0	0	13	0	0	18	0	25	0	32
-100	0	0	13	0	0	18	0	25	0	32
-50	0	0	13	0	0	18	0	25	0	32

Regarding the non-linear fitting, the following two equations were used. **Equation 5-7** and **Equation 5-8** applied in the case of single-salt electrolytes and dual-salt electrolytes, respectively.

$$MPE(E.D.) = \frac{MPE(Li_2O) \times \alpha + MPE(Li_2CO_3) \times \beta + MPE(Li_2C_2)}{\alpha + \beta + 1} \quad (5-7)$$

$$MPE(E.D.) = \frac{MPE(N-containing) \times \gamma + MPE(Li_2C_2)}{\gamma + 1} \quad (5-8)$$

Figure 5-18 shows the results of non-linear fitting. Typically, the obtained MPE(Li₂O) (19 for LF, 24 for LT) matches well with the MPE of predicted **Reaction (5-2-1)** (19 for LF, 25 for LT), further suggesting that Li₂O was only from LiFSI/LiTFSI decomposition. However, note that the calculated MPE(Li₂CO₃) and MPE(N-con.) values are very large, suggesting the existence of non-electrochemical reactions. This indicates that the non-electrochemical reactions predicted by FT-IRAS are plausible.

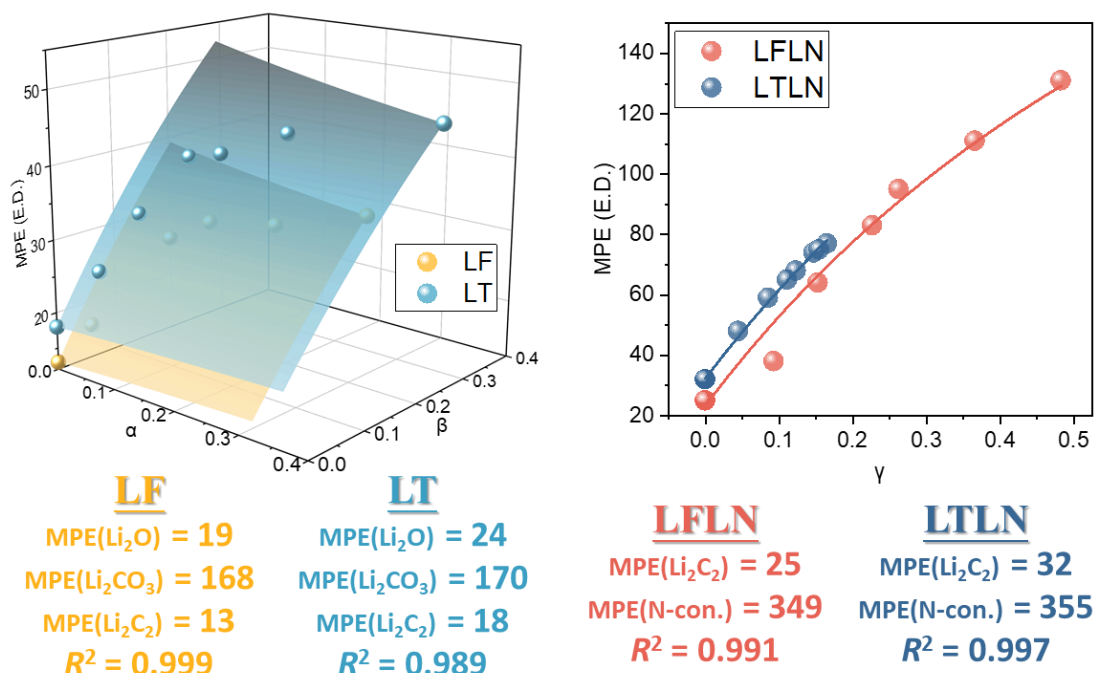


Figure 5-18. Fitting results for LF, LT, LFLN and LTLN. The α -MPE values of all E.D. reactions generating respective species as well as the R -squared value are shown for each electrolyte.

Scheme 5-2 lists up the predicted E.D. reactions (including electrochemical and non-electrochemical ones) associated with initial Li plating. The corresponding MPE of each E.D. reaction and the calculated α -MPE are summarized and classified by different electrolytes. The branching lines are used to map each α -MPE value to one or more reactions' MPE values.

Scheme 5-2. Proposed E.D. reactions during initial Li plating and the calculated α -MPE. “N-con.” represents N-containing species. All MPE values are accurate to one decimal place.

	Species	α -MPE	MPE	Possible reactions related to the respective species and the correspondent reaction number
LF	Li ₂ O	18.9	18.6	$\text{LiFSI} \xrightarrow{16\text{Li}^+ + 16\text{e}^-} \text{Li}_3\text{N} \downarrow + 2\text{Li}_2\text{S} \downarrow + 2\text{LiF} \downarrow + 4\text{Li}_2\text{O} \downarrow$ 5-2-1
	Li ₂ CO ₃	168.0	29.0	$\text{CH}_3\text{OLi} + \text{CO}_2 \xrightarrow{2\text{Li}^+ + 2\text{e}^-} \text{Li}_2\text{CO}_3 \downarrow + \text{CH}_3\text{Li} \downarrow$ 5-3
			∞	Non-electrochemical reaction to generate Li ₂ CO ₃ -
	Li ₂ C ₂	13.1	14.2	$\text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{Li}_2\text{C}_2 \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 4\text{LiH}$ 5-1
			12.7	$\text{LiFSI} + \text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{LiNFS}_2\text{O}_5\text{CH}_3 + \text{LiF} \downarrow + \text{CH}_3\text{OLi} \downarrow + \text{Li}_2\text{C}_2 \downarrow + 4\text{LiH}$ 5-2-2
LT	Li ₂ O	23.8	24.9	$\text{LiTFSI} \xrightarrow{16\text{Li}^+ + 16\text{e}^-} \text{Li}_3\text{N} \downarrow + 2\text{Li}_2\text{S} \downarrow + 2\text{LiCF}_3 \downarrow + 4\text{Li}_2\text{O} \downarrow$ 5-2-1
	Li ₂ CO ₃	169.8	29.0	$\text{CH}_3\text{OLi} + \text{CO}_2 \xrightarrow{2\text{Li}^+ + 2\text{e}^-} \text{Li}_2\text{CO}_3 \downarrow + \text{CH}_3\text{Li} \downarrow$ 5-3
			∞	Non-electrochemical reaction to generate Li ₂ CO ₃ -
	Li ₂ C ₂	17.9	14.2	$\text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{Li}_2\text{C}_2 \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 4\text{LiH}$ 5-1
			19.0	$\text{LiTFSI} + \text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{LiNCF}_3\text{S}_2\text{O}_5\text{CH}_3 + \text{LiCF}_3 \downarrow + \text{CH}_3\text{OLi} \downarrow + \text{Li}_2\text{C}_2 \downarrow + 4\text{LiH}$ 5-2-2
LF LN	Li ₂ C ₂	25.2	14.2	$\text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{Li}_2\text{C}_2 \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 4\text{LiH}$ 5-1
			25.9	$\text{LiFSI} + 2\text{DME} \xrightarrow{16\text{Li}^+ + 16\text{e}^-} \text{LiNS}_2\text{O}_6\text{C}_2\text{H}_6 + 2\text{LiF} \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 2\text{Li}_2\text{C}_2 \downarrow + 8\text{LiH}$ 5-2-2
	N-con.	348.6	52.0	$2\text{LiNO}_2 + \text{DME} \xrightarrow{2\text{Li}^+ + 2\text{e}^-} 2\text{CH}_3\text{OC}\equiv\text{N} \downarrow + 4\text{LiOH} \downarrow$ 5-4
			∞	Non-electrochemical reaction to generate R-C≡N and LiOH -
LT LN	Li ₂ C ₂	32.1	14.2	$\text{DME} \xrightarrow{8\text{Li}^+ + 8\text{e}^-} \text{Li}_2\text{C}_2 \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 4\text{LiH}$ 5-1
			32.2	$\text{LiTFSI} + 2\text{DME} \xrightarrow{16\text{Li}^+ + 16\text{e}^-} \text{LiNS}_2\text{O}_6\text{C}_2\text{H}_6 + 2\text{LiCF}_3 \downarrow + 2\text{CH}_3\text{OLi} \downarrow + 2\text{Li}_2\text{C}_2 \downarrow + 8\text{LiH}$ 5-2-2
	N-con.	355.4	52.0	$2\text{LiNO}_2 + \text{DME} \xrightarrow{2\text{Li}^+ + 2\text{e}^-} 2\text{CH}_3\text{OC}\equiv\text{N} \downarrow + 4\text{LiOH} \downarrow$ 5-4
			∞	Non-electrochemical reaction to generate R-C≡N and LiOH -

Based on these values as well as the SERS peak intensity ratios (**Figure 5-11**), the ratios of consumed charge for different E.D. reactions over total charges were calculated. The detailed process can be described as follows: First, the charges of reactions producing Li₂O, Li₂CO₃, Li₂C₂ and N-containing species are represented by $Q(\text{Li}_2\text{O})$, $Q(\text{Li}_2\text{CO}_3)$, $Q(\text{Li}_2\text{C}_2)$ and $Q(\text{N-con.})$, respectively. Similarly, the SERS integrated intensities of these species are represented by $I(\text{Li}_2\text{O})$, $I(\text{Li}_2\text{CO}_3)$, $I(\text{Li}_2\text{C}_2)$ and $I(\text{N-con.})$. Since there is only **Reaction (5-1)** and **Reaction (5-2-2)** (both producing Li₂C₂) remaining during Li plating with anodic scanning, which share the same $C(\text{e}^-)/C(\text{P})$ value (**Table 5-2**), the average I/Q ratio of these two reactions (regarded as one set of reaction) can be calculated based on **Figure 5-11**. Then, $Q(\text{Li}_2\text{C}_2)$ during cathodic scanning can be obtained through dividing $I(\text{Li}_2\text{C}_2)$ during cathodic scanning by the average I/Q ratio. After that, $Q(\text{N-con.})$ can be obtained by subtracting $Q(\text{Li}_2\text{C}_2)$ during cathodic scanning from the total charge in the case of dual-salt electrolytes. While for single-salt electrolytes, since the $C(\text{e}^-)/C(\text{P})$ value of Li₂O (= 4) is the half of Li₂C₂ (= 8) (**Table 5-2**), the I/Q ratio from Li₂O should be twice as much as that from Li₂C₂. Based on this, $Q(\text{Li}_2\text{O})$ and $Q(\text{Li}_2\text{CO}_3)$ can be obtained in the same manner as above. Regarding the charge ratio of **Reaction (5-1)** and **Reaction (5-2-2)**, if the charge ratio of **Reaction (5-1)** is set as x , the equation “ $14.2x - 12.7(1-x) = 13.1$ ” for LF can be established, where 14.2 and 12.7 are the MPE of **Reaction (5-1)** and **Reaction (5-2-2)**,

respectively, and 13.1 is $\text{MPE}(\text{Li}_2\text{C}_2)$ for LF. As a result, the x can be solved. Note that since there is no charge consumed for non-electrochemical reactions, only electrochemical reactions were taken into account for the calculation.

The calculated charge ratios of these electrochemical E.D. reactions over the total charges during initial Li plating (cathodic and anodic processes) for both single- and dual-salt electrolytes are summarized and shown in **Figure 5-19**. As previously reported, at potentials more positive than 0 V (including OCP), the E.D. process is predominantly driven by the electrochemical and chemical decomposition of Li salt, while the DME solvent remains relatively stable at OCP and starts to decompose by the applied potential.⁹ Besides, Qian et al. demonstrated that DME solvent has a more negative reduction potential against Li/Li^+ , making it stable even after Li plating starts.⁶⁶ However, the findings of this study suggest that the participation of DME in the E.D. process has already become significant during the initial stages of Li plating. Specifically, interactions between LiFSI/LiTFSI and DME (**Reaction (5-2-2)**) gradually took the vast majority of all electrochemical E.D. reactions as Li plating proceeds, whereas the direct reduction of DME (**Reaction (5-1)**) contributed less than 20% of the charges across all electrolytes. Additionally, reactions involving the formation of Li_2CO_3 or $\text{CH}_3\text{OC}\equiv\text{N}$ were nearly undetectable during anodic scanning.

As discussed in Section 5.2.5, the presence of LiNO_3 as a co-salt suppressed the decomposition of LiFSI/LiTFSI into smaller molecules, while enhancing their interactions with DME, which resulted in the increased production of Li_2C_2 . Consequently, the charge ratio of salt-solvent interactions over total charges further increased from approximately 80% for single-salt electrolytes to nearly 100% for dual-salt electrolytes (**Figure 5-19**). It is noteworthy, however, that there is no evidence suggesting that LiNO_3 regulates the overall decomposition degree of DME, including its direct reduction or its interactions with LiFSI/LiTFSI.

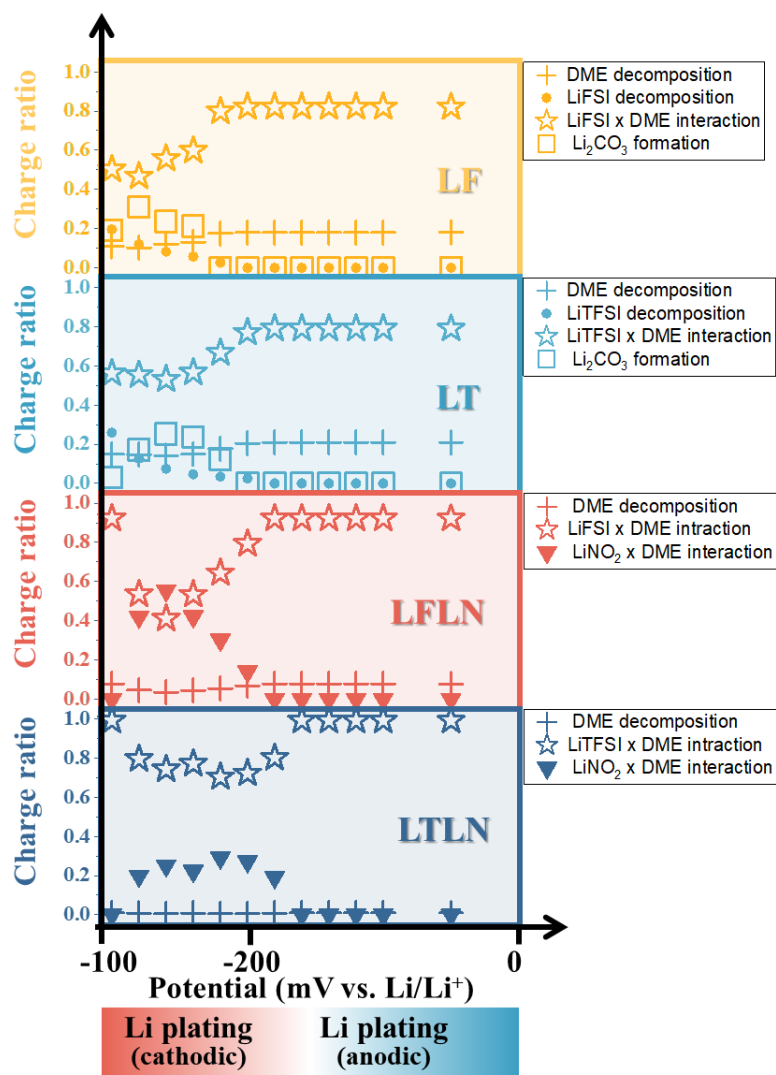


Figure 5-19. The potential-dependent charge ratio of several possible E.D. reactions during initial Li plating for LF, LT, LFLN and LTLN.

5.3 Conclusion

In this study, four DME-based electrolytes, i.e. LiFSI, LiTFSI, LiFSI-LiNO₃, and LiTFSI-LiNO₃ were prepared to investigate the detailed E.D. reactions associated by Li plating/stripping in the first cycle. The E.D. charge was successfully extracted from total charge via CA technique and data fitting by the modified “Li-SEI model”. Combined with QCM, the potential-dependent MPE values contributed by E.D. were obtained during initial Li plating/stripping. *In situ* SERS and FT-IRAS analysis revealed the dominant chemical species generated during initial Li plating/stripping for each electrolyte, as well as their potential dependencies. Based on these analyses, the prediction of possible E.D. reaction schemes and mechanisms was conducted. Furthermore, the charge ratio of each electrochemical E.D. reaction during initial Li

plating was calculated based on the proposed reaction schemes, showing that DME solvent related degradation processes consumed most charges. Moreover, this study emphasizes the key role of LiNO_3 in preventing the further decomposition of LiFSI/LiTFSI into smaller inorganic by-products, as well as in enhancing the interaction between LiFSI/LiTFSI and the DME solvent by favoring the replacement of functional groups within the lithium salts with DME fragments. However, LiNO_3 appears to have little effect on the overall decomposition of DME.

It should be noted that there are still evident limitations for this series of methodology. For example, the proposed methods were on the basis of several indirect analyses, hypotheses and evaluations. As such, inevitable errors or deviations at each stage of calculation could be accumulated, leading to improper conclusion. Nevertheless, this study can be regarded as an effective route to quantitatively interpret the complex electrolyte degradation process in the presence of deposited Li metal in real-time.

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Chapter 6

General Conclusion and Future Prospects

6.1 General Conclusion

In the present thesis, the composition and properties of SEI layers (including n-SEI pre-SEI and s-SEI) and E.D. mechanisms during the first cycle, as well as the stability of s-SEI during cycling were studied using Li||Cu anode model in the ether-based low-concentration (< 3 M) electrolytes. The role of LiNO_3 as additive and dual-salt was investigated in depth.

In Chapter 3, the behaviors of the adsorbed layer (including n-SEI and pre-SEI) on a Cu electrode surface before the initial Li plating in TEGDME-based low-concentration electrolytes were investigated. The study examined the effects of LiNO_3 as an additive or co-salt, exploring its role in the chemical and electrochemical reduction processes. Using QCM coupled with CV, mass changes and roughness variations of the surface were analyzed, highlighting potential-dependent shifts in surface composition based on MPE. FT-IRAS revealed the formation of organic species at OCP and during cathodic scanning, suggesting that increasing LiNO_3 ratio not only promoted the chemical and electrochemical decomposition of TEGDME but also put forward the ending of the further decomposition of TEGDME derivatives. In addition, the presence of LiNO_3 was found to suppress the formation of Li_2CO_3 during pre-SEI formation process. A preliminary model showing how the LiNO_3 ratio influenced SEI composition and roughness was proposed, emphasizing its dual role in regulating the species (particularly the organics) and the morphology of the adsorbed layer on Cu surface prior to initial Li plating.

In Chapter 4, the existence of an “oxidative subsequent SEI” formation process (named as OSS) was revealed by CV measurement, and it was found that Li plating/stripping efficiency and stability was greatly improved by either blocking OSS or adding LiNO_3 , while purely increasing concentration to 2.0 M did not function well. QCM analyses revealed the insight of such an improvement through the proof of more stabilized Li plating/stripping (MPE closer to 7), and smaller surface roughness owing to more even Li growth. XPS depth-profile analysis confirmed the formation of the protective Li_2O - and Li_2S_x -based subsequent SEI layers when blocking OSS in 0.4LT, which was considered to guarantee the improved stability of Li plating/stripping, while LiNO_3 additive helped suppressing the oxidation of Li_2O into Li_2O_2 and sustaining the

existence of Li_2O even with the occurrence of OSS, therefore substantially improving the CE performance. Meanwhile, the effect of increasing concentration to 2.0 M in the existence of 0.1 M LiNO_3 additive shifted the decisive SEI species from Li_2O to LiF , further assuring the enhanced CE performance in the low-concentration TEGDME-based electrolytes. By combining SERS analysis, a hypothesized model was proposed to summarize the major SEI component shift, and the correspondent morphology change via OSS process. These results together suggest the importance of adjusting operating potential range in a proper manner to achieve a better performance of Li plating/stripping in AFLMB.

In Chapter 5, the E.D. mechanisms during the initial-cycle Li plating/stripping were systematically investigated using DME-based electrolytes containing two common Li salts, LiFSI and LiTFSI, combined with LiNO_3 as a co-salt. A typical approach of multi-potential step chronoamperometry was employed alongside non-linear fitting using the modified “Li-SEI model” to extract E.D. charges during Li plating and stripping. QCM measurements facilitated the separation of mass changes specifically related to the E.D. process. Furthermore, *in situ* SERS and FT-IRAS revealed potential-dependent variations in surface chemical species, enabling the identification of possible E.D. reactions during the initial Li plating. The charge contributions of individual electrochemical E.D. reactions were calculated, and the effects of LiNO_3 as a co-salt were carefully examined in comparison to single-salt electrolytes. The findings highlight that LiNO_3 played a pivotal role in stabilizing the electrolyte system by suppressing the reduction of LiFSI/LiTFSI into smaller inorganic by-products. Additionally, LiNO_3 enhanced interactions between LiFSI/LiTFSI and DME, promoting the substitution of functional groups within Li salts by DME fragments, which significantly increased the charge ratio of salt-solvent interactions in the E.D. process. These results provide valuable insights into the design of dual-salt electrolyte systems for improving the performance of AFLMBs.

6.2 Future Prospects

This study shows that tailoring SEI composition and morphology via electrolyte modification is an effective approach to enhancing AFLMB performance. The pivotal role of LiNO_3 , functioning both as an additive and a co-salt, is underscored as essential for regulating SEI properties and E.D. mechanisms. However, there are still several

potential challenges to be addressed in the future, which are listed as follows:

In Chapter 3, the precise mechanism of LiNO_3 remains unclear, and additional evidence, such as observations of gas generation, is needed to support the conclusions. Moreover, this study maintains a constant total Li^+ concentration across electrolytes, with LiTFSI concentration decreasing in the order of $\text{LT} > \text{LN-add} > \text{LN-co}$, leaving the optimal $\text{LiTFSI}:\text{LiNO}_3$ ratio to be further explored. Besides, future investigations into the effects of the n-SEI and pre-SEI species on s-SEI evolution during prolonged cycles could enhance understanding of the battery system.

In Chapter 4, given the gradual consumption of the LiNO_3 additive during cycling, further optimization of the $\text{LiNO}_3:\text{LiTFSI}$ ratio is necessary as well. Meanwhile, the theoretical mechanisms showing how Li_2O affects CE, and how LiNO_3 prevents the oxidation of Li_2O in a higher potential region, need to be verified by more evidence. Additionally, alternative strategies such as the use of other additives or dissolved gases (e.g. CO_2 , N_2) to improve the composition and morphology impacted by the s-SEI formation process should be explored in future studies.

In Chapter 5, while E.D. was successfully separated during Li plating/stripping, the calculation of CE after excluding the E.D. charge portion has yet to be performed in a practical AFLMB configuration. Furthermore, as Li plating/stripping behaviors may differ between the initial and subsequent cycles in AFLMBs, cautions are required when applying the MUSCA method to subsequent cycles. It is also important to acknowledge the limitations of the methods used in this study, which rely on indirect analyses, hypotheses, and evaluations. This may introduce cumulative errors or deviations at various stages, potentially leading to inaccurate conclusions.

In summary, the possible future work based on the findings in this thesis contains optimizing electrolyte compositions, exploring alternative additives or dual-salts, and looking for other promising electrolyte systems such as weakly-solvated ether electrolytes. Moreover, employing advanced techniques is required to further elucidate interfacial phenomena. In particular, techniques like online mass spectroscopy for confirming the E.D. species more accurately, cross-sectional SEM/TEM or neutron reflectometry for checking the thickness of SEI layers, more powerful FT-IR techniques for reducing the bulk influence and exclusively investigating the surface species, can be applied.