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**Effect of Lithium Salt Concentration on Interfacial Solvation
Structure and Electrochemical Oxygen Reduction for
Nonaqueous Li-O₂ Battery**

(非水系 Li-O₂ 電池の界面溶媒和構造と電気化学的酸素還元にあつりチウム塩
濃度の影響)

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2021

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Chapter 1

Introduction

1.1 General Introduction

A steady, reliable source of energy is an integral part of our daily life. Currently, the world's main energy source is fossil fuel. However, the finite fossil fuel supply and environmental issues of greenhouse gases generated during the usage process hampered its use. To meet increasing global energy demand, alternative 'clean' energy sources, which do not depend on fossil fuels and environmentally friendly, must be developed.¹ The most convenient way is to transfer energy sources to electrical power. Several alternatives that relate to electricity generation have been widely concerned, such as, fuel cells, solar cells, and secondary batteries. A fuel cell is a device that converts the chemical potential energy of fuel into electrical energy. A proton exchange membrane cell uses hydrogen gas and oxygen gas as fuel. The products of the reaction in the cell are water, electricity, and heat. This is a big improvement over internal combustion engines, coal burning power plants, and nuclear power plants, all of which produce harmful by-products. However, if a better way of storing the hydrogen gas and low-cost oxygen reduction reaction catalyst could be developed, then proton exchange membrane cell would look much more promising.² Solar cell, an electronic device that directly converts the energy of light into electricity through the photovoltaic effect. The core component of a solar cell contains two semiconductor layers of different materials, i.e. p-type and n-type semiconductor. When a photon with suitable energy incident on the surface of a semiconductor layer, the electron would acquire energy from the photon and move to another semiconductor layer to generate current. In the past few years, several common semiconductor materials were emerging, such as GaAs film, CdTe film and CuInS₂ film et al. However, the high cost of these semiconductor films in photoelectric devices and low solar conversion efficiencies hinders the further development of solar cells.³ The secondary batteries such as lead-acid, nickel-cadmium (NiCd), nickel-metal hydride (NiMH), and lithium based secondary batteries including lithium ion batteries, polymer lithium ion batteries (PLiON) and lithium metal batteries, become much more promising compared with other techniques, as they can be recharged inexpensively many times before they need replacing. Among these, lithium based secondary batteries have the best

energy density and a slow loss of charge when not in use, as shown in Figure 1-1.⁴

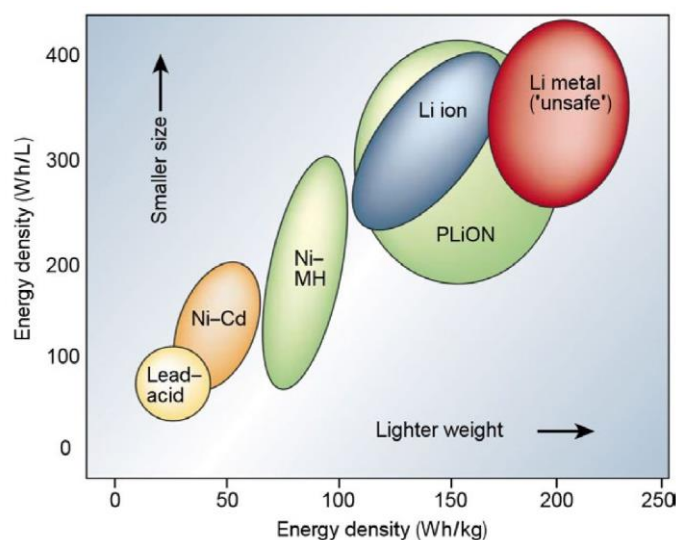


Figure 1-1. Comparison of energy densities and specific energy of different secondary rechargeable batteries.⁴

Since the 1970s, lithium based rechargeable batteries have undergone a great evolution involving the knowledge of intercalation chemistry and lithium-metal chemistry.⁵⁻⁶ Due to the safety problems of metallic lithium anodes, lithium ion battery technology based on an insertion-compound was introduced and developed by the Sony Corporation in the early 1990s. The commercialization of Li-ion rechargeable battery has enabled the wireless revolution of cell phones, laptop computers, digital cameras, and iPads that has transformed global communication. However, even fully developed, the highest energy storage that Li-ion batteries can deliver is too low to meet the demands of markets, such as an electric vehicle. Reaching beyond Li-ion batteries is a huge challenge; it requires the exploration of new chemistry, especially electrochemistry, and new materials.⁷⁻⁸ Rechargeable Li-air (Referred to as Li-O₂) and Li-S batteries, are receiving intense interest at the present time.⁹ The theoretical specific energies for Li-O₂ and Li-S batteries are 3505 Wh kg⁻¹ and 2600 Wh kg⁻¹, which is 9 and 6.6 times that of lithium ion batteries (387 Wh kg⁻¹), respectively. The increments of theoretical specific energies for Li-O₂ and Li-S batteries are because of Li₂O₂ and Li₂S in the cathode store more Li⁺ than LiCoO₂ per unit mass, and lithium metal stores more charge per unit mass than a graphite anode.¹⁰ With an increasement in energy density for Li-O₂ and Li-S batteries, the long-range all-electric vehicles could be developed, instead of cars driven by fossil fuels.

1.2 Lithium based secondary batteries

1.2.1 Lithium ion batteries (hereafter referred to as LIBs)

As shown in Figure 1-2, the traditional LIBs consist of graphite negative electrode (anode) and LiCoO_2 positive electrode (cathode), separated by a separator. Electrolytes are filled between cathode and anode, served as a medium to transport the Li^+ in the charging/discharging cycle of the cell. Lithium salts dissolved in organic solvents are used as the electrolyte for LIBs, the most common is 1 M LiFP_6 in dimethyl carbonate (DMC)/ethylene carbonate (EC) (1:1 v/v%) mixture, which has a low electrical resistance.¹¹ Solid electrolytes, including polymers¹² and inorganic compounds¹³⁻¹⁴, are used for solid-state batteries, which have advantages in terms of miniaturization and durability. Graphite anode has a layered structure, which can facilitate the movement of Li^+ in and out of its lattice space with minimum irreversibly. LiCoO_2 forms the $\alpha\text{-NaFeO}_2$ structure, which is a distorted rock-salt structure where the cations order in alternating (111) planes. This ordering results in a trigonal structure which allow Li^+ lithiation and delithiation.¹⁵ Thus, graphite and LiCoO_2 were used as a container for Li^+ storage during the electrode reaction.

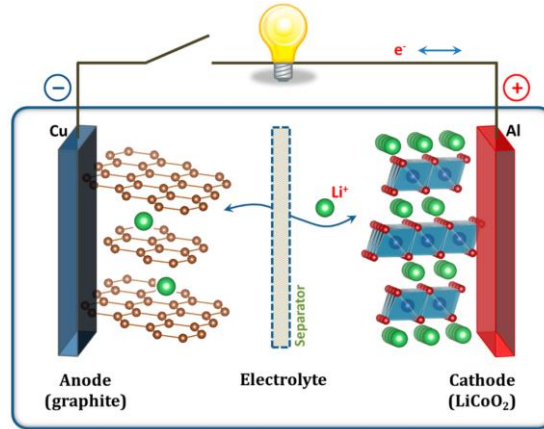
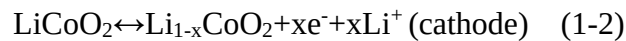
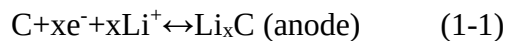


Figure 1-2. Schematic illustration of the LIBs ($\text{LiCoO}_2/\text{Li}^+$ electrolyte/graphite).¹⁶

The reaction at the cathode and anode is:



The overall reaction is,



During the charging process, Li^+ from the LiCoO_2 cathode passed through a separator, then inserted into a discharged graphite anode to form Li_xC compound (1-1). In the meantime, LiCoO_2 anode is oxidized into $\text{Li}_{1-x}\text{CoO}_2$ (1-2). During the discharging process, Li^+ deintercalated from Li_xC and insert to the LiCoO_2 cathode. $\text{Li}_{1-x}\text{CoO}_2$ is reduced into LiCoO_2 . The lithiation-delithiation potential of graphite is approximately 0.2 V vs. Li/Li^+ which is close to lithium deposition potential, while the potential for (1-2) is approximately 4.2 V vs. Li/Li^+ . Theoretically, a LIBs with an output voltage of approximately 4.0 V could be achieved considering the redox potential of reaction (1-1) and (1-2). The energy density is around 387 Wh kg^{-1} for LiCoO_2/C battery. It is worth noting that, the electrolyte is unstable at the lithiation-delithiation potential of graphite. The electrolyte would electrochemical degradation on the graphite surface during the first charging process and the insoluble products would deposit on the graphite surface to form a layer called solid electrolyte interphase (SEI). An SEI with good Li^+ permeability and good mechanical stability can serve as a very effective passivation film, and kinetically prevent the further reduction of the solution species.¹⁷⁻¹⁸ Because of the stable SEI-derived from carbonate electrolytes, which improves the cycle stability of LIBs and further promotes the commercialization of LIBs.

Compared with other rechargeable battery batteries, LIBs have the advantages of light weight, low self-discharge, no memory effect, and fast charging. However, it also suffers from several drawbacks such as, sensitivity to high temperature, aging effect, deep discharge, and safety concerns.¹⁹ And with the development of the electric vehicle industry, batteries with higher energy density become required for better endurance. In this context, Li-O_2 batteries came into being.

1.2.2 Li-O_2 batteries

The Li-O_2 batteries are an electrochemical cell that uses oxidation of lithium at the anode and reduction of oxygen at the cathode to induce a current flow. Although the concept of Li-O_2 batteries was proposed as early as 1996,²⁰ it recaptured scientific attention late in the first decade of the 2000 s due to advances in materials science.^{7, 21} In

2006, Bruce et al reported a Li-O₂ battery using manganese dioxide as the cathode catalyst.²¹ In this work, the author confirmed the decomposition of Li₂O₂ during charging by in-situ mass spectrometry. Although the charge overpotential of this battery is high, the extremely high capacity still attracts the researcher's attention. Since then, researches on Li-O₂ batteries has begun to flourish.

Generally, Li-O₂ batteries can be divided into nonaqueous and aqueous Li-O₂ batteries according to the use of electrolyte. As the name implies, the electrolyte of nonaqueous Li-O₂ battery uses organic solvents such as dimethyl sulfoxide (DMSO), dimethoxymethane (DME), glycol dimethyl ether (TEGDME) and acetonitrile as solvents, while the aqueous lithium battery uses water as the electrolyte solvent. The cathode electrode reaction of nonaqueous Li-O₂ battery involves the formation and decomposition of Li₂O₂, while the aqueous Li-O₂ battery is related to the formation and decomposition of LiOH. Note that the research object of the present thesis is the nonaqueous Li-O₂ battery because the aqueous Li-O₂ battery is more complicated due to the strong reactivity between lithium and water. Figure 1-3 shows the typical schematic of nonaqueous Li-O₂ battery during charging and discharging. On discharge, the Li metal negative electrode is oxidized, releasing Li⁺ into the electrolyte, and the process is reversed on charge. At the positive electrode, O₂ from the atmosphere enters the porous cathode, dissolves in the electrolyte, and is reduced at the electrode surface on discharge. In general, in aprotic nonaqueous electrolytes, the oxygen reacts with Li⁺ at the cathode surface to produce insoluble Li₂O₂ and cover the electrode surface during the discharging process. This process is also called an oxygen reduction reaction (ORR). On the reverse charging process, Li₂O₂ is decomposed into O₂, while electron and Li⁺ migrate back to the lithium anode for deposition. This process denoted as an oxygen evolution reaction (OER).

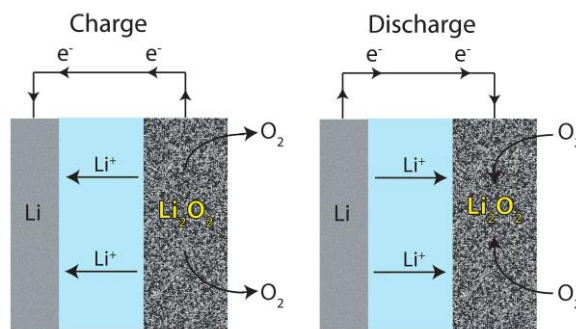
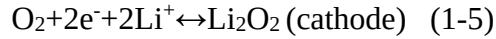
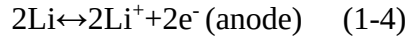
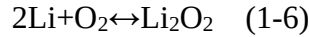


Figure 1-3. Schematic of nonaqueous Li-O₂ battery during charge and discharge cycles.

The electrode reaction is:

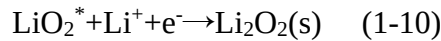
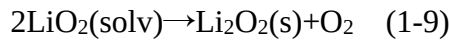
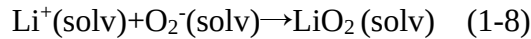
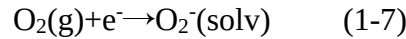


The overall reaction is,



The theoretic working potential for oxygen cathode is 2.96 V vs. Li/Li^+ , and for Li anode is 0 V vs. Li/Li^+ . Thus, the theoretic cell voltage of Li- O_2 battery is 2.96 V.

The ideal nonaqueous Li- O_2 battery is based on the electrochemical formation and decomposition of Li_2O_2 . In fact, the formation of lithium peroxide is a multi-step reaction process as follow,^{10, 22}



Oxygen is first converted to O_2^- on the electrode surface by one-electron reduction reaction (1-7), and then combined with Li^+ in the electrolyte to form a metastable LiO_2 (1-8). LiO_2 may subsequently undergo two different reaction pathways: 1. solution mechanism—chemical disproportionation of LiO_2 into Li_2O_2 molecule (1-9), or 2. surface mechanism—electrochemical reduction of LiO_2^* (* refers to species adsorbed on the electrode surface) into Li_2O_2 combined with an additional electron and Li^+ (1-10). Those reaction progresses are closely related to the surrounding conditions, including the choice of electrolyte, charge/discharge modes as well as the choice of electrode materials.²³⁻²⁵ As for the charging step, ideal nonaqueous Li- O_2 battery involves the electrooxidation of Li_2O_2 at air cathode and should follow the reverse process of the discharge reaction of (1-7)-(1-10).

As mentioned, the choice of electrolyte has a great influence on the reaction mechanism of the Li- O_2 battery. The researchers have found that the donor number (D.N.) and acceptor number (A.N.) of the solvent and anion of lithium salt have a great influence

on the stability of the LiO_2 intermediate, which in turn affects the mechanism of the Li- O_2 battery.²⁶⁻²⁸ LiO_2 shows high solubility in solvent with high D.N. to stabilize Li^+ and high A.N. to stabilize O_2^- , such as DMSO. The dissolved LiO_2 will further disproportionate into toroid-like Li_2O_2 and deposit on the electrode surface. While in solvent with low A.N. and D.N., such as DME, LiO_2 is poorly dissolved, LiO_2 accumulated on the electrode surface and then reduced into film-like Li_2O_2 . It is pointed that the film-like Li_2O_2 would passivate the electrode surface for further reaction once the Li_2O_2 grows to a certain thickness, which is so-called “sudden death” of a battery.²⁹ Whereas LiO_2 dissolved in the solution can be continuously deposited on the electrode surface, thus leading to a higher capacity.²⁷

In addition to the D.N. and A.N. of solvent, the D.N. and A.N. of the lithium salt anion have a greater impact on the discharge mechanism and capacity of the Li- O_2 battery. At the early stage of Li- O_2 battery, the donor number of lithium salts is rare mentioned, as most anions have similar and relatively small D.N. such as PF_6^- (D.N. = 2.5) and TFSI^- (D.N. = 5.4). However, it has been revealed recently by Burke et al. that anions with high D.N. were shown to enhance discharge capacity in low D.N. solvents such as 1 M LiNO_3/DME solution, whereas the counter anions did not influence discharge capacity in high D.N. solvents.²³ Their observation shows good agreement with the works by the other two groups,³⁰⁻³¹ which shows that anions with high D.N. can enhance Li^+-O_2^- solubility in low D.N. solvents and promotes the solution phase ORR pathway. It is widely believed that the discharge capacity is lower in low donor number solvents than that in high donor number solvents. Therefore, this finding indicates that the discharge capacitance in low donor number solvents can be adjusted by manipulating the donor number of the lithium salt cation. Although important progress of Li- O_2 battery has been made by many researchers, significant challenges remain, which will be discussed in a later section.

1.3 Challenges of nonaqueous Li- O_2 battery

1.3.1 Protection of Li metal anode

As mentioned previously, the electrode reaction for LMBs at the lithium anode

involves the electrodeposition and stripping of lithium (1-4). During this process, due to the high reactivity of lithium, most electrolytes (including solvent and lithium salts, or additives) that come in contact with lithium will decompose. Thus, an SEI which composed of insoluble decomposed products is generally formed on the Li anode due to electrolyte degradation during the first charge-discharge process. On one hand, the formation of SEI consumes the anode and electrolyte, resulting in low coulomb efficiency. On the other hand, SEI effectively prevents direct contact between the anode and the electrolyte, making the battery more stable.

Generally, after a long charge-discharge cycle, lithium will penetrate the SEI to form lithium dendrites and react with the electrolyte. The growth of lithium dendrites will induce low coulomb efficiency and safety hazards, thus hindering the commercialization of lithium metal batteries. Therefore, methods should be taken to prevent the growth of lithium dendrites in lithium metal batteries. Since the composition and property of SEI affect the Li-O₂ battery performance significantly, adjusting the composition and property of SEI would be a good strategy. Therefore, the modulation of electrolytes is the most efficient method to stabilize SEI.

Zhang reported the use of 0.05 M CsPF₆ as an additive in 1 M LiPF₆/PC solution to prevent the growth of lithium dendrites.³² Figure 1-4 shows the SEM images of Li foils surface deposited in the electrolyte with different CsPF₆ addition. It could be found that a large number of lithium dendrites on the surface of lithium metal were observed in the absence of additives (Figure 1-4a). However, even if a small amount of CsPF₆ (0.001 M) is added, the formation of lithium dendrites is substantially decreased (Figure 1-4b). In addition, lithium dendrites are gradually reduced with the concentration of CsPF₆ increases (Figure 1-4b to 4e). As the concentration of CsPF₆ reaches beyond 0.01 M, lithium dendrites can hardly be observed on the surface of lithium metal (Figure 1-4d to 4e). The explanation behind this phenomenon is attributed to lower reduction potential of Cs⁺ than that of Li⁺. During lithium deposition, Cs⁺ form a positively charged electrostatic shield around the initial Li dendrite. This prevent the continued growth of the lithium dendrites, and force Li⁺ to deposit in the adjacent area, eventually a smooth lithium surface was created.

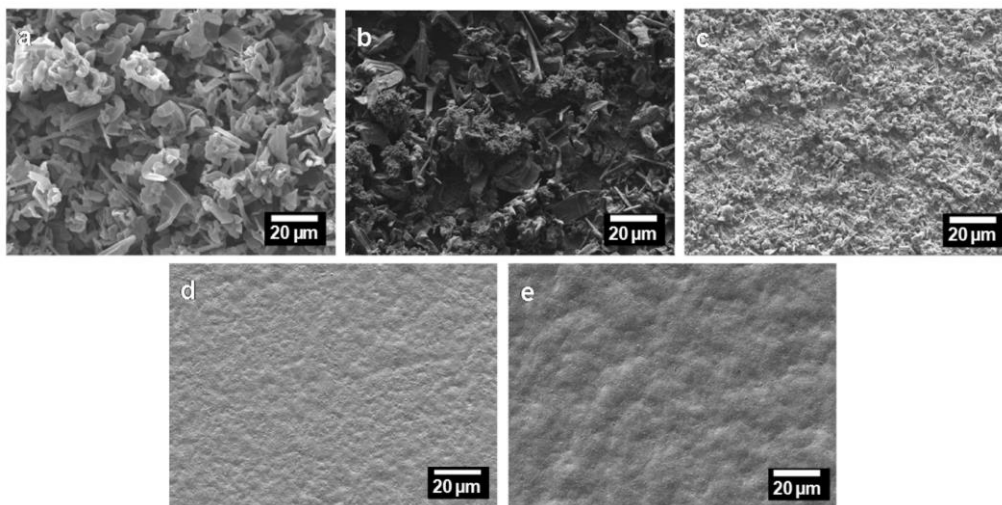


Figure 1-4. SEM images of Li films surface deposited in 1 M LiPF₆/PC solutions with CsPF₆ concentrations of (a) 0 M, (b) 0.001 M, (c) 0.005 M, (d) 0.01 M, and (e) 0.05 M, at a current density of 0.1 mA cm⁻².³²

However, if the cathodic reaction was taken into account, the problems of the lithium metal anode will be more serious. Unlike LIBs, the Li-O₂ battery is an open system with the cathode exposed to the gas phase. Oxygen and moisture will inevitably dissolve into the electrolyte from the oxygen cathode. Furthermore, various soluble by-products produced from the decomposition of electrolyte and carbon cathode induced by the nucleophilic attack of LiO₂ intermediate specie will also dissolve into the electrolyte. Recent studies have shown that even binders, such as polyvinylidene fluoride are difficult to escape from O₂⁻ attacks and produce byproducts.³³ Meanwhile, separator currently used could not ensure effective prevention of the diffusion of these soluble byproducts (crossover contaminations) to the lithium anode. Therefore, a series of side reactions will occur at the lithium anode. And as the charge/discharge proceeds, continuous crossover contaminations from the cathode would react with lithium metal, producing side products, such as LiOH, Li₂CO₃, and ROCO₂Li.³⁴ These side products would dramatically reduce the stability of Li anodes.

Recently, Xin et al. reported that the use of LiBr and LiNO₃ dual-salt electrolyte can stabilize the lithium anode of the Li-O₂ battery, even in the presence of oxygen.³⁵ As shown in Figure 1-5(a), the cells comprising LiBr-LiNO₃ electrolyte exhibited lower voltage increases in both O₂ (ca. 0.25 V) and Ar atmospheres (ca. 0.5 V) compared with

that in LiNO₃-only electrolyte (ca. 0.7 V). SEM images of the deposited Li foils after 100 hrs cycles show intact SEI in the LiBr-LiNO₃ dual-salt electrolyte under the O₂ atmosphere (Figure 1-5(e)), which is much better than the case in the LiNO₃-only electrolyte under O₂/Ar atmosphere and LiBr-LiNO₃ dual-salt electrolyte under the Ar atmosphere that thick/crack SEI could be observed (Figure 1-5(b) to 5(d)). They attribute this phenomenon to the formation of an ultrathin and homogeneous Li₂O-rich SEI layer in the discharge process. Br⁻ was thought to remove the initial passivation layer on lithium metal, while NO₃⁻ react with freshly exposed lithium to form the Li₂O layer. In addition, it is revealed by electron back scattered diffraction analysis that lithium is deposited by epitaxial growth during charging.

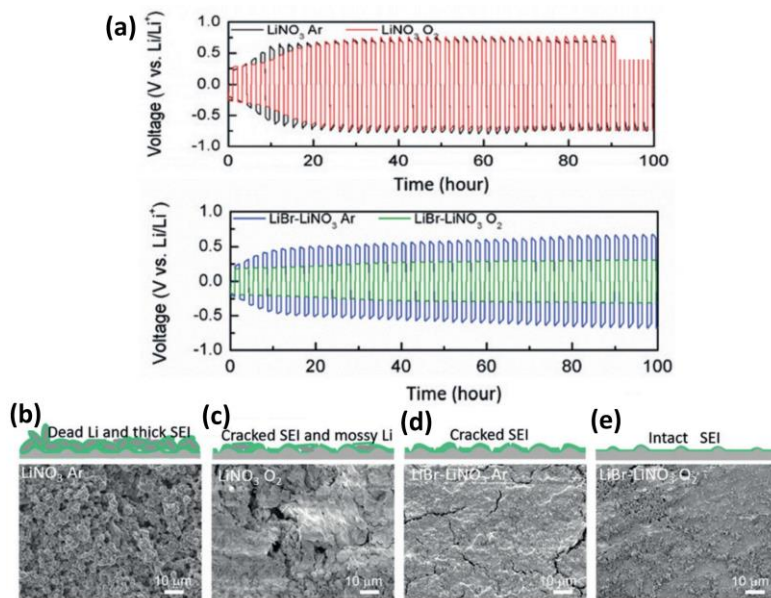


Figure 1-5. v-t profiles measured in the symmetrical Li/Li beaker cells cycled at 1 mA cm⁻² in (a) 1 M LiNO₃ and (b) 0.05 M LiBr-1 M LiNO₃ electrolytes under Ar or O₂. Top-view SEM images of the deposited Li foils after 100 hrs cycles in (b) 1 M LiNO₃ under Ar, (c) 1 M LiNO₃ under O₂, (d) 0.05 M LiBr-1 M LiNO₃ under Ar, and (e) 0.05 M LiBr-1 M LiNO₃ under O₂. The illustrations located at the top of sections (b)-(e) of the figure are schematic cross-sections of the surface of deposited Li, scale bar is 10 μm. Green is represented the SEI layer.³⁵

In an attempt to adjust the electrolyte composition, changing the electrolyte concentration has been widely studied. The commonly used electrolyte is within the range of 1-1.2 M based on optimized properties of electrolyte solution such as ionic conductivity, viscosity, and stability. Recently, electrolytes with superconcentrated lithium salts have received intensive attention due to the creation of a stable SEI to prevent the growth of lithium dendrite. The ratio of solvent and lithium salts affect the composition and property of the SEI layer significantly.³⁶⁻³⁸ In superconcentrated electrolyte, the SEI layer was thought to mainly derive from the decomposition of lithium salt anion, while in low-concentrated electrolyte, the SEI was mainly composed of degradation product of solvent. The detail explanation will be discussed in a later section.

1.3.2 Cathode materials design

In a Li-O₂ battery, the cathode is usually composed of materials with a rich pore structure, such as typical carbon nanotubes, Ketjen black et al., so that higher capacity could be achieved. As the main discharge product, Li₂O₂ is a wide band gap insulator with band gap around 4.9 eV.^{29, 39-40} The formation of Li₂O₂ film on the electrode easily passivates the active electrode surface, which rapidly increases the cell resistance during discharge, thus reducing the total capacity. In addition, the sluggish electrochemical oxidation kinetics of Li₂O₂ were also induced by this insulating film, which makes it difficult to oxidize Li₂O₂ and resulting in high charging overpotential. Hence, the development of cathode materials with ORR or OER active sites and facilitating mass transfer is essential to the Li-O₂ battery.⁴¹

Inspired by the fuel cell catalysts, the researchers used a series of catalytic materials, including Pt, Pd, Au, Ru, and MnO₂ into the Li-O₂ battery to reduce the overcharge potential.^{21, 42-46} Lu et al. report the intrinsic ORR activity of polycrystalline Pt, Pd, Au, Rh, and glassy carbon (GC) surfaces in 0.1 M LiClO₄-DME via rotating disk electrode measurements. They found ORR activity in Li⁺-contained nonaqueous solutions correlates to oxygen adsorption energy, in order of Pd > Pt > Ru ≈ Au > GC on bulk surfaces, forming a “volcano-type” trend.⁴⁵ Peng et al. reported a reversible and higher-

rate Li-O₂ battery in 0.1 M LiClO₄/DMSO solution with porous gold as cathode. The battery shows 95% capacity retention from 1st cycle to 100th cycles (Figure 1-6(a)). In addition, the charging potential reach as low as 3.1 V by using porous gold as cathode which is much lower than that employing carbon cathode (Figure 1-6(b)). Component analysis (not shown) shows that during charging and discharging, the gold surface involves highly reversible Li₂O₂ formation/decomposition, whereas partial Li₂O₂ formation/decomposition was occurring at carbon electrode. In addition, the kinetics of Li₂O₂ oxidation on charge at porous gold was found approximately 10 times faster than on carbon electrodes due to the catalytic effect of gold.

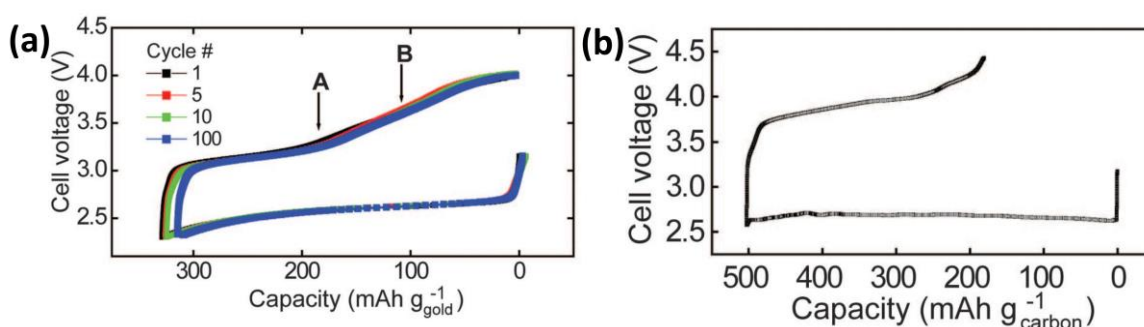


Figure 1-6. Charge-discharge curves employing (a) porous gold and (b) carbon cathode at 70 mA g⁻¹ cycling profile for a Li-O₂ cell with a 0.1 M LiClO₄-DMSO electrolyte.

In addition to the utilization of catalysts, fast mass transfer (electron, O₂, and Li⁺) is necessary as well, especially when the catalyst (such as transition metal oxide) has poor conductivity. Therefore, carbon materials are widely used as catalyst substrates to enhance the conductivity of electrodes. Since most OER catalysts are metal-based materials, the use of porous carbon materials can effectively reduce the loading of the catalyst, thereby increasing the specific capacity of the Li-O₂ battery. As shown in Figure 1-7, ruthenium nanoparticles were decorated on graphene sheets of graphene aerogels (Ru-GAs) and obtained a free-standing cathode for Li-O₂ battery. The ruthenium nanoparticles were demonstrated to significantly reduce the charge overpotential of the Li-O₂ battery comparing with pure graphene aerogels at a current density of 0.1 mA cm⁻², exhibiting a superior catalytic activity. Pd, Au, and their alloys were also applied as the catalyst material in a Li-O₂ battery and was not shown here.⁴⁷⁻⁴⁸

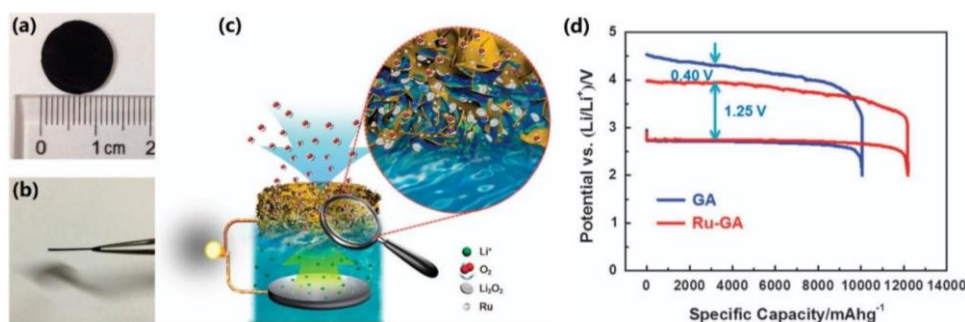


Figure 1-7. Ru-GA and its electrochemical performance. (a) A circular Ru particles functionalized graphene aerogel (Ru-GA) electrode with a diameter of 13 mm (b) free-standing electrode with a thickness of 1 mm (c) schematic representation of battery reaction for a Li-O₂ cell with Ru-GA cathode (d) Initial discharge-charge voltage profiles of Li-O₂ battery with graphene aerogel (GA) and Ru particles functionalized GA (Ru-GA) cathodes at a current density of 0.1 mA cm⁻².⁴⁹

It is worth noting that these noble metal ORR catalysts are also good OER catalysts. However, these highly active catalysts will inevitably electrooxidize the decomposition of electrolyte when oxidize Li₂O₂. McCloskey et al. shows the use of Au, Pt, MnO₂ nanoparticles supported on Vulcan XC 72 carbon black electrode achieves a low overcharge potential (Figure 1-8(a)), but differential electrochemical mass spectrometry (DEMS) results show that the by-product CO₂ was also detected along with the evolution of oxygen during the charging process (Figure 1-8(c)). Especially for Pt with high catalytic activity, charging process did not release oxygen, indicating side reaction is dominant instead of Li₂O₂ oxidation (Figure 1-8(b)). This work shows that the development of OER catalysts for Li-O₂ battery should not only focus on reducing the overcharge potential, but also avoid side reactions.⁴²

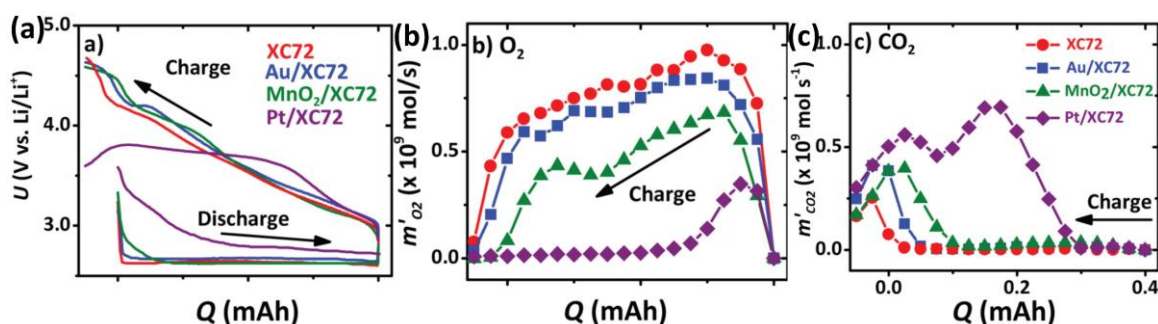


Figure 1-8. Gas evolution from cells employing DME. (a) Discharge-charge voltage curves, and corresponding O₂ (b) and CO₂ (c) evolution during charging of cells.

Compared with noble metal, the prices of transition metals and their oxides are more acceptable than precious metals. Due to the presence of oxygen vacancies and multivalent metal ions, transition metal oxides are capable of providing good catalytic activity. Therefore, a lot of work has applied transition metal materials in the field of Li-O₂ battery.^{43, 46, 50-52}

Cobalt oxide nanoparticle decorated on reduced graphene oxide (Co₃O₄/RGO) composite was reported by Nazar and coworkers, which shows good OER performance.⁴⁴ As shown in Figure 1-9(a) and 9(b), the XRD and selected area electron diffraction (SAED) pattern show cubic spinel of Co₃O₄, which is distributed on rGO. The composite loaded on Ketjen Black electrode shows a charge potential between 3.5~3.7 V which is 400 mV lower than that of a pure Ketjen Black electrode at a current density of 140 mA g_{carbon}⁻¹ (Figure 1-9(c)). They attributed the reduction in overcharge potential to the catalytic effect of Co₃O₄/RGO composite. The role of Co₃O₄/RGO is proposed to enhance the surface transport of Li_xO₂ species and hence lower the charging overpotential. Apart from cobalt and cobalt oxide, MnO₂ and Fe₂O₃ was also employed as the catalyst material in Li-O₂ battery.^{43, 46, 52-53}

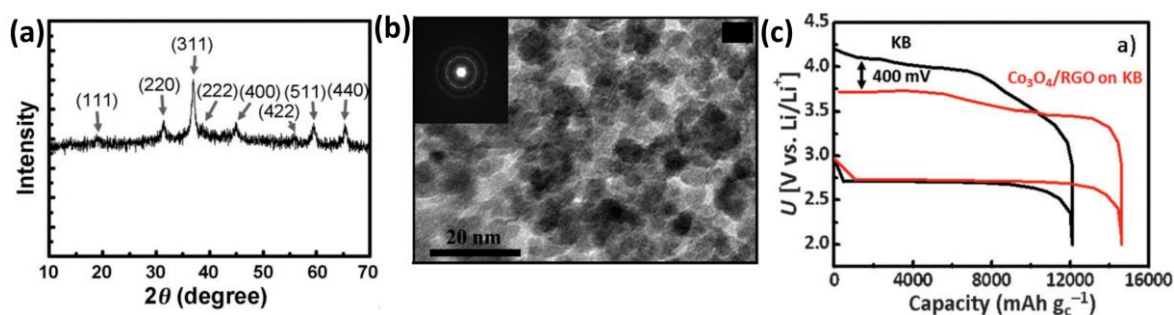


Figure 1-9. (a) XRD pattern of Co₃O₄/RGO, cubic spinel reflections. (b) HRTEM image of Co₃O₄/RGO, inset: SAED pattern of Co₃O₄.

While exploring the cathode catalysts, in fact, the corrosion of carbon electrodes has gradually begun to attract people's attention. Carbon electrodes are widely used in Li-O₂ battery, but they are not ideal cathodes because of carbon corrosion issues. The carbon cathode oxidation problem was first proposed by Luntz et al.⁵⁴ They used ¹³C-carbon black as cathode and employed DEMS to analyze the gas evolution. 40 % of ¹³CO₂ were found to evolve during charge, indicating carbon is involved in the parasitic reaction

(Figure 1-10). They revealed that the $^{13}\text{CO}_2$ comes from $\text{Li}_2^{13}\text{CO}_3$, which is generated by the reaction between Li_2O_2 and carbon electrodes. This finding indicates that the instability of the carbon electrode would lead to the formation of Li_2CO_3 , and the high overpotential required for the oxidation of Li_2CO_3 would cause more serious corrosion of the carbon electrode, which ultimately leads to a decrease in the active area of the electrode, thereby reducing the cycle performance of the battery. To address this problem, many efforts have been made, including the development of carbon-free electrodes such as, nanoporous gold⁴⁷, TiCs⁵⁵, Ni foam substrates⁵⁶⁻⁵⁷ et al.⁵⁸⁻⁶⁰

Although researches on cathode catalysts for the Li-O₂ battery has made some progress, it has not yet reached the level of commercialization. More effective cathode catalysts are yet to be developed. In the issue of lowering the charging potential, the application of soluble redox pairs seems to be more promising than the use of cathode catalysts, as will be discussed in a later section.

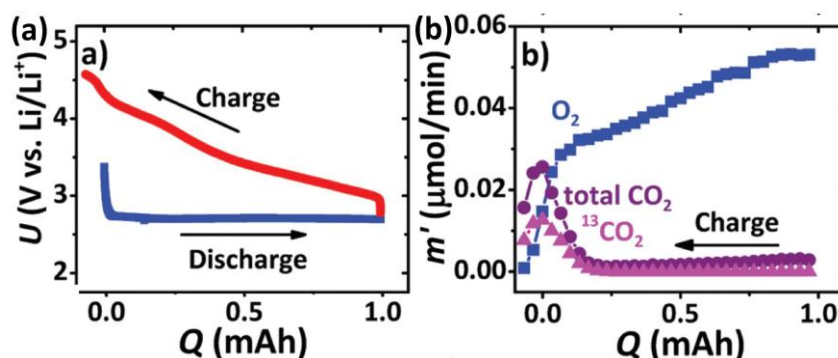


Figure 1-10 (a) Potential versus Li/Li^+ (U) versus discharge capacity (Q) for Li-O₂ galvanostatic discharge and charge at 200 μA of current on a ^{13}C cathode. (b) Quantitative evolution rates (m) for O_2 , $^{13}\text{CO}_2$, and $^{12}\text{CO}_2+^{13}\text{CO}_2$ during the charge in (a) as measured by quantitative DEMS.⁵⁴

1.3.3 Electrolytes

1.3.3.1 Solvent

In the early stages of Li-O₂ battery research, organic carbonate electrolytes which are commonly used in LIBs are applied. However, it has recently been reported that organic carbonates are vulnerable to be attacked by superoxide intermediate during

discharge, which is unstable under battery operation.⁶¹ Ever since then, various solvent-lithium salt combinations have been adopted as electrolytes, and their influence on electrochemistry has also been investigated.

Regarding the selection of solvent for nonaqueous Li-O₂ battery, the most important property lies its D.N. and A.N., because they have a great impact on the discharge reaction mechanism as mentioned previously. In addition to considering the effect of the D.N. and A.N. of the solvent on the ORR mechanism, the following aspects should also be noted: (1) electrolyte volatility, (2) stability of solvents to oxygen reduced species like LiO₂ and Li₂O₂. (3) electrochemical stability window and (4) solubility of lithium salt. These factors would affect the long-term stability of the Li-O₂ battery. Next, two commonly used solvents with significant different D.N. will be introduced, as well as faced problems and possible solutions.

DMSO is regarded as the representative of high D.N. solvent with D.N. of 30, which is the largest among the commonly used Li-O₂ battery solvents.⁶² Compared with a solvent with low donor numbers (DME and TEGDME), DMSO has the advantage of low volatility and viscosity, good oxygen diffusion, and high conductivity. The application of DMSO-based electrolyte to Li-O₂ battery was first proposed by Zhang et al.⁶³ The battery revealed a high capacity of 9400 mAh g⁻¹ at 0.05 mA cm⁻² and showed excellent rate performance with KB carbon as a cathode, LITFSI as lithium salt and DMSO as a solvent.(Figure 1-11) In addition, it also showed good electrochemical performance in the DMSO electrolyte by using Au and TiC as a cathode, respectively (not shown here).^{8, 47}

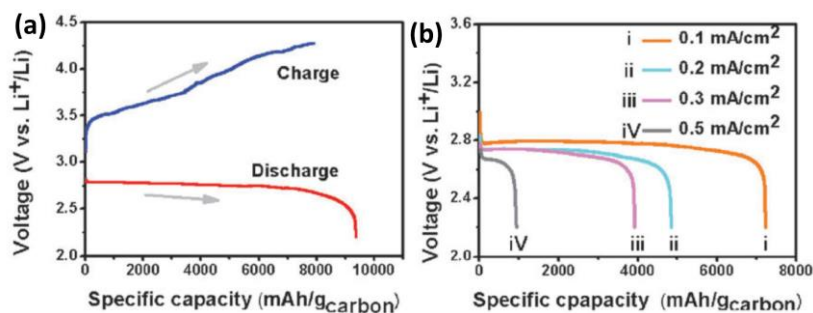


Figure 1-11. (a) Discharge and charge curves of Li-O₂ battery under 0.05 mA cm⁻²; (b) rate capacities under different current densities.⁶³

Since the solubility of LiO_2 intermediate in high D.N. solvents is high, the solution mechanism of ORR was thought to proceed in an electrolyte with DMSO as a solvent, which was confirmed by in situ surface enhanced Raman spectroscopy (SERS) measurement.²⁷ Figure 1-12(a) shows the cyclic voltammetry of ORR in 0.1 M $\text{LiClO}_4/\text{DMSO}$, two ORR peaks at ca. 2.6 V and ca. 2.35 V could be observed, revealing that ORR might be proceed by two steps. The corresponding Raman spectra with potential was shown in Figure 1-12(b), the vibrational peak of LiO_2 (ca. 1120 cm^{-1}) which reflects surface mechanism could not be detected on the electrode surface at any potential, while the signal of soluble O_2^- that relate to solution mechanism could be observed at low overpotential. And as the potential sweep negatively, the peak intensity of O_2^- gradually decreases, while that of Li_2O_2 increases, indicating that the O_2^- on the surface is electrochemically converted to Li_2O_2 . In addition, the presence of O_2^- in DMSO-contained electrolyte bulk solution was also confirmed by in-situ UV spectroscopy, demonstrating that the oxygen reduction intermediates species indeed go into the solution and follow solution mechanism.⁶⁴

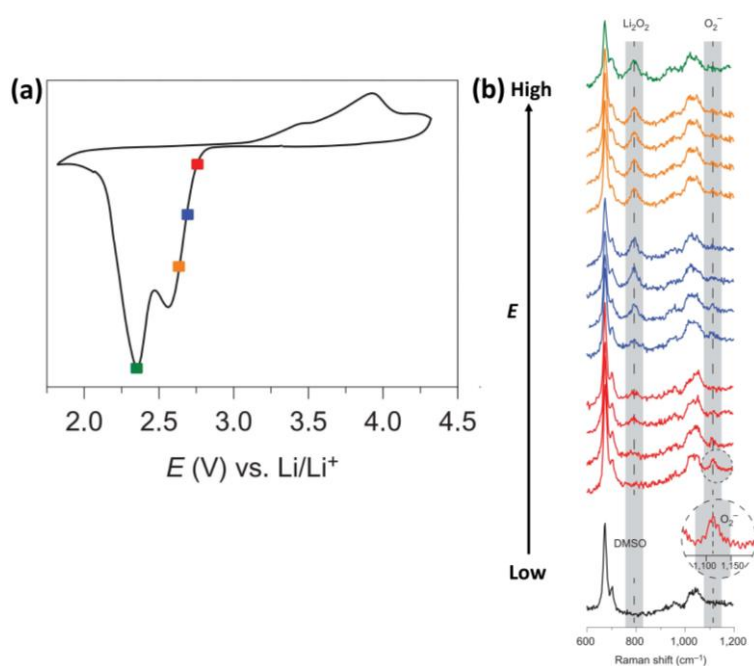


Figure 1-12. (a) Cyclic voltammetry of ORR in electrolyte with 0.1 M LiClO_4 in DMSO. (b) In situ SERS measurement spectra of the electrode surface in same electrolyte at various constant potentials indicated by the matching-colored markers in the CVs above each stack of spectra, vertical dotted lines with grey shading show positions of O_2^- , LiO_2 and Li_2O_2 . Insets: expanded areas of spectral regions outlined by the dashed circles. Spectra at the bottom were collected at the open circuit potential.²⁷

The disadvantage of DMSO is its chemical instability. It is shown that carbonate species would be produced under prolonged contact between DMSO and Li_2O_2 .⁶⁵ In addition, due to the high polarity of DMSO, it is also prone to be attacked by discharge intermediate LiO_2 . As shown in Figure 1-13, a chain reaction would be a trigger, leading to the formation of DMSO_2 , LiOH , Li_2SO_3 and Li_2SO_4 .⁶⁶ In addition, DMSO would anodizes at potential over than 4.2 V, which is much negative than that of ether-based solvent (DME and TEGDME).⁶⁷ The above results indicate that DMSO is unstable under ORR and OER processes on an oxygen electrode surface, not to mention the unresolved instability problem towards lithium anode.⁴⁷ Recently, it has been discovered that the use of DMSO-based superconcentrated electrolyte can effectively improve the stability of DMSO-based electrolytes in Li- O_2 battery due to the reduction of soluble O_2^- into the electrolyte, which will be discussed in a later section.

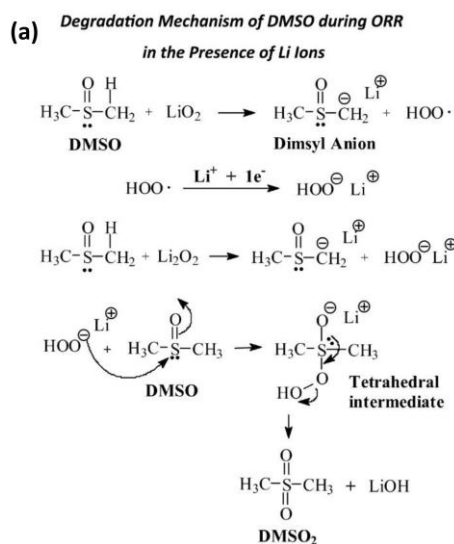


Figure 1-13. Degradation mechanism of DMSO during ORR in the presence of Li^+ .⁶⁸

Ethers are considered to be excellent Li- O_2 battery solvent because they can effectively resist the attack of oxygen reduced species and stabilize the lithium anode compared with DMSO.^{62, 69} It was found that DME shows better stability than carbonate electrolyte.⁷⁰ However, considering the high volatility of DME, it is not suitable for use in Li- O_2 battery because the air cathode is an open structure. To solve this problem, the researchers used triglyme (G3) and tetraglyme (G4, TEGDME) with low volatility as solvents and shows good cycle stability as well.⁷¹ As shown in Figure 1-14(a), the charge-

discharge curve demonstrates that the battery can cycle reversibly at a capacity of 1,100 mAh g_{carbon}⁻¹ with lower charge potential at ca. 3.6 V by using LiCF₃SO₃/TEGDME (molar ratio = 1:4) electrolyte. And the battery can be continuously cycled for at least 30 cycles at the current rate of 500 mA g_{carbon}⁻¹ without causing significant capacity loss as shown in Figure 1-14(b)). Because of relatively high chemical stability, ether electrolyte has become one of the most studied electrolytes in Li-O₂ battery.

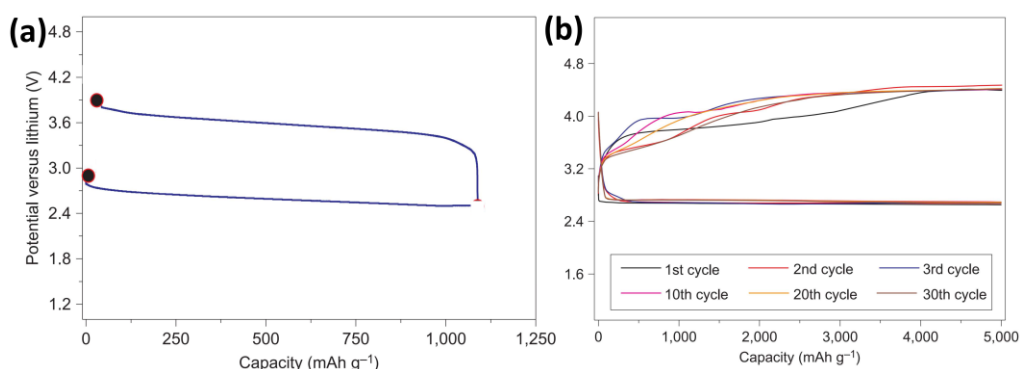


Figure 1-14. (a) Charge-discharge plots in LiCF₃SO₃/TEGDME (molar ratio = 1:4) electrolyte. (b) Cycling performance of the lithium/TEGDME–LiCF₃SO₃/O₂ battery under 500 mA g_{carbon}⁻¹.

Although polyether has better resistance to oxidation than carbonate, solvent degradation is still inevitable. The α -H and β -H on polyether molecules tend to be attacked by peroxide species and leading to the formation of a series of byproducts as shown in Figure 1-15.⁶⁶ Aiming at this problem, it's shown that by changing the LITFSI/ether molar ratio, the stability of G3 and G4 can be significantly enhanced.⁷² The appropriate coordination of Li⁺ by G3/G4 was thought to facilitate O₂⁻ access to Li⁺, and refrain glyme molecules from attacking. Besides, it is reported that replacing the DME backbone proton can effectively alleviate the attack of the solvent by oxygen reducing radicals and greatly improved cycle stability.⁷³

Apart from ether- and sulfone-based electrolyte, other types of solvents have also been studied, such as, dimethylformamide (DMF), *N,N*-dimethylacetamide and *N*-methylpyrrolidone (NMP). However, the SEI layer derived from these solvents are usually not stable. By applying a suitable lithium salt, such as LiNO₃, this problem can be alleviated well. In addition to commonly used organic solvents mentioned above, ionic

liquids are also often used as electrolytes for Li-O₂ battery due to low flammability, high ionic conductivity and less vulnerable to O₂⁻ attack.⁷⁴ However, poor solubility of lithium salt/oxygen and high viscosity are not good for Li-O₂ battery. By mixing ionic liquid with organic solvent such as diethylene glycol diethyl ether would be a good way to solve the problem.⁷⁵

Figure 1-15. Degradation mechanism of polyether solvents under the attack of Li_2O_2 .⁶⁶

1.3.3.2 Lithium salts

The degradation of LiPF_6 leads researchers to study other lithium salts, often relative to previously used in LIBs. LITFSI and LiTf have been widely used for Li- O_2 battery, but the degradation of lithium salts is still considered inevitable.^{77, 80-81} Both degradation products of LITFSI and LiTf contain LiF and $-\text{CF}_3$. To avoid the formation of LiF, the fluorine-free lithium salt is considered, such as lithium bis(oxalato)borate⁸⁰. However, degradation is still unavoidable by superoxide radicals.⁸² In this regard, LiClO_4 , which is considered unsafe for commercial, has been used in laboratory research because of its resistance to degradation.

Recently, the use of lithium nitrate (LiNO_3) as a lithium salt in Li- O_2 battery has attracted researchers' attention. LiNO_3 is normally used as an additive for a Li-S battery for protecting the Li anode from further reactions with the polysulfides. And it is also found to show superior performance in Li- O_2 battery. As shown in Figure 1-16(a), the charging voltage is about 3.8V after 30 cycles in 1M LiNO_3 /Diglyme solution, whereas the value in 1M LITFSI/Diglyme is 4.2 V (Figure 1-16(b)), which is higher than that in 1M LiNO_3 /Diglyme. The enhanced Li- O_2 battery performance could be ascribed to the following aspects. On one hand, LiNO_3 can stabilize the lithium anode by forming robust SEI on lithium anode through the following reaction:⁸³

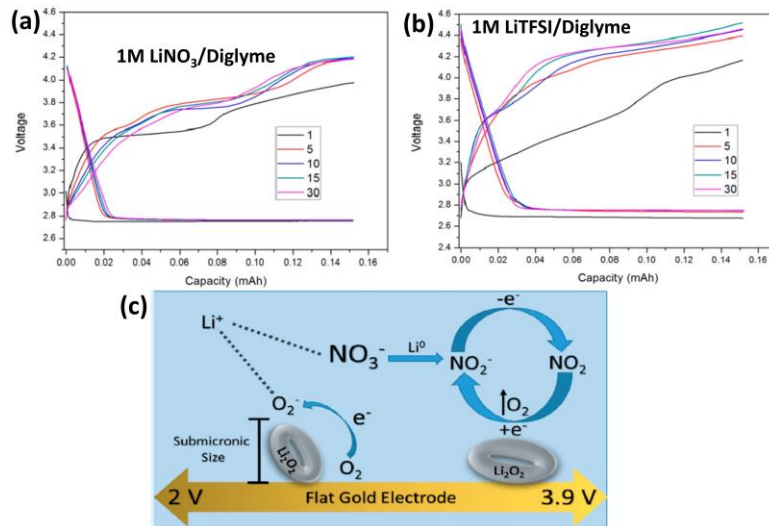
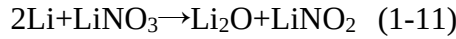


Figure 1-16. Charge-discharge of a Li- O_2 battery with (a) 1 M LiNO_3 or (b) 1 M LITFSI solutions in diglyme at 0.1 mA cm^{-2} using carbon paper cathodes. (c) Discharge mechanism in the presence of LiNO_3 .

On the other hand, NO_2^- that formed by the reduction of nitrate ions on the anode works as a redox mediator to help reduce the charge potential as shown in Figure 1-16(c). The oxidation forms NO_2 , which readily oxidizes to Li_2O_2 . The latter process moves the OER overpotentials down into a potential window suitable for polyether solvent-based cells. Although LiNO_3 shows so many benefits for Li- O_2 battery, nitrogen-containing groups are detected on the surface of the carbon cathode, indicating the instability of LiNO_3 under battery operation condition.⁸⁴

It seems that no specific lithium salt has perfect properties for Li- O_2 battery. Every salt has its own unique property. Combining lithium salts with different advantages into dual-salts or multi-salts electrolytes seems to be capable of improving the performance of the Li- O_2 battery by a synergic effect. This might be the reason why dual-salt electrolytes become popular recently.

1.3.3.3 Additives

The traditional electrolyte for lithium battery contains a solvent and a conductive lithium salt. Besides, the addition of a small number of additives can also greatly improve the performance of the battery. For example, the addition of vinylene carbonate (VC) and LiNO_3 could greatly improve the stability of lithium anode.⁸⁵

Although great progress has been made in the research of cathode catalysts, its defects have gradually emerged, that is, the immovability of discharge products. It is considered that electrocatalysis requires the products and reactants of the rate-determining step are mobile, so that the reactants can approach the catalyst surface and the products can diffuse away for the continuous catalytic reaction.⁴² However, the discharge product Li_2O_2 has no solution mobility.⁸⁶ In recent years, a new type of soluble additive called redox mediator (RM) which is capable of oxidizing solid Li_2O_2 has raised people's attention. Due to the immobility of Li_2O_2 , it seems that using a movable catalyst could address this problem. The mechanism of oxidation of Li_2O_2 by redox mediator is shown in Figure 1-17. The RM is first oxidized to RM^+ during charging. Then, one Li_2O_2 molecule was oxidized by two RM^+ and RM^+ was reduced back to RM.⁸⁷ Compared to solid catalysts, soluble RM is dissolved in the electrolyte, which allows it to fully contact Li_2O_2 , thereby oxidizing Li_2O_2 more effectively.

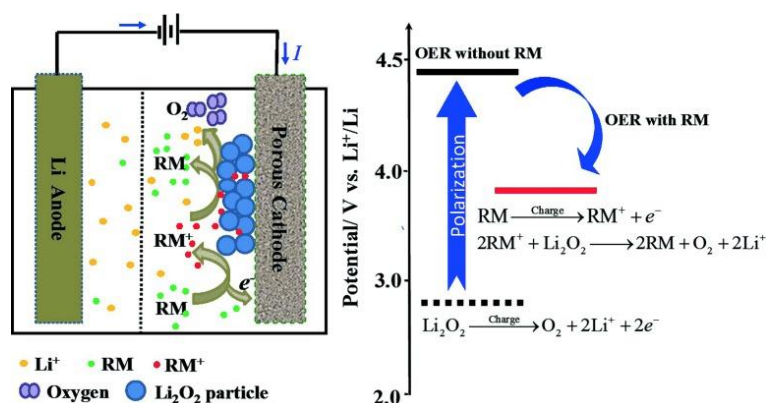


Figure 1-17. Proposed catalytic mechanism of the OER with a suitable redox mediator as the soluble catalyst in an aprotic Li-O₂ battery⁸⁷

Bruce et al first employed tetrathiafulvalene (TTF) mediator catalyst and nanoporous gold (NPG) electrode, Li-O₂ battery shows a significant drop in charge overpotential. (Figure 1-18(a))⁸⁸ It was shown by DEMS that the ratios of charge passed to O₂ evolved on the charge were very close to the theoretical value for Li₂O₂ decomposition, i.e. 2e⁻/O₂. (Figure 1-18(b)) This means that the Li₂O₂ indeed oxidized by TTF⁺ generated during charging. In addition, SERS and FTIR results show that Li₂O₂ was totally removed even after 100 cycles, which is difficult to achieve without TTF.(not shown here) In addition to TTF, other redox mediators have also been studied, such as LiI,⁸⁹ LiBr,⁹⁰ N-methylphenothiazine (MPT),⁹¹ 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)⁹² et al. All these redox mediators play a very good role in reducing the charging potential.

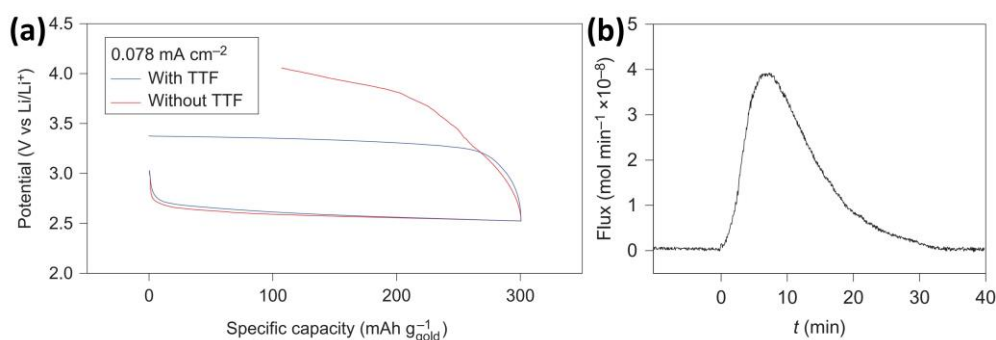


Figure 1-18. (a) First-cycle of charge-discharge plot in 1 M LiClO₄ in DMSO with 10 mM TTF (blue) and without TTF (red), the rates were increased from 0.078 mA cm⁻². (b) O₂ evolution from the reaction between oxidizing mediators and Li₂O₂.

Apart from redox mediator, the addition of protic additive such as water could transform discharge product Li_2O_2 into LiOH , or convert the ORR mechanism into solution process. It was found that the discharge product could be manipulated into LiOH by adding a trace of water into DMSO-based electrolyte with $\text{Ru}/\text{MnO}_2/\text{Super P}$ as cathode.⁹³ The charge/discharge mechanism is as follows: O_2 was first converted into Li_2O_2 , then react with water to form LiOH (step (i) and (ii)). The equilibrium of step (i) could be moved forward by catalytic conversion of H_2O_2 into H_2O over MnO_2 (step (ii)) and quickly transform Li_2O_2 to LiOH . On charging, LiOH would be oxidized at low overpotential with the assistance of Ru . As shown in Figure 1-19, the charging overpotential of $\text{Li}-\text{O}_2$ battery based on this system shows very low value, ca. 0.21 V. Other studies on the use of water as an additive in $\text{Li}-\text{O}_2$ battery have also shown excellent electrochemical performance.⁹⁴⁻⁹⁵

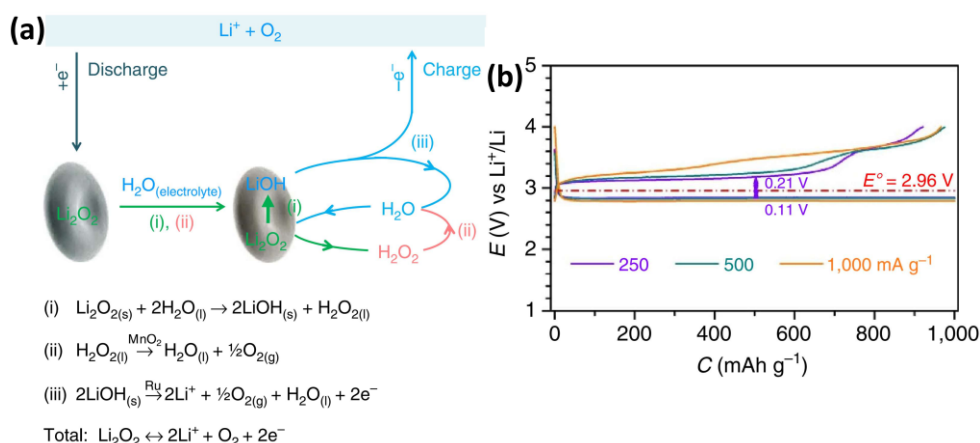


Figure 1-19. (a) Proposed reaction mechanism and (b) electrochemical performance of $\text{Li}-\text{O}_2$ battery with $\text{Ru}/\text{MnO}_2/\text{SP}$ as cathode in 0.5 M LiClO_4 with 120 ppm water.⁹³

Qiao et al. found when water was added as an additive in the absence of a catalyst, the discharge product was still Li_2O_2 . In this case, HO_2^- is the intermediate during the ORR/OER process as shown in Figure 1-20. Soluble HO_2^- allows the formation and decomposition of Li_2O_2 to proceed through the solution-phase chemical reaction, thus avoiding the slow kinetics between Li_2O_2 and the electrode, thereby reducing the overcharge potential.⁹⁶

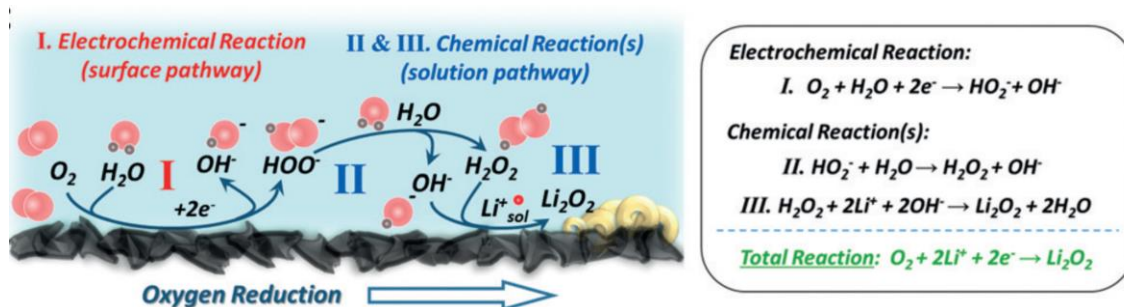


Figure 1-20. Proposed discharge mechanism of aprotic Li-O₂ battery with water addition.⁹⁶

1.4 Superconcentrated electrolytes for Li-O₂ batteries

Superconcentrated electrolyte is first used in the field of LIBs. Yamada et al. applied LITFSI-based superconcentrated electrolyte to various solvents in LIBs, such as, AN³⁷, DMSO³⁸, DME³⁶ and THF³⁸, which are considered incapable of forming a stable SEI on the graphite surface for the Li⁺ intercalations. By applying LITFSI-based superconcentrated electrolyte as a battery electrolyte, the reversible Li⁺ intercalation into a graphite electrode was observed, indicating more stable SEI than in dilute electrolyte. All results from in situ characterization^{36, 97-98} of SEI suggest that superconcentrated electrolytes tend to form anion-derived SEI full of inorganic compounds, whereas solvent-derived SEI rich in organic compounds was observed in a dilute electrolyte. The inorganic anion-derived SEI shows better mechanical stability and Li⁺ diffusion ability compared with organic solvent-derived SEI, which is the reason why anion-derived SEI is more stable.

Inspired by the superconcentrated electrolyte in LIBs, it was found that the superconcentrated electrolyte can not only stabilize the graphite anode, but also stabilize the lithium metal anode for lithium metal batteries. For example, in 4 M LITFSI/DME solution, a Li/Li symmetric cell could achieve 6000 cycles at 10 mA cm⁻², and the Li/Cu cell survives at 4 mA cm⁻² for more than 1000 cycles with a coulombic efficiency of 98.4%.⁹⁹ However, the cyclability in commonly 1 M LITFSI/DME solution was terrible. The enhanced cyclability in concentrated solution is attributed to FSI⁻ anions competitively react with Li and lead to the formation of a much thinner and denser inorganic SEI layer enriched by LiF that was decomposed from the salt. Besides LITFSI

and LITFSI salt mentioned above, concentrated electrolytes composed of LiNO_3 has also shown excellent passivating ability, such as in 4 M $\text{LiNO}_3/\text{DMSO}$ solution.¹⁰⁰ The component analysis show that the dense Li_2O -contained SEI formed by the reaction of LiNO_3 with lithium is the main reason for enhancing the cycle stability of the battery.

Since Li-O_2 battery belongs to lithium metal batteries, the use of superconcentrated electrolytes was thought to improve the cycle stability of the Li-O_2 battery. Recently, Liu et al. studied the effect of LITFSI concentration on the cycle stability of the Li-O_2 battery by using the LITFSI/DME solution. Cell with concentrated electrolyte shows a significant improvement in cyclability compared with that in diluted solutions. The author ascribes the improvement to that a stable SEI was created on the lithium anode in superconcentrated electrolyte.

Considering that SEI is composed of decomposition products of electrolyte, it is worth discussing the SEI formation from solvation structure of the electrolyte point of view. Based on Raman spectroscopy analysis, at low concentrations, the solvation structure of the electrolyte is mainly solvent-separated ion pairs (SSIP) and free solvent.³⁶ In the case of concentrated electrolyte, an anion of lithium salt joins the solvation shell due to the scare of free solvent to form contact ion pairs (CIPs) and cation-anion aggregates (AGGs). Anions are therefore participating in the formation of SEI by replacing solvent decomposition with the concentration of LITFSI increasing. (Figure 1-20). However, as SEI is forming by decomposing electrolyte on electrolyte/electrode interface instead of bulk solution. The solvation structure of electrolyte on electrolyte/electrode interface would reflect SEI formation more clearly. Therefore, the solvation structure of electrolyte on electrolyte/electrode interface would our one objective.

Yoo et al. also studied the effect of LiNO_3 concentration on the discharge capacity of Li-O_2 batteries in DMA.¹⁰¹ The Li-O_2 battery performance with 5 M LiNO_3/DMA exhibit a larger discharge capacity of 2 0000 mAh g^{-1} compared with that of 10000 mAh g^{-1} in 1 M LiNO_3/DMA solution. However, the reason of capacity enhancement is still not clear. The cell capacity in Li-O_2 battery is dependent on the reaction mechanism on air cathode. Liu et al. found that the discharge capacity of the Li-O_2 battery, is up to 600% greater within the concentration region of 10^{-3} to 5 M in LITFSI/TEGDME with different

concentrations. They believe that Li^+ concentration can regulate the morphology of Li_2O_2 on air cathode. and propose the nucleation and growth mechanism of Li_2O_2 .¹⁰² At low concentrations, Li_2O_2 tends to grow on the electrode surface as a film, which prevents electrons migrating through the film to forming more Li_2O_2 . At a medium concentration, Li_2O_2 growth three dimensionally, thus achieving high discharge capacity. When the concentration is higher than 4 M, the diffusion of oxygen is hindered by the discharge product, resulting in a low discharge capacitance. However, more experimental data is necessary to support this view. Although there have been many studies on the Li-O₂ battery performance with superconcentrated electrolytes, the effect of concentration on the reaction mechanism of oxygen electrodes is still limited. Especially using in-situ characterization to study the effect of lithium salt concentration on ORR mechanism in different donor number solvent like DMSO (with high donor number) and TEGDME (with low donor number).

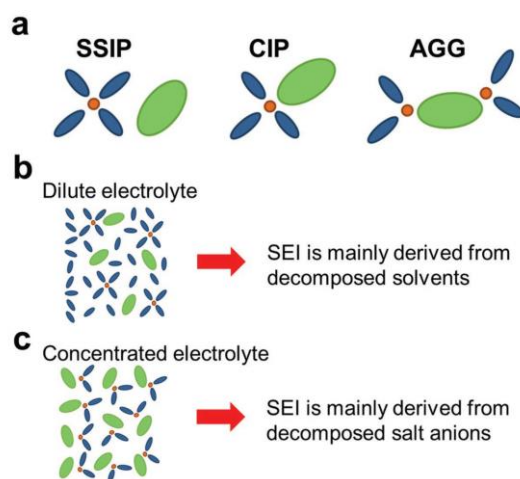


Figure 1-20. (a) Li^+ solvate species (SSIP, CIP and AGGs) in dilute and concentrated electrolytes. Schematic illustration of the electrolyte reduction mechanism at the electrode/electrolyte interface in (b) dilute and (c) concentrated electrolytes.¹⁰³

1.5 Objective and overview of the present thesis

The objective of this thesis is to study characteristics of the electrode/electrolyte interface in the superconcentrated electrolyte system for nonaqueous Li-O₂ battery, including the solvation structure at electrode/electrolyte interface, the effect of electrolyte concentration on ORR mechanism at air electrode under both DMSO and TEGDME

solutions, by using in-situ characterization methods such as electrochemical quartz crystal microbalance (EQCM) and Surface enhanced Raman spectroscopy (SERS) measurements.

In the present thesis, the gold electrode was used as model electrode for both anode and cathode of Li-O₂ battery because: (1) lithium metal is a very active metal, the electrolyte is unstable when it comes into contact with lithium, which makes it difficult to reveal the solvation structure at lithium/electrolyte interface. It's reported that lithium deposition/stripping would also develop on noble metal (i.e., Pt, Au and Ag) which is resemble on a lithium electrode in the same electrolyte.¹⁰⁴⁻¹⁰⁶ Thus, gold electrode was used as model electrode for lithium anode for understanding the interfacial solvation structure. (2) a). the use of gold rather than high surface area carbon for the air cathode has been shown to produce less Li₂CO₃ and limit the decomposition of DMSO, thus enhancing the cycling performance of Li-O₂ battery,^{47, 68, 88} b) the intrinsic ORR activity on gold electrode is much more active than glassy carbon during discharge.^{45, 107} c) the surface localized surface plasmons of gold allow for detecting species on electrode surface during electrochemistry by SERS.¹⁰⁸

In **Chapter 1**, the background of nonaqueous Li-O₂ battery is reviewed.

In **Chapter 2**, information about chemicals and setups, as well as experimental details are given.

In **Chapter 3**, the concentration-dependent solvation structure of LITFSI-DMSO on a gold model electrode has been investigated with various electrolyte concentrations using surface-enhanced Raman spectroscopy. At low concentrations, free DMSO and TFSI⁻ were found to be chemisorbed on the gold surface to form an adsorption layer. Among these, TFSI⁻ was chemisorbed via its oxygen atoms based on the observation of the $\nu(\text{Au-O})$ bond. Besides, chemisorbed TFSI⁻ at the gold surface did not coordinate with Li⁺ in the low concentration electrolyte. As the concentration gradually increased up to 2.31 M, chemisorbed TFSI⁻ started to coordinate with Li⁺. To further increase in LITFSI concentration above 2.31 M, chemisorbed DMSO was absent in the adsorption layer; instead, chemisorbed TFSI⁻ became the only species. The chemisorbed TFSI⁻ is proposed to be coordinated with Li⁺ by two of its oxygens in such high concentration, making its coordination saturated. The DMSO-free adsorption layer in electrolytes with

concentration above 2.31 M might help to form a dense and uniform SEI once an electrical field is applied, which contributes to improve the long-term cyclability of batteries.

In **Chapter 4**, in situ surface enhanced Raman spectroscopy (SERS) and electrochemical quartz crystal microbalance (EQCM) in combination with rotating ring/disk electrodes (RRDE) measurements were utilized for various concentration of LiNO_3 -DMSO solutions. It turns out that the effect of LiNO_3 concentration on oxygen reduction mainly achieved by affecting the O_2^- adsorbed on the electrode surface and LiO_2 dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. The dissolution of LiO_2 into bulk solution decrease with LiNO_3 concentration, suggesting surface reaction is promoted with concentration. While in the high-concentration electrolyte, due to the high viscosity of the electrolyte, a large amount of O_2^- is concentrated on the electrode surface, eventually failed to form Li_2O_2 .

In **Chapter 5**, the effect of LiNO_3 concentration in TEGDME, which is a most commonly used low donor number solvent, was investigated by EQCM and RRDE measurements. RRDE measurement shows that the dissolution of LiO_2 from disk electrode decrease as LiNO_3 concentration increase, which is due to the decrease of free TEGDME with concentration. EQCM measurement shows that, the concentration of LiNO_3 has almost no effect on the solid species deposition on electrode surface during ORR in LiNO_3 -TEGDME solution. O_2 was firstly electrochemically reduced into LiO_2 and leave electrode surface at low overpotential. At medium overpotential, O_2 is mainly converted to Li_2O_2 through surface two-electron reduction pathway, together with small part of LiO_2 dissolute into electrolyte. At high overpotential, oxygen is found to be reduced into LiO_2 on the surface of Li_2O_2 .

In **Chapter 6**, the general conclusion of the present thesis and future prospects are given

References

- (1) Dresselhaus, M. S.; Thomas, I. L. Alternative Energy Technologies. *Nature* **2001**, *414*, 332-337.
- (2) Steele, B. C. H.; Heinzel, A. Materials for Fuel-Cell Technologies. *Nature* **2001**, *414*, 345-352.
- (3) Gratzel, M. Photoelectrochemical Cells. *Nature* **2001**, *414*, 338-344.
- (4) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414*, 359-367.
- (5) Besenhard, J. O.; Eichinger, G. High-Energy Density Lithium Cells .1. Electrolytes and Anodes. *J. Electroanal. Chem.* **1976**, *68*, 1-18.
- (6) Yazami, R.; Touzain, P. A Reversible Graphite Lithium Negative Electrode for Electrochemical Generators. *J. Power Sources* **1983**, *9*, 365-371.
- (7) Bruce, P. G. Energy Storage Beyond the Horizon: Rechargeable Lithium Batteries. *Solid State Ionics* **2008**, *179*, 752-760.
- (8) Bruce, P. G.; Scrosati, B.; Tarascon, J. M. Nanomaterials for Rechargeable Lithium Batteries. *Angew. Chem. Int. Ed.* **2008**, *47*, 2930-2946.
- (9) Bruce, P. G.; Hardwick, L. J.; Abraham, K. M. Lithium-Air and Lithium-Sulfur Batteries. *MRS Bull.* **2011**, *36*, 506-512.
- (10) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. Li-O₂ and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19-29.
- (11) Abraham, D. P.; Furczon, M. M.; Kang, S. H.; Dees, D. W.; Jansen, A. N. Effect of Electrolyte Composition on Initial Cycling and Impedance Characteristics of Lithium-Ion Cells. *J Power Sources* **2008**, *180*, 612-620.
- (12) Stephan, A. M.; Nahm, K. S. Review on Composite Polymer Electrolytes for Lithium Batteries. *Polymer* **2006**, *47*, 5952-5964.
- (13) Knauth, P. Inorganic Solid Li Ion Conductors: An Overview. *Solid State Ionics* **2009**, *180*, 911-916.
- (14) Thangadurai, V.; Weppner, W. Recent Progress in Solid Oxide and Lithium Ion Conducting Electrolytes Research. *Ionics* **2006**, *12*, 81-92.
- (15) Akimoto, J.; Gotoh, Y.; Oosawa, Y. Synthesis and Structure Refinement of LiCoO₂ Single Crystals. *J Solid State Chem* **1998**, *141*, 298-302.

- (16) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. *JACS* **2013**, *135*, 1167-1176.
- (17) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air Battery. *J. Phys. Chem. C* **2010**, *114*, 9178-9186.
- (18) Wang, A. P.; Kadam, S.; Li, H.; Shi, S. Q.; Qi, Y. Review on Modeling of the Anode Solid Electrolyte Interphase (Sei) for Lithium-Ion Batteries. *Npj Computational Materials* **2018**, *4*.
- (19) Deng, D. Li-Ion Batteries: Basics, Progress, and Challenges. *Energy Science & Engineering* **2015**, *3*, 385-418.
- (20) Abraham, K. M.; Jiang, Z. A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery. *J. Electrochem. Soc.* **1996**, *143*, 1-5.
- (21) Ogasawara, T.; Debart, A.; Holzapfel, M.; Novak, P.; Bruce, P. G. Rechargeable Li₂O₂ Electrode for Lithium Batteries. *JACS* **2006**, *128*, 1390-1393.
- (22) Lu, J.; Li, L.; Park, J. B.; Sun, Y. K.; Wu, F.; Amine, K. Aprotic and Aqueous Li-O-2 Batteries. *Chem. Rev.* **2014**, *114*, 5611-5640.
- (23) Burke, C. M.; Pande, V.; Khetan, A.; Viswanathan, V.; McCloskey, B. D. Enhancing Electrochemical Intermediate Solvation through Electrolyte Anion Selection to Increase Nonaqueous Li-O-2 Battery Capacity. *Proceedings of the National Academy of Sciences of the United States of America* **2015**, *112*, 9293-9298.
- (24) Wu, S. C.; Zhu, K.; Tang, J.; Liao, K. M.; Bai, S. Y.; Yi, J.; Yamauchi, Y.; Ishida, M.; Zhou, H. S. A Long-Life Lithium Ion Oxygen Battery Based on Commercial Silicon Particles as the Anode. *Energy Environ. Sci.* **2016**, *9*, 3262-3271.
- (25) Khetan, A.; Luntz, A.; Viswanathan, V. Trade-Offs in Capacity and Rechargeability in Nonaqueous Li-O-2 Batteries: Solution-Driven Growth Versus Nucleophilic Stability. *Journal of Physical Chemistry Letters* **2015**, *6*, 1254-1259.
- (26) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Applications. *J. Phys. Chem. C* **2009**, *113*, 20127-20134.
- (27) Johnson, L.; Li, C. M.; Liu, Z.; Chen, Y. H.; Freunberger, S. A.; Ashok, P. C.; Praveen, B. B.; Dholakia, K.; Tarascon, J. M.; Bruce, P. G. The Role of LiO₂ Solubility

in O₂ Reduction in Aprotic Solvents and Its Consequences for Li-O₂ Batteries. *Nature Chemistry* **2014**, *6*, 1091-1099.

(28) Scheers, J.; Lidberg, D.; Sodeyama, K.; Futera, Z.; Tateyama, Y. Life of Superoxide in Aprotic Li-O₂ Battery Electrolytes: Simulated Solvent and Counter-Ion Effects. *PCCP* **2016**, *18*, 9961-9968.

(29) Viswanathan, V.; Thygesen, K. S.; Hummelshøj, J. S.; Nørskov, J. K.; Girishkumar, G.; McCloskey, B. D.; Luntz, A. C. Electrical Conductivity in Li₂O₂ and Its Role in Determining Capacity Limitations in Non-Aqueous Li-O₂ Batteries. *J. Chem. Phys.* **2011**, *135*.

(30) Sharon, D.; Hirsberg, D.; Salama, M.; Afri, M.; Frimer, A. A.; Noked, M.; Kwak, W.; Sun, Y. K.; Aurbach, D. Mechanistic Role of Li⁺ Dissociation Level in Aprotic Li-O₂ Battery. *Acs Applied Materials & Interfaces* **2016**, *8*, 5300-5307.

(31) Kwon, H. M.; Thomas, M. L.; Tatara, R.; Nakanishi, A.; Dokko, K.; Watanabe, M. Effect of Anion in Glyme-Based Electrolyte for Li-O₂ Batteries: Stability/Solubility of Discharge Intermediate. *Chem. Lett.* **2017**, *46*, 573-576.

(32) Ding, F., et al. Dendrite-Free Lithium Deposition Via Self-Healing Electrostatic Shield Mechanism. *JACS* **2013**, *135*, 4450-4456.

(33) Black, R.; Oh, S. H.; Lee, J. H.; Yim, T.; Adams, B.; Nazar, L. F. Screening for Superoxide Reactivity in Li-O₂ Batteries: Effect on Li₂O₂/LiOH Crystallization. *JACS* **2012**, *134*, 2902-2905.

(34) Shui, J. L.; Okasinski, J. S.; Kenesei, P.; Dobbs, H. A.; Zhao, D.; Almer, J. D.; Liu, D. J. Reversibility of Anodic Lithium in Rechargeable Lithium-Oxygen Batteries. *Nat. Commun.* **2013**, *4*.

(35) Xin, X.; Ito, K.; Dutta, A.; Kubo, Y. Dendrite-Free Epitaxial Growth of Lithium Metal During Charging in Li-O₂ Batteries. *Angewandte Chemie-International Edition* **2018**, *57*, 13206-13210.

(36) Yamada, Y.; Yaegashi, M.; Abe, T.; Yamada, A. A Superconcentrated Ether Electrolyte for Fast-Charging Li-Ion Batteries. *Chem. Commun.* **2013**, *49*, 11194-11196.

(37) Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A. Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries. *JACS* **2014**, *136*, 5039-5046.

- (38) Yamada, Y.; Usui, K.; Chiang, C. H.; Kikuchi, K.; Furukawa, K.; Yamada, A. General Observation of Lithium Intercalation into Graphite in Ethylene-Carbonate-Free Superconcentrated Electrolytes. *Acs Applied Materials & Interfaces* **2014**, *6*, 10892-10899.
- (39) Garcia-Lastra, J. M.; Bass, J. D.; Thygesen, K. S. Communication: Strong Excitonic and Vibronic Effects Determine the Optical Properties of Li_2O_2 . *J. Chem. Phys.* **2011**, *135*.
- (40) Chen, J. Z.; Hummelshoj, J. S.; Thygesen, K. S.; Myrdal, J. S. G.; Norskov, J. K.; Vegge, T. The Role of Transition Metal Interfaces on the Electronic Transport in Lithium-Air Batteries. *Catal. Today* **2011**, *165*, 2-9.
- (41) Harding, J. R.; Lu, Y. C.; Tsukada, Y.; Shao-Horn, Y. Evidence of Catalyzed Oxidation of Li_2O_2 for Rechargeable Li-Air Battery Applications. *PCCP* **2012**, *14*, 10540-10546.
- (42) McCloskey, B. D.; Scheffler, R.; Speidel, A.; Bethune, D. S.; Shelby, R. M.; Luntz, A. C. On the Efficacy of Electrocatalysis in Nonaqueous Li-O₂ Batteries. *JACS* **2011**, *133*, 18038-18041.
- (43) Qin, Y., et al. In Situ Fabrication of Porous-Carbon-Supported Alpha-MnO₂ Nanorods at Room Temperature: Application for Rechargeable Li-O₂ Batteries. *Energy Environ. Sci.* **2013**, *6*, 519-531.
- (44) Black, R.; Lee, J. H.; Adams, B.; Mims, C. A.; Nazar, L. F. The Role of Catalysts and Peroxide Oxidation in Lithium-Oxygen Batteries. *Angew. Chem. Int. Ed.* **2013**, *52*, 392-396.
- (45) Lu, Y. C.; Gasteiger, H. A.; Shao-Horn, Y. Catalytic Activity Trends of Oxygen Reduction Reaction for Nonaqueous Li-Air Batteries. *JACS* **2011**, *133*, 19048-19051.
- (46) Debart, A.; Paterson, A. J.; Bao, J.; Bruce, P. G. Alpha-MnO₂ Nanowires: A Catalyst for the O₂ Electrode in Rechargeable Lithium Batteries. *Angew. Chem. Int. Ed.* **2008**, *47*, 4521-4524.
- (47) Peng, Z. Q.; Freunberger, S. A.; Chen, Y. H.; Bruce, P. G. A Reversible and Higher-Rate Li-O₂ Battery. *Science* **2012**, *337*, 563-566.
- (48) Sevim, M.; Sener, T.; Metin, O. Monodisperse Mpd (M: Co, Ni, Cu) Alloy Nanoparticles Supported on Reduced Graphene Oxide as Cathode Catalysts for the

Lithium-Air Battery (Vol 40, Pg 10876, 2015). *Int. J. Hydrogen Energy* **2016**, *41*, 3318-3318.

(49) Li, F. J.; Chen, Y.; Tang, D. M.; Jian, Z. L.; Liu, C.; Golberg, D.; Yamada, A.; Zhou, H. S. Performance-Improved Li-O₂ Battery with Ru Nanoparticles Supported on Binder-Free Multi-Walled Carbon Nanotube Paper as Cathode. *Energy Environ. Sci.* **2014**, *7*, 1648-1652.

(50) Riaz, A.; Jung, K. N.; Chang, W.; Lee, S. B.; Lim, T. H.; Park, S. J.; Song, R. H.; Yoon, S.; Shin, K. H.; Lee, J. W. Carbon-Free Cobalt Oxide Cathodes with Tunable Nanoarchitectures for Rechargeable Lithium-Oxygen Batteries. *Chem. Commun.* **2013**, *49*, 5984-5986.

(51) Park, C. S.; Kim, K. S.; Park, Y. J. Carbon-Sphere/Co₃O₄ Nanocomposite Catalysts for Effective Air Electrode in Li/Air Batteries. *J. Power Sources* **2013**, *244*, 72-79.

(52) Ming, J.; Wu, Y. Q.; Park, J. B.; Lee, J. K.; Zhao, F. Y.; Sun, Y. K. Assembling Metal Oxide Nanocrystals into Dense, Hollow, Porous Nanoparticles for Lithium-Ion and Lithium-Oxygen Battery Application. *Nanoscale* **2013**, *5*, 10390-10396.

(53) Feng, N. N.; Mu, X. W.; Zheng, M. B.; Wang, C. Q.; Lin, Z. X.; Zhang, X. P.; Shi, Y.; He, P.; Zhou, H. S. A Multi-Layered Fe₂O₃/Graphene Composite with Mesopores as a Catalyst for Rechargeable Aprotic Lithium-Oxygen Batteries. *Nanotechnology* **2016**, *27*.

(54) McCloskey, B. D.; Speidel, A.; Scheffler, R.; Miller, D. C.; Viswanathan, V.; Hummelshøj, J. S.; Nørskov, J. K.; Luntz, A. C. Twin Problems of Interfacial Carbonate Formation in Nonaqueous Li-O₂ Batteries. *Journal of Physical Chemistry Letters* **2012**, *3*, 997-1001.

(55) Thotiyl, M. M. O.; Freunberger, S. A.; Peng, Z. Q.; Chen, Y. H.; Liu, Z.; Bruce, P. G. A Stable Cathode for the Aprotic Li-O₂ Battery. *Nat. Mater.* **2013**, *12*, 1049-1055.

(56) Liu, Z. Q.; Feng, N. N.; Shen, Z. H.; Li, F. J.; He, P.; Zhang, H. G.; Zhou, H. S. Carbon-Free O₂ Cathode with Three-Dimensional Ultralight Nickel Foam-Supported Ruthenium Electrocatalysts for Li-O₂ Batteries. *Chemsuschem* **2017**, *10*, 2714-2719.

(57) Xu, J. J.; Chang, Z. W.; Yin, Y. B.; Zhang, X. B. Nanoengineered Ultralight and Robust All-Metal Cathode for High-Capacity, Stable Lithium-Oxygen Batteries. *Acs Central Science* **2017**, *3*, 598-604.

- (58) Li, F. J.; Tang, D. M.; Jian, Z. L.; Liu, D. Q.; Golberg, D.; Yamada, A.; Zhou, H. S. Li-O₂ Battery Based on Highly Efficient Sb-Doped Tin Oxide Supported Ru Nanoparticles. *Adv. Mater.* **2014**, 26, 4659-+.
- (59) Kundu, D.; Black, R.; Adams, B.; Harrison, K.; Zavadil, K.; Nazar, L. F. Nanostructured Metal Carbides for Aprotic Li-O₂ Batteries: New Insights into Interfacial Reactions and Cathode Stability. *Journal of Physical Chemistry Letters* **2015**, 6, 2252-2258.
- (60) Adams, B. D.; Black, R.; Radtke, C.; Williams, Z.; Mehdi, B. L.; Browning, N. D.; Nazar, L. F. The Importance of Nanometric Passivating Films on Cathodes for Li-Air Batteries. *Acs Nano* **2014**, 8, 12483-12493.
- (61) Mizuno, F.; Nakanishi, S.; Kotani, Y.; Yokoishi, S.; Iba, H. Rechargeable Li-Air Batteries with Carbonate-Based Liquid Electrolytes. *Electrochemistry* **2010**, 78, 403-405.
- (62) Li, Y.; Wang, X. G.; Dong, S. M.; Chen, X.; Cui, G. L. Recent Advances in Non-Aqueous Electrolyte for Rechargeable Li-O₂ Batteries. *Adv. Energy Mater.* **2016**, 6.
- (63) Xu, D.; Wang, Z. L.; Xu, J. J.; Zhang, L. L.; Zhang, X. B. Novel Dmso-Based Electrolyte for High Performance Rechargeable Li-O₂ Batteries. *Chem. Commun.* **2012**, 48, 6948-6950.
- (64) Qiao, Y.; Ye, S. Spectroscopic Investigation for Oxygen Reduction and Evolution Reactions with Tetrathiafulvalene as a Redox Mediator in Li-O₂ Battery. *J. Phys. Chem. C* **2016**, 120, 15830-15845.
- (65) Younesi, R.; Norby, P.; Vegge, T. A New Look at the Stability of Dimethyl Sulfoxide and Acetonitrile in Li-O₂ Batteries. *ECS Electrochem. Lett.* **2014**, 3, A15-A18.
- (66) Sharon, D.; Etacheri, V.; Garsuch, A.; Afri, M.; Frimer, A. A.; Aurbach, D. On the Challenge of Electrolyte Solutions for Li-Air Batteries: Monitoring Oxygen Reduction and Related Reactions in Polyether Solutions by Spectroscopy and Eqcm. *Journal of Physical Chemistry Letters* **2013**, 4, 127-131.
- (67) Mozhzhukhina, N.; De Leo, L. P. M.; Calvo, E. J. Infrared Spectroscopy Studies on Stability of Dimethyl Sulfoxide for Application in a Li-Air Battery. *J. Phys. Chem. C* **2013**, 117, 18375-18380.
- (68) Sharon, D.; Afri, M.; Noked, M.; Garsuch, A.; Frimer, A. A.; Aurbach, D. Oxidation of Dimethyl Sulfoxide Solutions by Electrochemical Reduction of Oxygen. *Journal of Physical Chemistry Letters* **2013**, 4, 3115-3119.

- (69) Bryantsev, V. S.; Giordani, V.; Walker, W.; Blanco, M.; Zecevic, S.; Sasaki, K.; Uddin, J.; Addison, D.; Chase, G. V. Predicting Solvent Stability in Aprotic Electrolyte Li-Air Batteries: Nucleophilic Substitution by the Superoxide Anion Radical ($O_2^{\cdot-}$). *J. Phys. Chem. A* **2011**, *115*, 12399-12409.
- (70) McCloskey, B. D.; Bethune, D. S.; Shelby, R. M.; Girishkumar, G.; Luntz, A. C. Solvents' Critical Role in Nonaqueous Lithium-Oxygen Battery Electrochemistry. *Journal of Physical Chemistry Letters* **2011**, *2*, 1161-1166.
- (71) Jung, H. G.; Hassoun, J.; Park, J. B.; Sun, Y. K.; Scrosati, B. An Improved High-Performance Lithium-Air Battery. *Nature Chemistry* **2012**, *4*, 579-585.
- (72) Li, F. J.; Zhang, T.; Yamada, Y.; Yamada, A.; Zhou, H. S. Enhanced Cycling Performance of Li-O₂ Batteries by the Optimized Electrolyte Concentration of Litfsa in Glymes. *Adv. Energy Mater.* **2013**, *3*, 532-538.
- (73) Adams, B. D.; Black, R.; Williams, Z.; Fernandes, R.; Cuisinier, M.; Berg, E. J.; Novak, P.; Murphy, G. K.; Nazar, L. F. Towards a Stable Organic Electrolyte for the Lithium Oxygen Battery. *Adv. Energy Mater.* **2015**, *5*.
- (74) Kuboki, T.; Okuyama, T.; Ohsaki, T.; Takami, N. Lithium-Air Batteries Using Hydrophobic Room Temperature Ionic Liquid Electrolyte. *J. Power Sources* **2005**, *146*, 766-769.
- (75) Liu, Q. C., et al. Artificial Protection Film on Lithium Metal Anode toward Long-Cycle-Life Lithium-Oxygen Batteries (Vol 27, Pg 5241, 2015). *Adv. Mater.* **2015**, *27*, 6089-6089.
- (76) Younesi, R.; Urbonaitė, S.; Edstrom, K.; Hahlin, M. The Cathode Surface Composition of a Cycled Li-O₂ Battery: A Photoelectron Spectroscopy Study. *J. Phys. Chem. C* **2012**, *116*, 20673-20680.
- (77) Veith, G. M.; Nanda, J.; Delmau, L. H.; Dudney, N. J. Influence of Lithium Salts on the Discharge Chemistry of Li-Air Cells. *Journal of Physical Chemistry Letters* **2012**, *3*, 1242-1247.
- (78) Aetukuri, N. B.; McCloskey, B. D.; Garcia, J. M.; Krupp, L. E.; Viswanathan, V.; Luntz, A. C. Solvating Additives Drive Solution-Mediated Electrochemistry and Enhance Toroid Growth in Non-Aqueous Li-O₂ Batteries. *Nature Chemistry* **2015**, *7*, 50-56.

- (79) Meini, S.; Piana, M.; Tsiouvaras, N.; Garsuch, A.; Gasteiger, H. A. The Effect of Water on the Discharge Capacity of a Non-Catalyzed Carbon Cathode for Li-O-2 Batteries. *Electrochemical and Solid State Letters* **2012**, *15*, A45-A48.
- (80) Nasybulin, E.; Xu, W.; Engelhard, M. H.; Nie, Z. M.; Burton, S. D.; Cosimbescu, L.; Gross, M. E.; Zhang, J. G. Effects of Electrolyte Salts on the Performance of Li-O-2 Batteries. *J. Phys. Chem. C* **2013**, *117*, 2635-2645.
- (81) Gunasekara, I.; Mukerjee, S.; Plichta, E. J.; Hendrickson, M. A.; Abraham, K. M. Microelectrode Diagnostics of Lithium-Air Batteries. *J. Electrochem. Soc.* **2014**, *161*, A381-A392.
- (82) Oh, S. H.; Yim, T.; Pomerantseva, E.; Nazar, L. F. Decomposition Reaction of Lithium Bis(Oxalato)Borate in the Rechargeable Lithium-Oxygen Cell. *Electrochemical and Solid State Letters* **2011**, *14*, A185-A188.
- (83) Sharon, D.; Hirsberg, D.; Afri, M.; Chesneau, F.; Lavi, R.; Frimer, A. A.; Sun, Y. K.; Aurbach, D. Catalytic Behavior of Lithium Nitrate in Li-O-2 Cells. *Acs Appl Mater Inter* **2015**, *7*, 16590-16600.
- (84) Kang, S. J.; Mori, T.; Narizuka, S.; Wilcke, W.; Kim, H. C. Deactivation of Carbon Electrode for Elimination of Carbon Dioxide Evolution from Rechargeable Lithium-Oxygen Cells. *Nat. Commun.* **2014**, *5*.
- (85) Guo, J.; Wen, Z. Y.; Wu, M. F.; Jin, J.; Liu, Y. Vinylene Carbonate-LiNO₃: A Hybrid Additive in Carbonic Ester Electrolytes for SEI Modification on Li Metal Anode. *Electrochem. Commun.* **2015**, *51*, 59-63.
- (86) Aurbach, D.; McCloskey, B. D.; Nazar, L. F.; Bruce, P. G. Advances in Understanding Mechanisms Underpinning Lithium-Air Batteries. *Nature Energy* **2016**, *1*.
- (87) Feng, N. N.; He, P.; Zhou, H. S. Enabling Catalytic Oxidation of Li₂O₂ at the Liquid-Solid Interface: The Evolution of an Aprotic Li-O-2 Battery. *ChemSuschem* **2015**, *8*, 600-602.
- (88) Chen, Y. H.; Freunberger, S. A.; Peng, Z. Q.; Fontaine, O.; Bruce, P. G. Charging a Li-O-2 Battery Using a Redox Mediator. *Nature Chemistry* **2013**, *5*, 489-494.
- (89) Lim, H. D., et al. Superior Rechargeability and Efficiency of Lithium-Oxygen Batteries: Hierarchical Air Electrode Architecture Combined with a Soluble Catalyst. *Angew. Chem. Int. Ed.* **2014**, *53*, 3926-3931.

- (90) Kundu, D.; Black, R.; Adams, B.; Nazar, L. F. A Highly Active Low Voltage Redox Mediator for Enhanced Rechargeability of Lithium-Oxygen Batteries. *Acs Central Science* **2015**, *1*, 510-515.
- (91) Feng, N. N.; Mu, X. W.; Zhang, X. P.; He, P.; Zhou, H. S. Intensive Study on the Catalytical Behavior of N-Methylphenothiazine as a Soluble Mediator to Oxidize the Li₂O₂ Cathode of the Li-O₂ Battery. *Acs Applied Materials & Interfaces* **2017**, *9*, 3733-3739.
- (92) Lee, D. J.; Lee, H.; Kim, Y. J.; Park, J. K.; Kim, H. T. Sustainable Redox Mediation for Lithium-Oxygen Batteries by a Composite Protective Layer on the Lithium-Metal Anode. *Adv. Mater.* **2016**, *28*, 857-863.
- (93) Li, F. J.; Wu, S. C.; Li, D.; Zhang, T.; He, P.; Yamada, A.; Zhou, H. S. The Water Catalysis at Oxygen Cathodes of Lithium-Oxygen Cells. *Nat. Commun.* **2015**, *6*.
- (94) Wu, S. C.; Tang, J.; Li, F. J.; Liu, X. Z.; Zhou, H. S. Low Charge Overpotentials in Lithium-Oxygen Batteries Based on Tetraglyme Electrolytes with a Limited Amount of Water. *Chem. Commun.* **2015**, *51*, 16860-16863.
- (95) Liu, T.; Leskes, M.; Yu, W. J.; Moore, A. J.; Zhou, L. N.; Bayley, P. M.; Kim, G.; Grey, C. P. Cycling Li-O₂ Batteries Via LiOH Formation and Decomposition. *Science* **2015**, *350*, 530-533.
- (96) Qiao, Y.; Wu, S. C.; Yi, J.; Sun, Y.; Guo, S. H.; Yang, S. X.; He, P.; Zhou, H. S. From O₂(-) to HO₂⁻ : Reducing by-Products and Overpotential in Li-O₂ Batteries by Water Addition. *Angew. Chem. Int. Ed.* **2017**, *56*, 4960-4964.
- (97) Jeong, S. K.; Inaba, M.; Iriyama, Y.; Abe, T.; Ogumi, Z. Interfacial Reactions between Graphite Electrodes and Propylene Carbonate-Based Solutions: Electrolyte-Concentration Dependence of Electrochemical Lithium Intercalation Reaction. *J. Power Sources* **2008**, *175*, 540-546.
- (98) Nie, M. Y.; Abraham, D. P.; Seo, D. M.; Chen, Y. J.; Bose, A.; Lucht, B. L. Role of Solution Structure in Solid Electrolyte Interphase Formation on Graphite with LiPF₆ in Propylene Carbonate. *J. Phys. Chem. C* **2013**, *117*, 25381-25389.
- (99) Qian, J. F.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J. G. High Rate and Stable Cycling of Lithium Metal Anode. *Nat. Commun.* **2015**, *6*.

- (100) Togasaki, N.; Momma, T.; Osaka, T. Enhanced Cycling Performance of a Li Metal Anode in a Dimethylsulfoxide-Based Electrolyte Using Highly Concentrated Lithium Salt for a Lithium-Oxygen Battery. *J. Power Sources* **2016**, *307*, 98-104.
- (101) Yoo, E.; Qiao, Y.; Zhou, H. S. Understanding the Effect of the Concentration of LiNO_3 Salt in Li-O₂ Batteries. *Journal of Materials Chemistry A* **2019**, *7*, 18318-18323.
- (102) Liu, Y.; Suo, L.; Lin, H.; Yang, W.; Fang, Y.; Liu, X.; Wang, D.; Hu, Y. S.; Han, W.; Chen, L. Novel Approach for a High-Energy-Density Li-Air Battery: Tri-Dimensional Growth of Li_2O_2 Crystals Tailored by Electrolyte Li^+ Ion Concentrations. *Journal of Materials Chemistry A* **2014**, *2*, 9020-9024.
- (103) Zheng, J. M.; Lochala, J. A.; Kwok, A.; Deng, Z. Q. D.; Xiao, J. Research Progress Towards Understanding the Unique Interfaces between Concentrated Electrolytes and Electrodes for Energy Storage Applications. *Adv. Sci.* **2017**, *4*.
- (104) Aurbach, D.; Daroux, M.; Faguy, P.; Yeager, E. The Electrochemistry of Noble-Metal Electrodes in Aprotic Organic-Solvents Containing Lithium-Salts. *J. Electroanal. Chem.* **1991**, *297*, 225-244.
- (105) Ely, Y. E.; Aurbach, D. Identification of Surface-Films Formed on Active Metals and Nonactive Metal-Electrodes at Low Potentials in Methyl Formate Solutions. *Langmuir* **1992**, *8*, 1845-1850.
- (106) Aurbach, D.; Moshkovich, M.; Cohen, Y.; Schechter, A. The Study of Surface Film Formation on Noble-Metal Electrodes in Alkyl Carbonates/Li Salt Solutions, Using Simultaneous in Situ Afm, Eqcm, Ftir, and Eis. *Langmuir* **1999**, *15*, 2947-2960.
- (107) Lu, Y. C.; Gasteiger, H. A.; Crumlin, E.; McGuire, R.; Shao-Horn, Y. Electrocatalytic Activity Studies of Select Metal Surfaces and Implications in Li-Air Batteries. *J. Electrochem. Soc.* **2010**, *157*, A1016-A1025.
- (108) Campion, A.; Kambhampati, P. Surface-Enhanced Raman Scattering. *Chem. Soc. Rev.* **1998**, *27*, 241-250.

Chapter 2

Experimental

2.1 Materials

H₂SO₄ (96~98%), KCl (99.5%) and LiNO₃ (99%) were purchased from Wako Pure Chemical Industries. Alumina slurries (1, 0.3 and 0.05 μm) were supplied by Baikowski International. Mill-Q water was used for preparing aqueous solutions. Ultrapure Ar and O₂ gas (99.999%) were used throughout the experiment. Gold foil was purchased from the Nilaco Corporation. Li wire (99%), ferrocene (98%) (denote as Fc) and tetrabutylammonium nitrate (TBANO₃, 97%) were purchased from Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl)imide salt (LITFSI, 99.9%) and anhydrous dimethyl sulfoxide (DMSO, 99%) were purchased from Kishida Chemical. All the solvents were dried with 4A molecular sieves for at least 7 days, and used after filtering with a 200 nm pore-sized nylon filter in the glove box (H₂O <0.5 ppm, O₂ <0.2 ppm). Before use, LiNO₃ and LITFSI was dried at 120 °C for 1 day to remove moisture. The drying setup was shown in Figure 2-1. All organic solvents and lithium salts are stored in the glove box. Water content in electrolyte solutions was measured by coulometric karl-fischer moisture meter (model: CA-21).

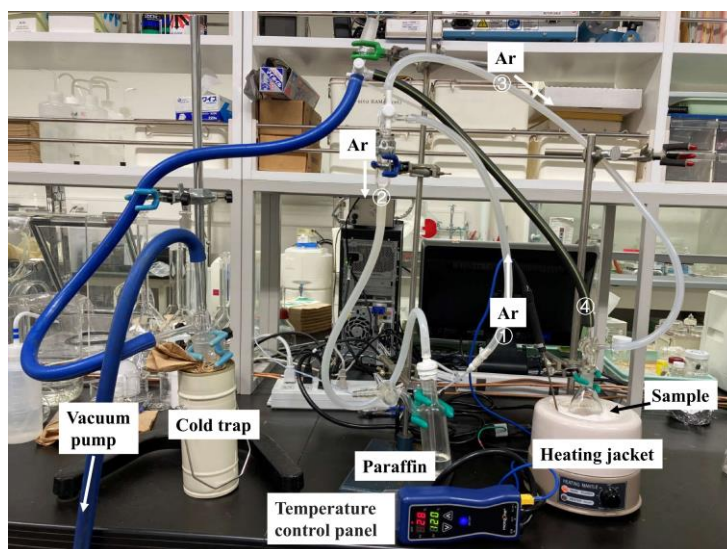


Figure 2-1. Setup for drying lithium salts and molecule sieves.

2.2 Surface enhance Raman spectroscopy (SERS) measurements

2.2.1 Principle of SERS measurement

In order to get the molecule information of species on the electrode surface, SERS was used. SERS is a surface-sensitive technology, which is capable of enhancing the Raman scattering signal of molecules in the vicinity of rough metal surface. The enhancement factor could reach as high as 10^{10} , which means single molecule could be detected by this technique.¹⁻² Electromagnetic mechanism and chemical mechanism were widely accepted as the origin of SERS.³⁻⁵ Electromagnetic mechanism refers to the enhanced intensity of Raman signal for adsorbate on the metal particle surface (e.g. Pt, Au and Ag) by electric field near the surface. When the incident light irradiates the surface, the surface localized surface plasmons are excited. The enhancement becomes higher, when the plasma frequency is in resonance with the radiation. To allow scattering to occur, rough metal surfaces or nanoparticles with specific arrangements are required as these surfaces provide enough localized collective oscillations. It is generally believed that when the distance between nanoparticles is less than 10 nm, a significant Raman enhancement would be produced.⁶⁻⁸ These localized areas are referred as “hotspots”. For example, as shown in Figure 2-2, analytes between gold particles shows stronger Raman scattering signal than that located at the gold monomer surface.⁹

Chemical mechanism means charge transfer between the analyte molecules and nanoparticle. It only occurs when analyte is chemisorbed on the particle surface. The electronic configuration of the chemical species changes more or less upon adsorption, leading to the change in the Raman cross section. The enhancement of the Raman cross section comes from intensity-borrowing from the metal, which has a high scattering cross section. SERS of species in direct contact with the surface are often different from those of species in the condensed phase in relative intensity and in position of Raman bands. The “chemical” enhancement is a kind of resonance Raman effect, it has chemical specificity, the relative intensity of Raman bands may change in the SER spectra, and the enhancement factor changes significantly from system to system. In addition, the “chemical” enhancement may take place for species adsorbed on solid substrates other than free-electron metals. The adsorption on transition metals, however, gives rise to high affinity levels and the resulting enhancement is low.

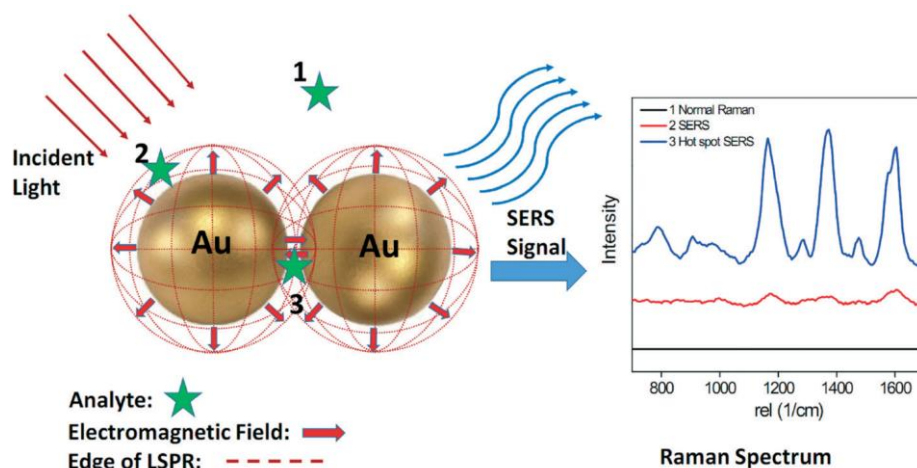


Figure 2-2. Schematic of SERS effect for an organic analyte on Au nanoparticles.⁹

2.2.2 SERS substrate preparation

In the present study, SERS substrate was prepared by electrochemical roughening and gold was used as substrate because it's chemically stable under the operating potential region. The detail procedure is as follows. Gold foil (thickness 1 mm, 10×10 mm² wide, 99.95% pure, Nilaco Corporation, Japan) was first polished by 400# sand paper to pre-roughen gold surface, then cleaned by ultrasonication in an ethanol and Milli-Q water mixture for 10 min to remove surface contamination. The gold foil was then electrochemically cleaned in a 0.5 M H₂SO₄ aqueous solution from -0.2 to 1.5 V at 50 mV s⁻¹ for five cycles with a potentiostat (HZ-7000, Hokuto Denko). The surface of the clean gold foil was rinsed with Milli-Q water to remove remaining H₂SO₄. The clean foil was immersed in 0.1 M KCl aqueous solutions and electrochemically roughened by cycling for several cycles in the potential range of -0.3 to 1.4 V at a scan rate of 0.2 V s⁻¹ using an Ag/AgCl electrode saturated with NaCl as the reference electrode and Pt wire as the counter electrode, as shown in Figure 2-3. The modified gold foil was rinsed and stored in Milli-Q water for further use. Before Raman measurement, the Milli-Q water on SERS substrate was flushed away by Ar gas gun. The electrochemical surface area of as-prepared gold substrate is 0.56 cm² for in situ SERS measurements using oxide stripping charge in Ar-saturated 0.1 M H₂SO₄ by conversion factor of 440 μC cm⁻².¹⁰⁻¹¹ In order to obtain a SERS substrate with a high enhancement factor, the roughness of the sandpaper and the cycle number during electrochemical roughening were studied.

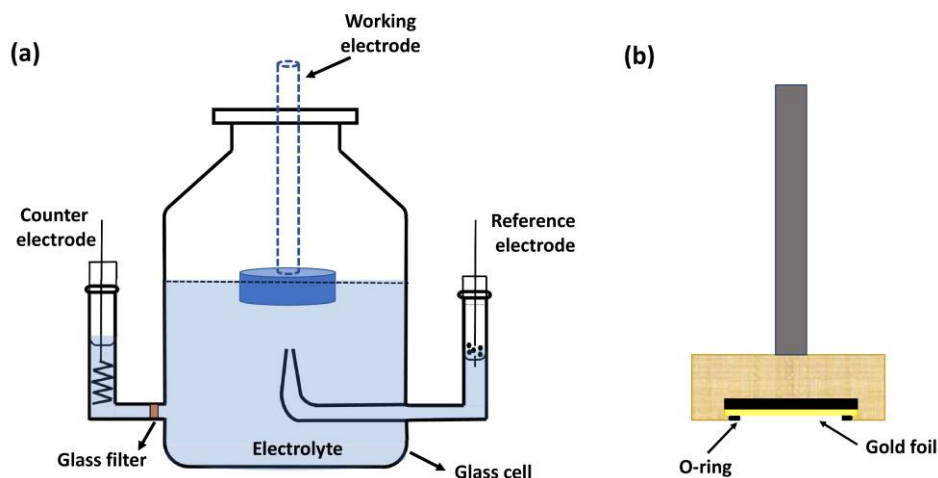


Figure 2-3. (a) Schematic illustration of typical three-electrode electrochemical cell for gold SERS substrate preparation. (b) Cross section views of working electrode.

2.2.3 Parameter of Raman measurements

Concentration-dependence Raman spectra for LITFSI-DMSO and LiNO₃-DMSO solutions in chapter 3 were recorded using a confocal microscope spectrometer (RamanTouch-VIS-NIR). The excitation light of a cooled diode laser at a wavelength of 785 nm was focused on the gold surface through a 10× long working distance lens (Olympus America Inc.). The power of the laser beam incident on the gold surface was 3 mW and the exposure time was 20 s; the grating was 300 grooves mm⁻¹ with a spectral resolution of 3.5 cm⁻¹. Raman measurements were performed in a superdry room (water contents: <0.1 ppm, 297 K, Shinryo Corp). A Gaussian-Lorentzian (pseudo-Voigt) function was used to deconvolute the Raman peaks at designated frequency regions.

In situ SERS was carried out in PTFE-made three-electrode Raman cell with Li wire as counter and reference electrode. The SERS working electrode was fixed to the Raman cell via chemically stable O-ring (inner diameter = 6.8 mm). (Figure 2-4) The electrolyte was purged by high-purity Ar/O₂ for 30 min before injecting into the Raman cell. The 785 nm laser was irradiated onto the electrode surface through a quartz window (thickness= 1 mm). Spectra were collected for every 20 s during cyclic voltammetry in the potential region of OCP to 2.0 V vs. Li/Li⁺ at 2 mV s⁻¹.

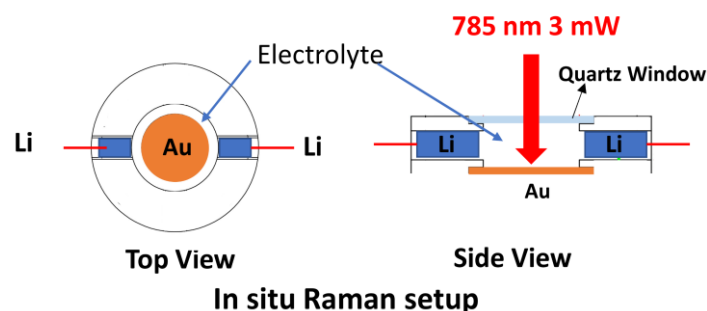


Figure 2-4. Schematic illustration of in situ Raman cell.

2.3 Electrochemical quartz crystal microbalance (EQCM) measurements

2.3.1 Principle of EQCM measurements

EQCM is a technique that is very sensitive to surface mass change in the order of ng and is used to measure the mass change on electrode during electrochemical process.¹²⁻¹⁴ The electrode was made from a thin AT-cut crystal (at an angle of approximately 35° with respect the *x*-axis) deposited by metal thin film on both sides of the crystal. The use of EQCM is based on the piezoelectric effect of quartz crystal.¹⁵⁻¹⁶ Once alternating current was applied to the quartz, the oscillation would be induced. The frequency of oscillation could be affected by the addition and remove rigid species on the electrode surface. The change of frequency could be monitored in real time with potential to get the information of molecules interact with electrode, such as metal deposition and oxidation, etc. The frequency change could be converted into mass change by the well-known Sauerbrey equation:¹⁷

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (2-1)$$

Where f_0 is the resonant frequency of the fundamental mode (Hz), Δf is normalized frequency change (Hz), Δm is a mass change (g), A is piezoelectrically active crystal area (area between the electrodes, cm²), ρ_q is the density of quartz (2.648 g cm⁻³) and μ_q is the shear modulus of quartz for AT-cut crystal (2.947×10¹¹ g cm⁻¹ s⁻²). When the working electrode is selected, except Δf and Δm , all parameters have specific values, thus the Sauerbrey equation could be expressed as follows:

$$\Delta m = -S \cdot \Delta f \quad (2-2)$$

, in which S is the sensitivity factor of the equipment ($\text{ng Hz}^{-1} \text{cm}^{-2}$).

2.3.2 Parameter for EQCM measurements

EQCM measurements were carried out by the QCA-922 system (Seiko EG & G Co., Ltd.). The working electrode was AT-cut quartz crystal deposited by gold thin films ($\varphi = 5.3 \text{ mm}$, roughness $< 0.06 \mu\text{m}$, fundamental resonant frequency: 9 MHz). A three-electrode electrochemical cell made by PTFE and glass was used for the measurement. (Figure 2-5) The reference electrode was Ag/Ag^+ , which Ag wire was put into in a compartment filled with DMSO solution of 10 mM AgNO_3 and $0.1 \text{ M NBu}_4\text{PF}_6$. The potential of Ag/Ag^+ was converted to quasi-reversible Li/Li^+ electrode by the potential of a ferrocene/ferrocenium redox couple (Fc/Fc^+) in the Ar saturated electrolyte solution containing 7.5 mM ferrocene (see below). The Pt wire was used as counter electrode. The electrolyte solution was purged with high-purity O_2 for 30 min before the experiment and the cell was purged thought the whole experiment. The gate time for the experiment was 0.1 s . The sensitivity factor of the present system was determined by Ag deposition in 0.01 AgPF_6 - 0.1 M LiPF_6 DMSO solution and the value was $5.5 \text{ ng Hz}^{-1} \text{cm}^{-2}$. The frequency and resistance were recorded during cyclic voltammetry in the potential region of OCP to -1.6 V vs. Ag/Ag^+ . The electrochemical surface area of Au EQCM substrate for electrochemistry is 0.27 cm^2 using oxide stripping charge in Ar-saturated $0.1 \text{ M H}_2\text{SO}_4$.

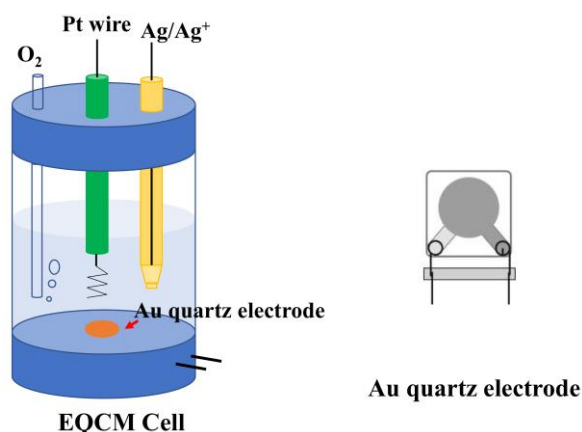


Figure 2-5. Schematic illustration of EQCM cell and Au quartz electrode.

2.4 Rotating ring disk electrode (RRDE) measurements

2.4.1 Principle of RRDE measurement

Rotating ring/disk electrode is an effective electrochemical technique for studying soluble products. The configuration of the working electrode is shown in Figure 2-6, there are usually two kinds of electrodes, RRDE and RDE. RDE is made of a round electrode material such as Pt, glassy carbon, etc. embedded in the center of a non-conductive material such as PTFE. In RRDE, a ring surrounds the disk electrode with an insulating material between them. When the electrode rotates, the electrolyte will move towards the disk electrode vertically due to convection, and move towards the ring electrode after contacting the electrode surface. The thickness of diffusion layer for soluble species are dependent on the rotation rate. If potential is applied to disk electrode, the soluble species generated on the surface of the disk electrode will be brought to the surface of the ring electrode. At this time, if a potential sufficient to trigger an electrochemical reaction of the soluble species is applied to the ring electrode, the amount of the soluble species could be calculated from the ring current.

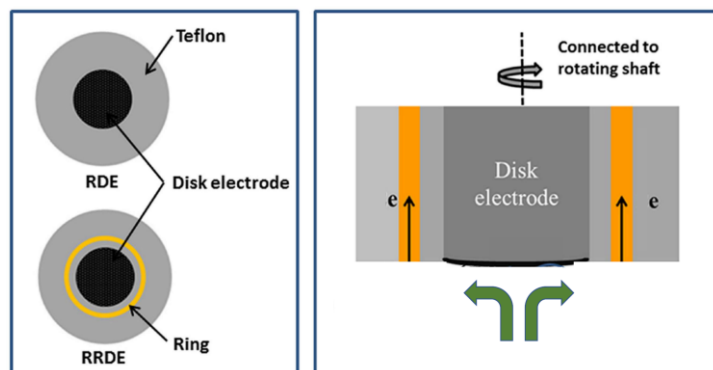


Figure 2-6. Schematic illustration of RDE and RRDE electrode. Left is top view of RDE and RRDE electrode, right is cross view of RRDE electrode.¹⁸

2.4.2 Parameter of RRDE measurement

In the present study, RRDE experiments were performed in a gastight beak-type RRDE cell with Au ring ($\phi_{\text{I.D.}} = 5.5$ mm, $\phi_{\text{O.D.}} = 8.2$ mm)-Au disk ($\phi = 5.3$ mm) as working electrodes, Ag/Ag⁺ as reference electrode and Pt wire as counter electrode. All the experiments were carried out in the superdry room with a speed control unit (Pine

Research Instruments, AFMSRCE-2743). The electrolyte solution was purged with high-purity O_2 for 30 min before the experiment and the cell was purged throughout the whole experiment. The electrochemical surface area of polished RRDE gold electrode is 0.25 cm^2 using oxide stripping charge in Ar-saturated $0.1\text{ M H}_2\text{SO}_4$. The collection efficiency of the RRDE evaluated from ring/disk charge ratio verified with the O_2/O_2^- redox couple in O_2 saturated- $0.1\text{ M TBANO}_3/\text{DMSO}$ solution as shown in Figure 2-7, is 0.23. The potential on disk was scanned from -0.5 V to -1.8 V vs. Ag/Ag^+ at a scan rate of 10 mV s^{-1} with the rotation speed of 1600 rpm . With the potential scan negatively, a cathodic current was observed, which is corresponding to the reduction of O_2 into O_2^- :



The generated O_2^- during this process was transferred to the ring electrode due to convection induced by the rotation of the electrode. The ring potential was held at 0.3 V vs. Ag/Ag^+ , at which the O_2^- was electrooxidized back to O_2 as shown in the reaction:

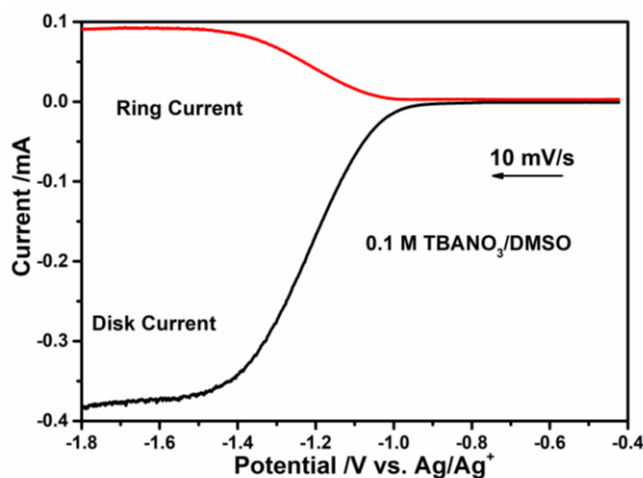
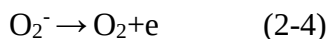


Figure 2-7. Rotating ring disk voltammograms of O_2/O_2^- system in $0.1\text{ M TBANO}_3/\text{DMSO}$ solution at 10 mV s^{-1} with a rotation speed of 1600 rpm .

2.5 Calibration of Ag/Ag^+ reference electrode in $\text{LiNO}_3\text{-DMSO}$ solutions

The Ag/Ag^+ reference electrode was used in EQCM and RRDE measurements in chapter 4 because of its mechanical stability, voltage stability and long lifetime. To note that the electrode potential in lithium batteries is usually referred against the Li/Li^+ couple.

In order to convert potential vs. Ag/Ag^+ to potential vs. Li/Li^+ , calibration should be done against a true reference electrode. In the present study, Fc/Fc^+ couple in nonaqueous solution was used since it is among the best example of solvent- and concentration-independent redox system.¹⁹

The Fc/Fc^+ redox potential against Ag/Ag^+ reference electrode and the Li/Li^+ electrode was determined under setup in Figure 2-8. In this experiment, gold foil was used as working electrode, Pt wire was used as counter electrode, lithium wire and Ag/Ag^+ was used as reference electrode, respectively. The electrolytes investigated were 0.58 M, 1.14 M, 2.21 M, 2.87 M and 4.13 M $\text{LiNO}_3/\text{DMSO}$ solutions, corresponding to the $\text{LiNO}_3/\text{DMSO}$ molar ratio of 1:24, 1:12, 1:6, 1:5 and 1:3, respectively (Note: the solution is saturated in 4.13 M solution). During the operation, electrolyte solution with 7.5 mM Fc was injected into the main chamber of the cell, separated from the reference chamber by a glass filter. Since Fc and lithium metal cannot coexist stably, when measuring Fc/Fc^+ redox potential vs. Li/Li^+ , the reference chamber should be filled with investigated solution without Fc . For Ag/Ag^+ potential calibration, the potential window was set between -0.8 V and 0.6 V with scan rate of 10 mV/s, while in the case of Li/Li^+ potential, potential window is from 2.8 V to 4.2 V. All experiments were carried out in the glove box.

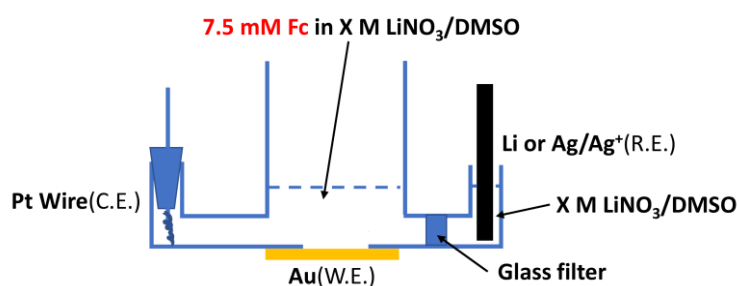
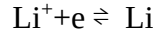


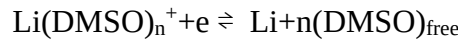
Figure 2-8. Experimental setup for calibration of reference electrode.

Figure 2-9(a) and (b) shows cyclic voltammogram for various concentrations of $\text{LiNO}_3/\text{DMSO}$ solutions with 7.5 mM ferrocene by using lithium wire and Ag/Ag^+ as reference electrode, respectively. A reduction and an oxidation peak could be observed for each concentration which corresponds to the one-electron reduction and oxidation of Fc/Fc^+ redox couple.²⁰ It can be found that as the concentration of LiNO_3 increases, the

formal potential $(E_{pa}+E_{pc})/2$ of Fc/Fc^+ redox/oxidation couple shifts to negative potential. Since Fc/Fc^+ potential is independent of the Li salt concentration, the shift in the peak position reflects the shift in the reference electrode potential caused by the concentration change. This shift is more obvious for the lithium reference electrode, compared with Ag/Ag^+ reference electrode. For lithium reference electrode, electrode reaction is not only,



instead,



Li^+ cannot exist itself in DMSO solution, it will coordinate with free DMSO to form $Li(DMSO)_n^+$. The coordination structure of $Li^+(Li(DMSO)_n^+)$ is different under different concentration electrolyte. Thus, the shift potential of the Li reference electrode is due to different activities of the $Li(DMSO)_n^+$ complex and free $(DMSO)_{free}$ instead of Li^+ activity alone. As for Ag/Ag^+ reference electrode, the electrode reaction is,

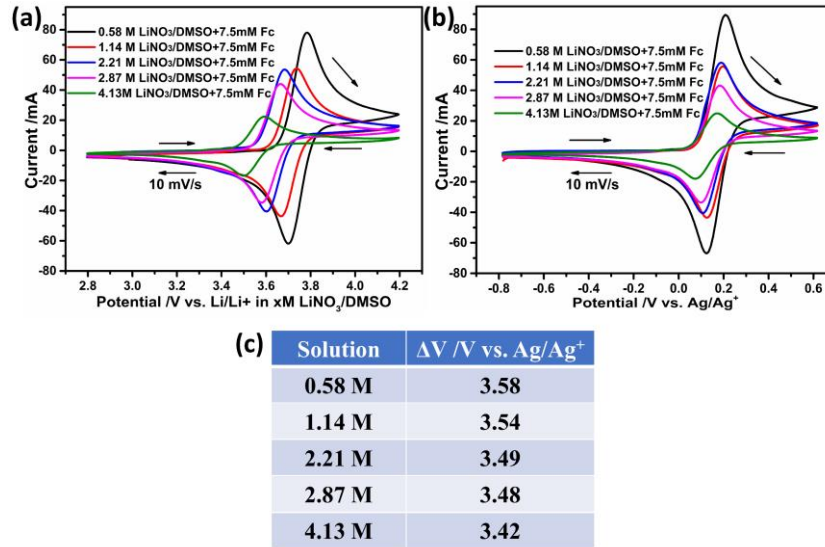
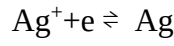


Figure 2-9. Comparison of cyclic voltammogram for 0.58, 1.14, 2.21, 2.87 and 4.13 M $LiNO_3/DMSO$ solutions with 7.5 mM ferrocene with (a) Li wire, and (b) Ag/Ag^+ electrode as reference electrode, (c) the difference between lithium reference electrode and Ag/Ag^+ reference electrode in different concentrated $LiNO_3/DMSO$ solutions.

Lithium salt is not involved in electrode reaction, the slightly shift of electrode potential is probably due to the different ionic mobility between the solution in the electrode tube and the investigated solutions. The table in Figure 2-9(c) shows the difference in electrode potential between lithium reference electrode and Ag/Ag^+ reference electrode in different concentrated $\text{LiNO}_3/\text{DMSO}$ solutions. It can be found that the difference in value between them is gradually decreasing as the concentration increases.

References

- (1) Le Ru, E. C.; Blackie, E.; Meyer, M.; Etchegoin, P. G. Surface Enhanced Raman Scattering Enhancement Factors: A Comprehensive Study. *J. Phys. Chem. C* **2007**, *111*, 13794-13803.
- (2) Blackie, E. J.; Le Ru, E. C.; Etchegoin, P. G. Single-Molecule Surface-Enhanced Raman Spectroscopy of Nonresonant Molecules. *JACS* **2009**, *131*, 14466-14472.
- (3) Haes, A. J.; Van Duyne, R. P. A Unified View of Propagating and Localized Surface Plasmon Resonance Biosensors. *Analytical and Bioanalytical Chemistry* **2004**, *379*, 920-930.
- (4) Mrozek, I.; Otto, A. Quantitative Separation of the Classical Electromagnetic and the Chemical Contribution to Surface Enhanced Raman-Scattering. *J. Electron. Spectrosc. Relat. Phenom.* **1990**, *54*, 895-911.
- (5) Link, S.; El-Sayed, M. A. Spectral Properties and Relaxation Dynamics of Surface Plasmon Electronic Oscillations in Gold and Silver Nanodots and Nanorods. *J. Phys. Chem. B* **1999**, *103*, 8410-8426.
- (6) Qin, L. D.; Zou, S. L.; Xue, C.; Atkinson, A.; Schatz, G. C.; Mirkin, C. A. Designing, Fabricating, and Imaging Raman Hot Spots. *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 13300-13303.
- (7) Im, H.; Bantz, K. C.; Lindquist, N. C.; Haynes, C. L.; Oh, S. H. Vertically Oriented Sub-10-Nm Plasmonic Nanogap Arrays. *Nano Lett.* **2010**, *10*, 2231-2236.
- (8) Wang, H.; Levin, C. S.; Halas, N. J. Nanosphere Arrays with Controlled Sub-10-Nm Gaps as Surface-Enhanced Raman Spectroscopy Substrates. *JACS* **2005**, *127*, 14992-14993.
- (9) Wei, H.; Abtahi, S. M. H.; Vikesland, P. J. Plasmonic Colorimetric and SERS Sensors for Environmental Analysis. *Environmental Science-Nano* **2015**, *2*, 120-135.
- (10) Angerstein-Kozłowska, H.; Conway, B. E.; Hamelin, A.; Stoicoviciu, L. Elementary Steps of Electrochemical Oxidation of Single-Crystal Planes of Au .1. Chemical Basis of Processes Involving Geometry of Anions and the Electrode Surfaces. *Electrochim. Acta* **1986**, *31*, 1051-1061.
- (11) Noda, H.; Wan, L. J.; Osawa, M. Dynamics of Adsorption and Phase Formation of P-Nitrobenzoic Acid at Au(111) Surface in Solution: A Combined Surface-Enhanced Infrared and STM Study. *PCCP* **2001**, *3*, 3336-3342.

- (12) Sugawara, Y.; Yadav, A. P.; Nishikata, A.; Tsuru, T. Electrochemical Quartz Crystal Microbalance Study on Dissolution of Platinum in Acid Solutions. *Electrochemistry* **2007**, 75, 359-365.
- (13) Tsai, W. Y.; Taberna, P. L.; Simon, P. Electrochemical Quartz Crystal Microbalance (Eqcm) Study of Ion Dynamics in Nanoporous Carbons. *JACS* **2014**, 136, 8722-8728.
- (14) Varela, H.; Malta, M.; Torresi, R. M. Low Cost in Situ Techniques in Electrochemistry: The Quartz Crystal Microbalance. *Quim. Nova* **2000**, 23, 664-679.
- (15) Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J. The Imide Ion: Potential Energy Surface and Geometries. *Electrochim. Acta* **1998**, 43, 1375-1379.
- (16) Erdem, U. Applications of Piezoelectric Quartz Crystal Microbalances - Lu, C., Czanderna, A. W. *Journal of Physics E-Scientific Instruments* **1984**, 17, 1100-1101.
- (17) Sauerbrey, G. Verwendung Von Schwingquarzen Zur Wagung Dunner Schichten Und Zur Mikrowagung. *Zeitschrift Fur Physik* **1959**, 155, 206-222.
- (18) Masa, J.; Ozoemena, K.; Schuhmann, W.; Zagal, J. H. Oxygen Reduction Reaction Using N-4-Metallomacrocyclic Catalysts: Fundamentals on Rational Catalyst Design. *J. Porphyrins Phthalocyanines* **2012**, 16, 761-784.
- (19) Kottam, P. K. R.; Kalkan, D.; Wohlfahrt-Mehrens, M.; Marinaro, M. Influence of Li-Salt Concentration on Redox Potential of Lithium Metal and Electrochemistry of Ferrocene in DmsO-Based Electrolytes. *J. Electrochem. Soc.* **2019**, 166, A1574-A1579.
- (20) Lewandowski, A.; Waligora, L.; Galinski, M. Ferrocene as a Reference Redox Couple for Aprotic Ionic Liquids. *Electroanalysis* **2009**, 21, 2221-2227.

Chapter 3

Effect of Electrolyte Concentration on the Solvation Structure of Gold/LITFSI-DMSO and Gold/LiNO₃-DMSO Solutions Interface

3.1 Introduction

Lithium metal batteries (LMBs) such as lithium-air and lithium-sulfur batteries exhibit larger specific capacity of lithium (3860 mAh g⁻¹) that is ten times that of its counterpart graphite (370 mAh g⁻¹) in LIBs, which would thus meet the power density demand for electric vehicles and portable devices.¹⁻³ However, the commercial application of LMBs is strongly hampered due to poor cyclability and safety issues that result from the growth of lithium dendrites at the lithium anode during charge-discharge cycling.^{1, 4-5} A solid electrolyte interphase (SEI) layer is generally formed on the lithium metal anode due to electrolyte (including solvent, lithium salt, or additives) degradation during the first charge-discharge process. The SEI layer consists of insoluble inorganic and organic components from reductive degradation of the electrolyte. A stable SEI layer can significantly impede the formation of lithium dendrites by preventing lithium anode from further reaction with more electrolyte.^{1, 3-4} The choice of electrolyte and its stability have a significant influence on the properties of the SEI layer and thus battery performance.

The utilization of dimethyl sulfoxide (DMSO) in lithium-air batteries has been demonstrated to facilitate the reversible formation and oxidation of Li₂O₂ compared to other aprotic solvents studied⁶ and the solution-phase mechanism is promoted at the oxygen cathode.⁶⁻⁹ However, the SEI layer derived from DMSO degradation in a conventional dilute electrolyte (e.g., 0.1 M LiClO₄/DMSO) cannot passivate the lithium anode well; therefore, the cycle life of a lithium-air battery with DMSO as a solvent in the electrolyte is relatively low.¹⁰ Recently, lithium bis(trifluoromethanesulfonyl)imide (LITFSI) and LiNO₃-based high-concentration electrolyte was reported to effectively suppress lithium dendrite formation, and a significant improvement of cycle performance of the lithium battery was realized due to the formation of a stable SEI layer derived from the degradation of lithium salt anion.¹¹⁻¹⁴ Most solvents and lithium salts are thermodynamically unstable over the range of lithium deposition potentials. It is

universally accepted that the prior decomposition of solvent molecules or lithium salt anions contributes the main ingredients that compose the SEI layer.¹⁵⁻¹⁷ Note that the SEI component is strongly dependent on the solvation structure, i.e., the electrolyte characteristics at the electrode surface, which is rarely understood in LITFSI- and LiNO₃-based electrolytes. To understand how the LITFSI and LiNO₃ concentration affects the interface electrochemistry, it is crucial to determine the solvation structure of the electrolyte near the electrode surface.

Surface-enhanced Raman spectroscopy (SERS) is a very useful and sensitive technique that enables the detection of ultralow concentrations of molecule in the vicinity of an electrode surface¹⁸⁻¹⁹ and was used in this work to detect ion-solvent/anion complexes at the electrode/electrolyte interface in LiNO₃-DMSO and LITFSI-DMSO solutions with various lithium salt concentrations. A gold substrate was used as a model electrode because it resembles a lithium electrode in the same electrolyte for lithium deposition/stripping.²⁰⁻²² In this work, DMSO molecules were found to interact with the gold substrate and form Au-O and Au-S bonds, while TFSI⁻ was adsorbed by the formation of Au-O bonds. However, there is no indication that NO₃⁻ interacts with gold through chemical adsorption. In the superconcentrated LITFSI-DMSO electrolytes, chemisorbed TFSI⁻ is the only species on the gold surface, while NO₃⁻ and Li(DMSO)₃⁺NO₃⁻ complex is dominant in superconcentrated LiNO₃-DMSO solutions. High proportion of salt anion (TFSI⁻ and NO₃⁻) dominant gold surface in superconcentrated DMSO electrolytes might benefit for the formation of dense SEI-derived from salt anion, which is the reason for good battery cycle performance.

3.2 Results and discussion

3.2.1 Raman spectra of pure DMSO, LITFSI-DMSO and LiNO₃-DMSO solutions in the bulk and at the gold surface

In this study, traditional Raman spectroscopy is used to study molecular information of bulk solutions, while SERS is used to reveal information on the gold surface. **Figure 3-1** shows Raman spectra between 250 and 1500 cm⁻¹ of pure DMSO, 1.72 M LITFSI-DMSO, 2.21 M LiNO₃-DMSO solutions, and that at the gold substrate. (NOTE: For both 1.72 M LITFSI-DMSO and 2.21 M LiNO₃-DMSO solutions, lithium

salt/DMSO ratio = 1:6. The selection of this molar ratio is to make the Raman peak of lithium salt more obvious for comparison with that of DMSO). Peak frequencies and assignments are given in Table 1.²³⁻²⁵ The Raman bands observed in pure DMSO at 310, 338, and 387 cm^{-1} are due to the CSC out-of-plane bending ($\delta_{\text{op}}(\text{CSC})$), CSO out-of-plane bending ($\delta_{\text{op}}(\text{CSO})$), and CSO in-plane rocking ($\rho_{\text{ip}}(\text{CSO})$) modes, respectively (**Figure 3-1(a)**). A prominent Raman band at 672 cm^{-1} and a band at 702 cm^{-1} were assigned to the CSC symmetric stretching ($\nu_{\text{s}}(\text{CSC})$) and CSC asymmetric stretching ($\nu_{\text{a}}(\text{CSC})$) modes, respectively.²⁶ These two bands are known to be sensitive to the solvation of Li^+ .²⁷⁻²⁸ The band observed at 1044 cm^{-1} is due to the S=O stretching mode ($\nu(\text{SO})$) of different forms of DMSO. Bands at 956 and 1423 cm^{-1} correspond to the CH_3 rocking ($\rho(\text{CH}_3)$) and deforming mode ($\delta_{\text{def}}(\text{CH}_3)$), respectively. Upon addition of LITFSI to DMSO, four small bands at 282, 405, 554, and 575 cm^{-1} were observed in the Raman spectrum of the 1.72 M LITFSI-DMSO solution, which correspond to the CF_3 rocking ($\rho(\text{CF}_3)$), SN symmetric rocking ($\rho_{\text{s}}(\text{SN})$), SO_2 symmetric bending ($\delta_{\text{s}}(\text{SO}_2)$), and CF_3 asymmetric bending ($\delta_{\text{a}}(\text{CF}_3)$) modes of TFSI^- , respectively. The bands at 744, 1142, and 1246 cm^{-1} , which are due to the SNS symmetric stretching ($\nu_{\text{s}}(\text{SNS})$), SO_2 symmetric stretching ($\nu_{\text{s}}(\text{SO}_2)$), and CF_3 symmetric stretching ($\nu_{\text{s}}(\text{CF}_3)$) modes from TFSI^- , respectively, were also observed.²⁹⁻³⁰ In the Raman spectrum of 2.21 M LiNO_3 , a sharp peak at 1047 cm^{-1} was overlapped with S=O stretching mode ($\nu(\text{SO})$) of DMSO, which is due to symmetric stretching mode of NO_3^- ($\nu_{\text{s}}(\text{NO}_3^-)$), as shown in **Figure 3-1(b)**.

In contrast to the Raman spectrum of the bulk solution, two small peaks located at 285 and 453 cm^{-1} were observed in the SERS spectrum of pure DMSO, 1.72 M LITFSI-DMSO and 2.21 M LiNO_3 -DMSO solutions on the gold substrate (**Figures 3-1(c) and (d)**). Parker et al. reported the Raman spectrum of $[\text{Au}_{25}(\text{SC}_2\text{Ph})_{18}]^{0/1-}$ had a peak at around 290 cm^{-1} that was assigned to an Au-S stretching vibration band.³¹ Varnholt et al. also observed the presence of the Au-S bond from the Raman spectrum of thiolate-protected gold clusters, as evidenced by a band in the frequency range from 250 to 325 cm^{-1} .³² Thus, the band located at 285 cm^{-1} was assigned as the Au-S stretching vibrational mode ($\nu(\text{Au-S}_{\text{DMSO}})$) in this study. Freeman et al. reported the Au-O bond from several gold tetracoordinate complexes in aqueous solution from Raman spectroscopy measurements.³³ They assigned the Au-O stretching vibration band of the complexes in the wavenumber range from 406 to 445 cm^{-1} .

Table 1. Peak frequencies and band assignments of Raman spectra for pure DMSO, 1.72 M LITFSI-DMSO and 2.21 M LiNO₃-DMSO in bulk solution and at the gold surface.

Assignment	Raman shift /cm ⁻¹					
	Pure DMSO Raman	1.72 M LITFSI-DMSO Raman	2.21 M LiNO ₃ -DMSO Raman	Pure DMSO SERS	1.72 M LITFSI-DMSO SERS	2.21 M LiNO ₃ -DMSO SERS
CF ₃ rocking		282				
Au-S _{DMSO} stretching				285		285
CSC out-of-plane bending	310	307	310	311	308	311
CSO out-of-plane bending	338	338	338	340	340	341
CSO in-plane rocking	387	387	387	389	388	388
SN symmetric rocking		405			405	
Au-O _{DMSO} stretching				459		459
Au-O _{TFSI} ⁻ stretching					453	
Au(OH) ₂ ⁻ or impurity				533	531	531
SO ₂ symmetric bending		554			554	
CF ₃ asymmetric bending		575			575	
CSC symmetric stretching	672	678	678	675	678	678
CSC asymmetric stretching	702	710	709	703	712	711
SNS symmetric stretching		744			744	
CH ₃ rocking	956	959	961	961	956	956
NO ₃ ⁻ symmetric stretching			1047			1043
SO symmetric stretching	1044	1057		1048	1048	
SO ₂ symmetric stretching		1142			1143	
CF ₃ symmetric stretching		1246			1246	
CH ₃ deformation	1423	1423	1423	1423	1423	1423

A Raman peak centered at 491 cm⁻¹ was identified by several researchers on a gold electrode during the oxygen reduction reaction in an aprotic electrolyte.³⁴⁻³⁵ They assigned this band as the Au-O stretching mode for a superoxide adsorbed on the gold surface. DMSO is considered to have a trigonal pyramidal molecular geometry with two methyl groups that occupy the corners and an S=O bond at the edges. Both the oxygen and sulfur atoms of DMSO possess lone pair electrons, so that they can act as electron donors to bind to a gold substrate.³⁶ Therefore, the new band at 459 cm⁻¹ was assigned to the Au-O stretching mode ($\nu(\text{Au-O}_{\text{DMSO}})$) of DMSO chemisorbed on the gold substrate. DMSO was found to form bidentate adsorption structure on gold via Au-O and Au-S bonds by other researchers through thermal desorption spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission microscopy measurements.³⁷⁻³⁸ Overall, DMSO molecules interact with a gold substrate through Au-O bonds and Au-S bonds. A broad band was also observed at 533 cm⁻¹, which may be due to [Au(OH)₂]⁻ adsorbed on the gold substrate during preparation of the SERS substrate.³⁹⁻⁴⁰ Apart from bands relative to TFSI⁻ observed in the surface Raman signals of the electrolyte with LITFSI addition, a small band centered at 453 cm⁻¹ was also observed, which was assigned as the Au-O stretching mode ($\nu(\text{Au-O}_{\text{TFSI}})$) originated from TFSI⁻ interaction with the gold substrate.

However, this band couldn't be observed in surface Raman signals of the electrolyte with LiNO_3 addition. A detailed explanation of this band is given in a later section.

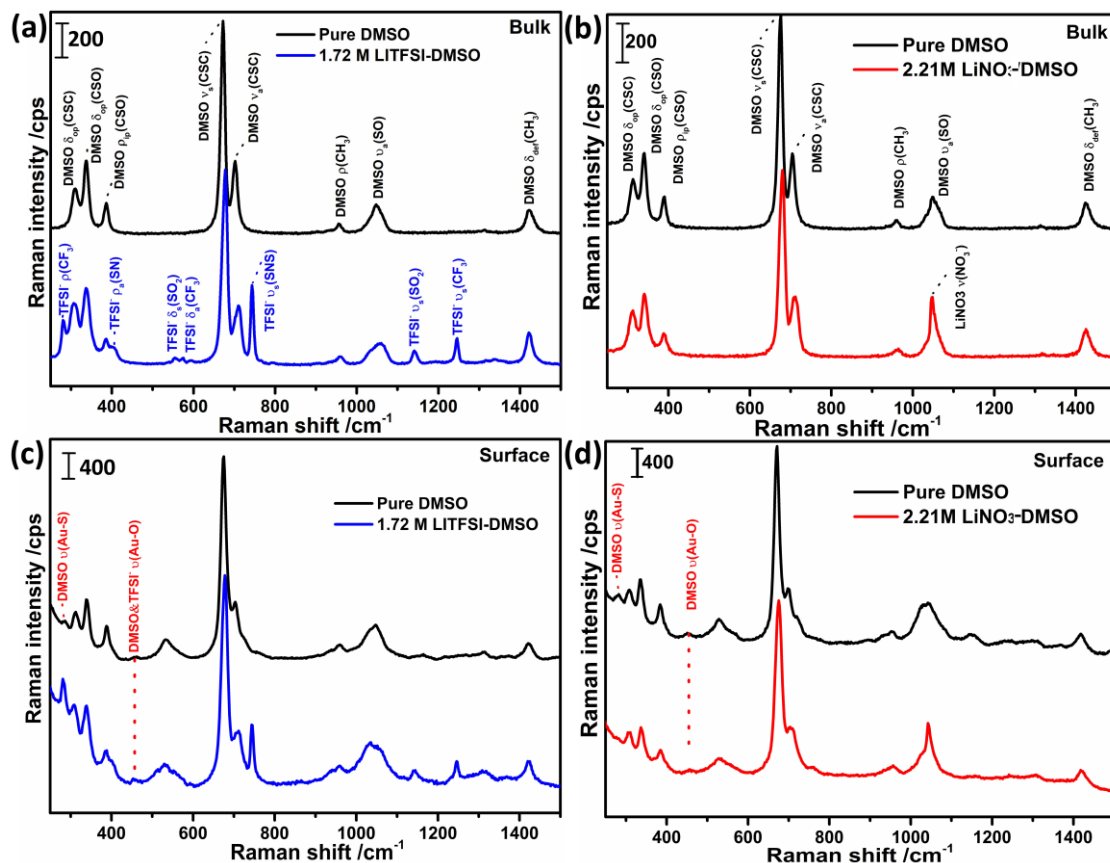


Figure 3-1. (a, b) Raman spectra of pure DMSO (black line), 1.72 M LiTFSI-DMSO solution (blue line) and 2.21 M LiNO_3 -DMSO solution (red line). (c, d) SERS spectra of pure DMSO (black line), 1.72 M LiTFSI-DMSO solution (blue line) and 2.21 M LiNO_3 -DMSO solution (red line) on a gold substrate.

3.2.2 Effects of LiTFSI and LiNO_3 concentration on solvation structure in LiTFSI-DMSO and LiNO_3 -DMSO bulk solutions

Solvation is an interaction between a solute and solution, which facilitates stabilization of the solute in the solvent. As a strong Lewis-acid, Li^+ tends to bind with electrolyte components that have the characteristics of a Lewis-base such as DMSO molecules and the TFSI⁻ or NO_3^- anion to form a specific solvation structure. The solvation structure of the electrolyte varies with different concentrations of lithium salts, in turn altering the ionic conductivity,⁴¹ electrochemical stability,⁴² cyclability,^{10, 43} SEI

formation,⁴⁴ and the overcharge tolerance.⁴⁵ **Figure 3-2(a)** show the fitting of the Raman spectra of LITFSI-DMSO electrolytes in the bulk solution in the range from 650 to 730 cm^{-1} . LITFSI-DMSO solutions with molar concentrations of 0, 0.53, 1, 1.72, 2.31, and 2.76 M were prepared (LITFSI/DMSO molar ratio is 0, 1:24, 1:12, 1:6, 1:4, and 1:3, respectively). A straight line between 630 and 730 cm^{-1} was used as a baseline of spectrum fitting. As mentioned in previous section, these two broad bands in this frequency region correspond to $\nu_a(\text{CSC})$ and $\nu_s(\text{CSC})$ vibration bands of DMSO, which is sensitive to Li^+ coordination. In order to facilitate the comparison of the effect of LITFSI concentration on the intensity of these two bands, the integral peak intensity was fixed as 1 in this region after baseline subtraction. Peak fitting for the bulk electrolytes revealed that peaks at ca. 672 and 702 cm^{-1} are each composed of two bands. The bands at ca. 672 and 702 cm^{-1} were related to free DMSO, while the other bands at 678 and 713 cm^{-1} were attributed to Li^+ solvated DMSO.^{27-28, 46} The peak intensity of solvated DMSO gradually increased with the LITFSI concentration. The free and solvated vibrational bands could be separated well by peak fitting and were used to calculate the solvation number for DMSO (N_{DMSO}) because the relative intensity of these bands is directly proportional to the DMSO concentration. It is easier to differentiate the $\nu_a(\text{CSC})$ band between free DMSO and solvated DMSO (ca. 11 cm^{-1} difference) compared with that of $\nu_s(\text{CSC})$ (ca. 6 cm^{-1} difference); therefore, the $\nu_a(\text{CSC})$ band is used to quantify the solvation number. It was assumed that the coordinated DMSO molecule had the same Raman scattering coefficient as the uncoordinated DMSO molecule.⁴⁷ The solvation number of Li^+ can be calculated from the following equation:²⁷

$$N_{\text{DMSO}} = \frac{[\text{DMSO}]_{\text{solv}}}{[\text{Li}^+]} = \frac{[\text{DMSO}]}{[\text{Li}^+] \left(1 + \frac{[\text{DMSO}]_{\text{free}}}{[\text{DMSO}]_{\text{solv}}} \right)}$$

where $[\text{Li}^+]$ and $[\text{DMSO}]$ denote the molar concentrations of lithium salt and DMSO in a given electrolyte, respectively, and $[\text{DMSO}]_{\text{free}}/[\text{DMSO}]_{\text{solv}}$ is the integral peak ratio of free DMSO to solvated DMSO.

The calculated solvation numbers for bulk solution with different LITFSI concentrations in DMSO is shown in **Figure 3-2(b)**. The calculated N_{DMSO} is 3.9 in 0.53 M LITFSI-DMSO bulk solution, which indicates that four DMSO molecules form a $\text{Li}(\text{DMSO})_4^+$ cluster by coordination with one Li^+ . It is universally accepted that a

solvation number around four best describes the coordination of Li^+ in DMSO solvent, which confirms that the present calculation is reliable.^{27, 48} For an electrolyte concentration range from 0.53 to 2.31 M, N_{DMSO} shows a slight decrease from 3.9 to 3.5 as the concentration increases, which means that the dominant solvation structure in bulk solution is $\text{Li}(\text{DMSO})_4^+$ cluster. Further increase in the concentration to 2.76 M causes a decrease of N_{DMSO} to 3, which suggests that one DMSO molecule in the solvation sheath was substituted by one TFSI⁻ anion to form contact ion pairs (CIP) or aggregates from solvent separated ion pairs (SSIP).⁴⁹ This could be attributed to the different electron-donating ability between DMSO and TFSI⁻. The reported Gutmann donor number (DN) of DMSO is 30, which is much higher than that of TFSI⁻ (DN = 7) and indicates the higher electron-donating ability of DMSO.⁵⁰ Therefore, Li^+ preferentially coordinates with DMSO when Li^+ coexist with DMSO and TFSI⁻. Li^+ coordinates with TFSI⁻ only when there is insufficient DMSO.

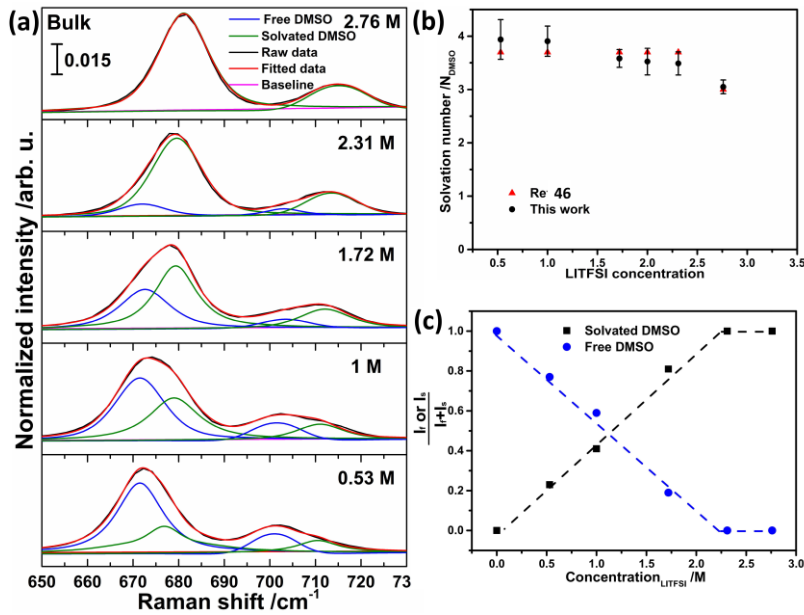


Figure 3-2. (a) Peak fitting of Raman spectra from electrolytes in bulk solution with increased LITFSI concentrations. The frequency range corresponds to $\nu_s(\text{CSC})$ and $\nu_a(\text{CSC})$ of DMSO. (b) The solvation number of Li^+ in LITFSI-DMSO bulk solutions, solvation number from Ref. 46 for increased LITFSI concentrations. The error bar indicates standard deviation of calculated solvation number based on at least three measurements at the same electrolyte. (c) concentration-dependence of integrate peak ratio of free or solvated DMSO to over DMSO based on $\nu_a(\text{CSC})$ band in (a).

The concentration-dependence of integrate peak ratio of free or solvated DMSO to over DMSO based on $\nu_a(\text{CSC})$ band was fitted and shown in Figure 3-2(c). As LITFSI concentration increase, free DMSO decrease with solvated DMSO increase. In addition, when the concentration is over than 2.31 M, free DMSO is almost completely transit to solvated DMSO. Note that the molar ratio of LITFSI to DMSO is exactly 1:4 in the 2.31 M solution of LITFSI-DMSO. According to the tetra-coordination solvation structure of DMSO, all DMSO molecules are coordinated by Li^+ in this concentration. That is to say, free DMSO only present in those electrolytes with LITFSI concentrations lower than 2.31 M, whereas all DMSO molecules coordinate with Li^+ at higher concentrations of LITFSI. The solvation number determined in the present study was compared with a similar study reported by Tatara et al.⁴⁶, which is also shown in Figure 3-2(b). The solvation number taken from Tatara et al. was 3.7 as the LITFSI concentration lower than 2.31 M. Our calculated solvation numbers show very close value with their studies in this concentration range. In addition, When the LITFSI concentration reaches to 2.76 M, the calculated solvation number is 3, which is also consistent with the result of Tatara et al. The solvation number in present study shows a slight downward trend with increasing concentration, whereas that of Tatara et al. is constant, which may be due to the difference in the calculation method. Overall, our results show consistent with their results.

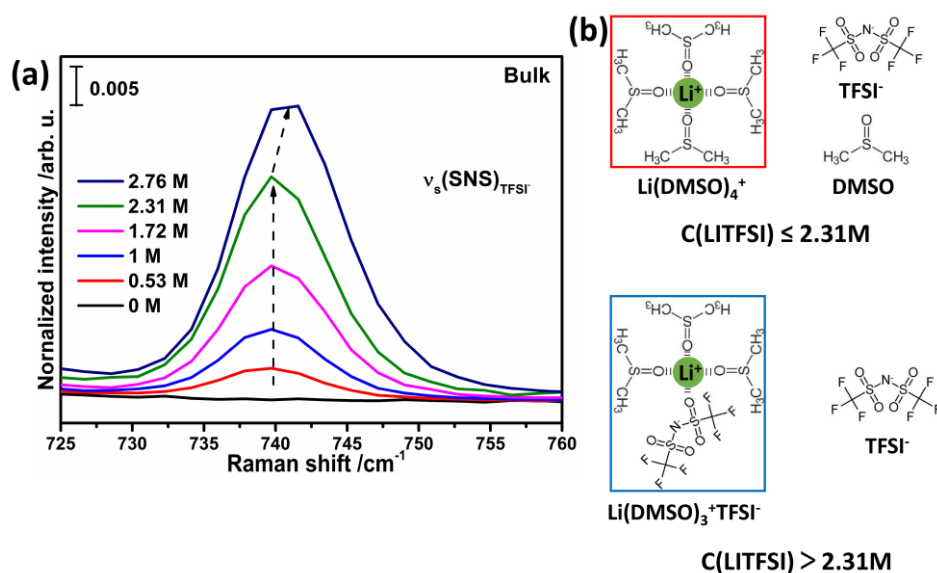


Figure 3-3. (a) Concentration-dependence of Raman spectra of LITFSI-DMSO bulk solutions in vibration region of $\nu_s(\text{SNS})_{\text{TFSI}^-}$. (b) Proposed solvation structure in bulk LITFSI-DMSO solutions at different LITFSI concentration.

The SNS symmetric stretching band ($\nu_s(\text{SNS})$) of TFSI^- is sensitive to Li^+ coordination as well. As can be seen, the intensity of $\nu_s(\text{SNS})$ increase as the LITFSI concentration increased (**Figure 3-3(a)**). The peak center of the $\nu_s(\text{SNS})$ band for the bulk solution remains unchanged at 740 cm^{-1} in the electrolytes with concentrations $\leq 2.31\text{ M}$, while a blue-shift to 744 cm^{-1} was observed when the electrolyte concentrations is 2.76 M . Tatara et al. observed the same trend in various concentrations of LITFSI-DMSO electrolytes by Raman spectroscopy. The band at 740 cm^{-1} was attribute to free TFSI^- , while the band at 744 cm^{-1} was Li^+ solvated TFSI^- . Thus, this phenomenon could be explained by Li^+ being only solvated by DMSO molecules to form $\text{Li}(\text{DMSO})_4^+$ clusters when the electrolyte concentration is lower than 2.31 M , while the TFSI^- begins to participate in the formation of a solvation shell as $\text{Li}(\text{DMSO})_3^+\text{TFSI}^-$ with higher concentrations, which is consistent with the solvation number discussed previously.

Therefore, according to the above discussion, the solvation structure of LITFSI-DMSO bulk electrolytes is as follows (**Figure 3-3(b)**): 1) $\text{Li}(\text{DMSO})_4^+$, free TFSI^- and free DMSO is present in the electrolyte range from 0 to 2.31 M , where the amount of free DMSO gradually decreases with the increase of LITFSI concentration, whereas the amount of $\text{Li}(\text{DMSO})_4^+$ and free TFSI^- increase. 2) For electrolytes with a concentration higher than 2.31 M , $\text{Li}(\text{DMSO})_3^+\text{TFSI}^-$ and free TFSI^- become the dominant species.

Similarly, the solvation number of DMSO in LiNO_3 -DMSO solutions was also studied based on $\nu_s(\text{CSC})$ vibration bands of DMSO. LiNO_3 -DMSO solutions with molar concentrations of 0, 0.58, 1.14, 2.21, 3.18, and 4.13 M were investigated (LiNO_3 -DMSO molar ratio 0, 1:24, 1:12, 1:6, 1:4, and 1:3, respectively). It can be found in **Figure 3-4(a)** that as the concentration of LiNO_3 increases, Raman intensity of $\nu_s(\text{CSC})$ vibration band for Li^+ coordinated-DMSO increase, whereas the intensity of $\nu_s(\text{CSC})$ vibration band for free DMSO decrease. The concentration-dependence of solvation number of DMSO in bulk solution was calculated based on this band and was shown in **Figure 3-4(b)**. When the concentration of LiNO_3 is lower than 2.21 M , the solvation number of DMSO is close to four, indication of tetra-coordination solvation structure of DMSO in low LiNO_3 concentration. Further increasing LiNO_3 concentration would reduce the solvation number to 3 at 4.13 M , which means $\text{Li}(\text{DMSO})_4^+$ cluster was gradually convert to $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ by replacing one DMSO molecule with one NO_3^- . The solvation number of DMSO in present study was consistent with work reported by Togasaki et al.

in the same electrolytes.⁵¹

The $\nu_s(\text{NO}_3^-)$ band of LiNO_3 is sensitive to Li^+ coordination as well. As can be seen in **Figure 3-4(c)**, the peak position of $\nu_s(\text{NO}_3^-)$ band was constant at 1044 cm^{-1} at LiNO_3 concentration lower than 2.21 M and blue-shifted to 1045 cm^{-1} at higher concentration. The former band was attribute to free NO_3^- , while the band at 1045 cm^{-1} was Li^+ solvated NO_3^- . Thus, the behavior of $\nu_s(\text{NO}_3^-)$ band for LiNO_3 shows consistent with solvation number. Based on above analysis, concentration-dependence solvation structure of bulk LiNO_3 -DMSO solutions could be drawn (**Figure 3-4(d)**). 1) $\text{Li}(\text{DMSO})_4^+$, free NO_3^- and free DMSO is present in the electrolyte range from 0 to 2.21 M , where the amount of free DMSO gradually decreases with the increase of LiNO_3 concentration, whereas the amount of $\text{Li}(\text{DMSO})_4^+$ and free NO_3^- increase. 2) For electrolytes with a concentration higher than 2.21 M , $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ and free NO_3^- become the dominant species.

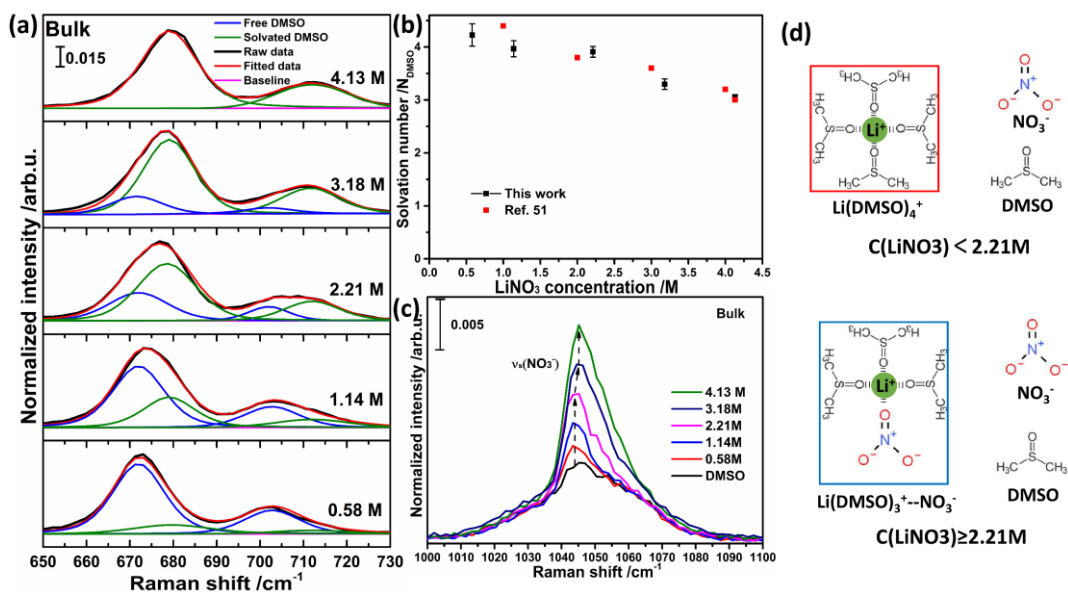


Figure 3-4. (a) Peak fitting of Raman spectra from electrolytes in bulk solution with increased LiNO_3 molar concentrations. The frequency range corresponds to $\nu_s(\text{CSC})$ and $\nu_a(\text{CSC})$ of DMSO. (b) The solvation number of Li^+ in LiNO_3 -DMSO bulk solutions, solvation number from Ref. 51 for increased LiNO_3 molar concentrations. The error bar indicates standard deviation of calculated solvation number based on at least three measurements at the same electrolyte. (c) Concentration-dependence of Raman spectra of LiNO_3 -DMSO bulk solutions in vibration region of $\nu(\text{NO}_3^-)$. (d) Proposed solvation structure in bulk LiNO_3 -DMSO solutions at different LiNO_3 concentration.

Compared with the solvation structure of bulk LITFSI-DMSO and LiNO₃-DMSO solutions, it is worth noting that for the LITFSI-DMSO solutions, the TFSI⁻ start to join solvation shell occurred at above 2.31 M (LITFSI/DMSO molar ratio = 1:4). However, in case of LiNO₃-DMSO solutions, NO₃⁻ has already been added to the solvation shell when the concentration is over 2.21 M (LiNO₃/DMSO molar ratio = 1:6). The difference is due to varied DN of NO₃⁻ and TFSI⁻. The donor number of TFSI⁻, NO₃⁻ and DMSO follow the order of TFSI⁻ (7) < NO₃⁻ (21) < DMSO (30).⁵⁰ Since DN of TFSI⁻ is much lower than that of DMSO, DMSO shows stronger electron affinity towards Li⁺ to form Li(DMSO)₄⁺ cluster. Only when all the free DMSO is coordinated with Li⁺, TFSI⁻ would start to coordinate with the Li⁺, i.e. molar ratio of LITFSI to DMSO = 1:4. However, compared with TFSI⁻, the DN of NO₃⁻ is much higher, showing that the affinity of NO₃⁻ towards Li⁺ is stronger than that of TFSI⁻. In other words, NO₃⁻ is easier to join the Li⁺ solvation shell compared with TFSI⁻. Therefore, NO₃⁻ join the solvation shell in LiNO₃-DMSO solutions with molar ratio of LiNO₃ to DMSO above 1:6, which is lower than that of LITFSI-DMSO solutions. In that case, free DMSO is still exist in electrolyte solution when NO₃⁻ start to coordinate with Li⁺, which is not observed in LITFSI-DMSO solution, where no free DMSO is coexist when TFSI⁻ start to coordinate with Li⁺.

3.2.3 Effects of LITFSI and LiNO₃ concentration on the solvation structure of TFSI⁻ and NO₃⁻ at gold/electrolyte interface

As discussed in section 3.2.1, the Raman band at around 459 cm⁻¹ for DMSO at the gold surface is attributed to $\nu(\text{Au-O}_{\text{DMSO}})$ from the interaction between DMSO and the gold substrate. **Figure 3-5(a)** shows the peak at 459 cm⁻¹ when the concentration is lower than 1 M, and another peak at 453 cm⁻¹ become apparent with higher LITFSI concentration. Peak fitting and quantitative analysis of the integral ratio of peaks at 459 and 453 cm⁻¹ to the total $\nu(\text{Au-O})$ band are shown in **Figure 3-5(a) and 5(b)**, respectively. In Figures 3-5(a), straight line between 440 and 475 cm⁻¹ was used as a baseline of spectrum fitting. An immediate observation in Figure 3-5(b) is that the ratio for the peak at 459 cm⁻¹ decreases, whereas that for the peak at 453 cm⁻¹ increases with the LITFSI concentration to 2.31 M. In addition, the behavior of $\nu(\text{Au-O}_{\text{DMSO}})$ and $\nu(\text{Au-O}_{\text{TFSI}^-})$ band against LITFSI concentration is similar as that of free DMSO and TFSI⁻ in bulk electrolyte in Figure 3-5(b). This suggests that the peak at 453 cm⁻¹ is associated with

TFSI⁻ because the proportion of TFSI/DMSO at the interface increases with the LITFSI concentration. However, this peak was not observed in the Raman spectrum of the bulk solution containing LITFSI (**Figure 3-5(c)**), which suggests that this peak is related to the interaction between TFSI⁻ and the gold substrate.

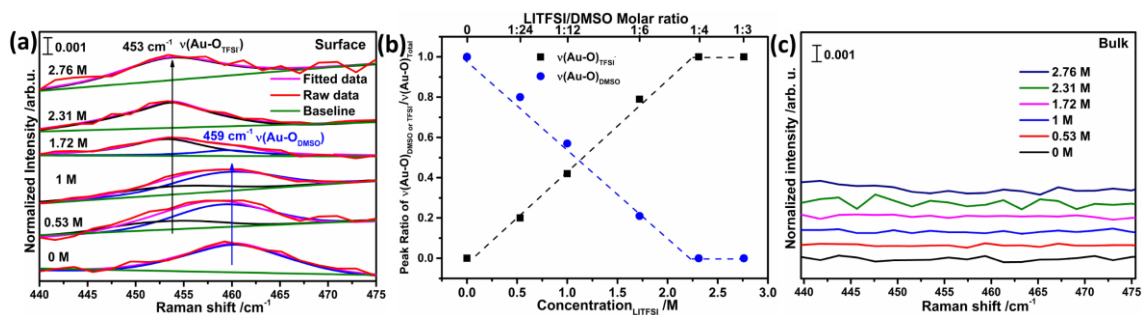


Figure 3-5. (a) Peak fitting of Raman spectra of LITFSI-DMSO electrolytes at the gold surface. Frequency regions correspond to $\nu(\text{Au-O})$ of DMSO and TFSI⁻ interacted with the gold substrate. (b) Variation in the ratio of $\nu(\text{Au-O}_{\text{DMSO}})$ and $\nu(\text{Au-O}_{\text{TFSI}^-})$ over the sum of $\nu(\text{Au-O})_{\text{Total}}$ as a function of the LITFSI concentration. (c) Raman spectra of LITFSI-DMSO bulk solutions with increased concentrations in the same frequency regions as shown in (a).

In LiNO₃-DMSO solutions case, the $\nu(\text{Au-O}_{\text{DMSO}})$ band appeared at 459 cm⁻¹ in Raman spectra of surface solution (**Figure 3-6(a)**) which is not observed in that of bulk solution (**Figure 3-6(c)**). The intensity of the $\nu(\text{Au-O}_{\text{DMSO}})$ band decreased with the addition of LiNO₃ as shown in Figure 3-6(a) and (b), which behaved same as LITFSI-DMSO solution case, indicating chemisorbed DMSO on gold surface replaced by NO₃⁻ with LiNO₃ addition. However, there is no sign that NO₃⁻ is chemisorbed on the gold surface from present Raman spectroscopy. According to the literature survey, study on the interaction between NO₃⁻ and gold is limited and mainly focused on aqueous system. F.C. Nart et al. shows that NO₃⁻ adsorb on polycrystalline gold electrodes in acidic aqueous solution under two-fold coordination by in situ FTIRS.⁵² Fawcett et al. reported that NO₃⁻ was adsorbed to the Au(111) surface through one of its oxygen atoms by in situ IR reflection spectroscopy in 0.01 M HNO₃ aqueous solution.⁵³ However, the vibrational mode of Au-O bond between NO₃⁻ and gold was not observed for both works, probably the adsorption of NO₃⁻ on gold is not enough to form a chemical bond.

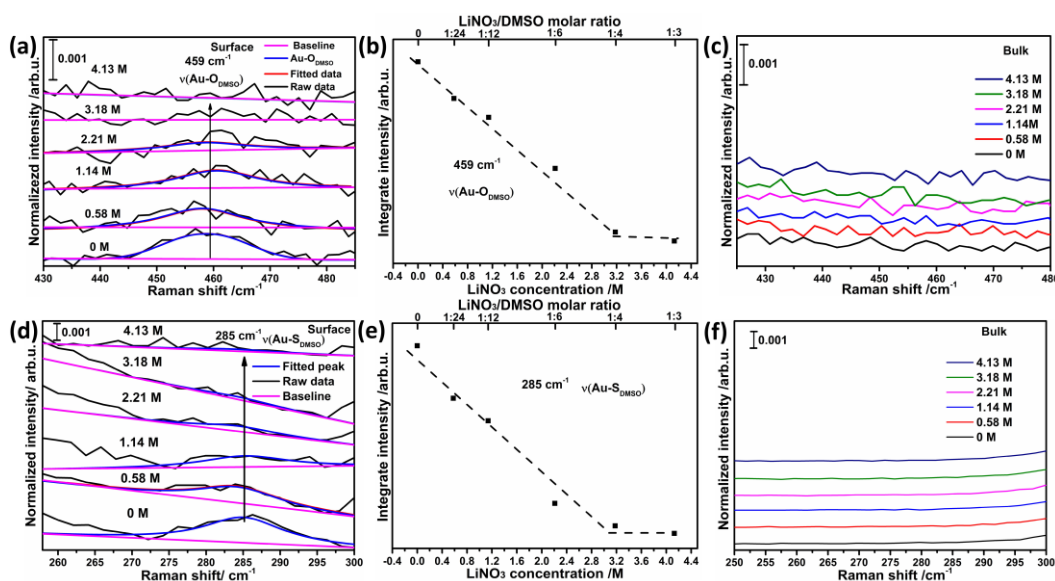


Figure 3-6. (a) Peak fitting of Raman spectra of LiNO₃-DMSO electrolytes at the gold surface. Frequency region correspond to $\nu(\text{Au-O})$ of DMSO interacted with the gold. (b) integrate intensity of $\nu(\text{Au-O}_{\text{DMSO}})$ as a function of LiNO₃ concentration. (c) Raman spectra of LiNO₃-DMSO bulk solutions with increased concentration in the same frequency region as shown in (a). (d) Peak fitting of Raman spectra in the frequency region correspond to $\nu(\text{Au-S}_{\text{DMSO}})$ of DMSO interacted with the gold, (e) integrate intensity of $\nu(\text{Au-S}_{\text{DMSO}})$ as a function of LiNO₃ concentration. (f) Raman spectra of LiNO₃-DMSO bulk solutions with concentration in the same region shown in (d).

For better explanation, the adsorption model of NO_3^- on gold electrode would be drawn in latter section based on F.C. Nart et al.'s description because the SERS substrate is polycrystalline. Concentration-dependence of integrate intensity of $\nu(\text{Au-O}_{\text{DMSO}})$ band in **Figure 3-6(b)** shows the intensity of $\nu(\text{Au-O}_{\text{DMSO}})$ band decreasing with LiNO_3 concentration until molar ratio of $\text{LiNO}_3/\text{DMSO} = 1:4$. Further increase the concentration of LiNO_3 would result disappearing of this band. This behavior is consistent with the tendency of $\nu(\text{Au-S}_{\text{DMSO}})$ band. As shown in **Figure 3-6(d)**, the vibrational band of Raman spectra of surface solution at 285 cm^{-1} was attributed to $\nu(\text{Au-S}_{\text{DMSO}})$ mode as discussed previously, which is not observed in bulk case (**Figure 3-6(f)**). The intensity of this band decreased with LiNO_3 concentration and eventually this band was not be observed in solution with molar ratio of 1:4 (**Figure 3-6(e)**).

Figure 3-7 shows Raman spectra of electrolytes on the gold surface and the bulk solution with various LITFSI concentrations. As discussed previously, the peak position of the $\nu_s(\text{SNS})$ band of TFSI^- in bulk electrolytes remains unchanged in the electrolytes $\leq 2.31\text{ M}$, while a blue-shift was observed when the electrolyte concentrations is 2.76 M . (**Figure 3-7(a)**) For the electrolyte with a concentration of 0.53 M at the gold surface, the peak center of the $\nu_s(\text{SNS})$ band was more positive than that in the bulk solution due to chemisorption of TFSI^- on the gold substrate. (**Figure 3-7(d)**) The $\nu_s(\text{SNS})$ band was centered at 746 cm^{-1} for the electrolyte with a concentration of 0.53 M , whereas a gradual red-shift to 743 cm^{-1} was observed for the electrolyte with a higher concentration of 2.31 M . However, the frequency position of this band remains unchanged at 743 cm^{-1} with further increase in the concentration. Note that chemisorbed TFSI^- at the gold surface is affected not only by interfacial chemisorption, but also by the Li^+ coordination as the concentration changes. TFSI^- has extensive charge delocalization at SO_2 bonds; thus, the coordination of Li^+ and adsorption by gold substrate affect the charge distribution significantly.⁵⁴ Therefore, the red-shift of the $\nu_s(\text{SNS})$ band with the increased LITFSI in the electrolyte concentration, indicating different vibrational energy states of the SNS bond, will provide information of chemisorbed TFSI^- coordination with Li^+ .

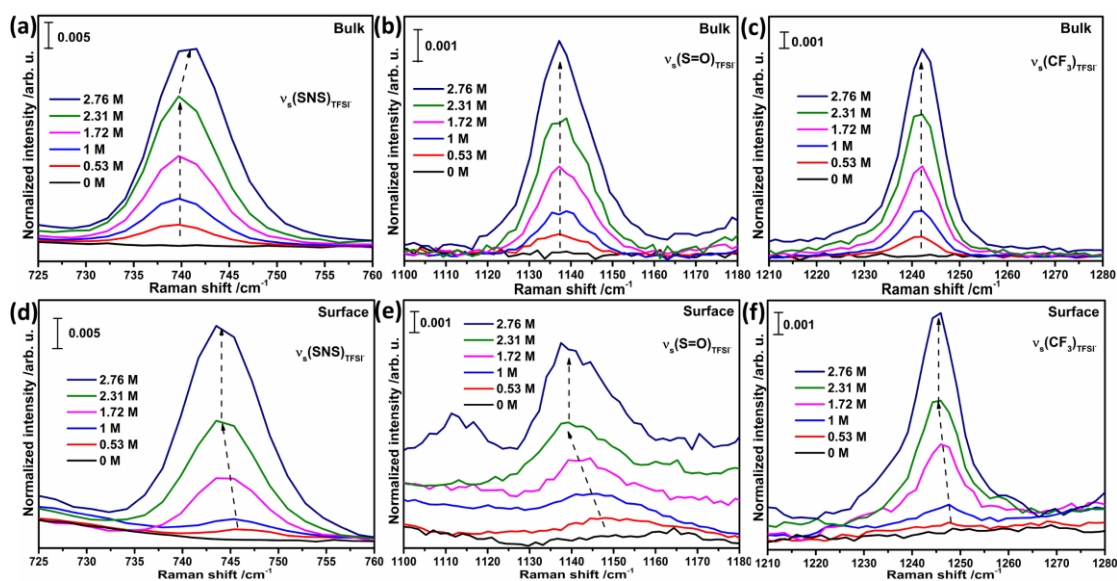


Figure 3-7. Raman spectra of LITFSI-DMSO electrolytes with increased concentrations. (a-c) in the bulk solution and (d-f) electrolytes at the gold surface. The regions correspond to (a, d) $\nu_s(\text{SNS})_{\text{TFSI}^-}$, (b, e) $\nu_s(\text{S=O})_{\text{TFSI}^-}$, and (c, f) $\nu_s(\text{CF}_3)_{\text{TFSI}^-}$ of TFSI⁻ anions.

TFSI⁻ has two types of low-energy conformations, cis and trans conformers.⁵⁵⁻⁵⁶ The cis conformer is considered to be preferred in the first solvation shell of Li⁺ in an aprotic solution owing to the dipole moment of the cis conformer is significantly larger than that of the trans conformer, and will be used as the molecular model in this study.^{48,}
⁵⁷ TFSI⁻ is chemisorbed on the gold surface through Au-O bonds; however, the four oxygens of one TFSI⁻ are not on the same plane; therefore, TFSI⁻ cannot fully interact with gold substrate through four oxygens.^{54, 56} Furthermore, it can be inferred from the asymmetric shape of the peak that the peak consists of at least two or three bands. The possible adsorption state of TFSI⁻ on the gold substrate is shown in Scheme 1 (red dotted area) to explain the red-shift of the $\nu_s(\text{SNS})$ band. In a low-concentration electrolyte, such as at 0.53 M, two S=O bonds on one side of the nitrogen atom interact with the gold surface via lone pair electrons, which leaves the remaining two S=O bonds on the other side of the nitrogen atom uncoordinated (a-TFSI⁻). Due to the electron-withdrawing of gold and the delocalization of π electrons, the π electrons on the S=O bond that are away from the gold surface are partially delocalized to the SNS bond. This increases the force constant of the SNS bond, which in turn strengthens the SNS bond and thus leads to the higher wavenumber of the $\nu_s(\text{SNS})$ band in the SERS spectrum, in contrast to the

conventional Raman spectrum.⁵⁸ As the LITFSI concentration increases, one of the uncoordinated S=O terminals of chemisorbed TFSI⁻ is coordinated by one Li⁺ (a-TFSI⁻··Li⁺). The attraction of the coordinated Li⁺ to the π bond on the S=O bond means the π electron cloud that could delocalize to the SNS bond is reduced, which results in a weaker SNS bond. Similarly, further increase in the LITFSI concentration over 2.31 M means another S=O will also be coordinated by one Li⁺ (a-TFSI⁻··2Li⁺). The presence of two pairs of Li⁺··O=S bonds attract the π electron cloud, so that the electron cloud on the SNS bond is further dispersed, which in turn weakens the bond strength of the SNS bond. Thus, the red-shift of the $\nu_s(\text{SNS})$ band in the concentration range of 2.31 M is mainly due to the dispersion of the chemisorbed TFSI⁻ skeleton electrons induced by Li⁺ coordination. This band no longer shifts with further increase in the concentration over 2.31 M, because all oxygen atoms of chemisorbed TFSI⁻ have already been coordinated by Li⁺. A similar redshift behavior can also be observed for the SO₂ symmetric stretching ($\nu_s(\text{SO}_2)$) (**Figure 3-7(b)**) and CF₃ symmetric stretching ($\nu_s(\text{CF}_3)$) (**Figure 3-7(c)**) of LITFSI from Raman spectrum at the gold surface in various electrolyte concentrations. It should be noted that the $\nu_s(\text{SO}_2)$ band exhibited a red-shift with a rate of $-4.49 \text{ cm}^{-1} \text{ M}^{-1}$, while this value for $\nu_s(\text{CF}_3)$ and $\nu_s(\text{SNS})$ was respectively -1.68 and $-1.12 \text{ cm}^{-1} \text{ M}^{-1}$ as the concentration increased. This indicates that the LITFSI concentration has the most significant influence on the S=O bond of chemisorbed TFSI⁻, i.e., coordination with Li⁺. The CF₃ group and SNS bonds are located at both sides of the S=O bond; therefore, it is reasonable that the coordination of Li⁺ with the S=O bond causes the electrons of the CF₃ and SNS bonds to be delocalized to the S=O bond, which is consistent with our proposed model. However, the peak positions of the $\nu_s(\text{CF}_3)$ and $\nu_s(\text{SNS})$ bands for the bulk solution do not change with the concentration of the LITFSI, which suggests that these two groups are weakly affected by Li⁺ coordination in the bulk solution (**Figure 3-7(e) and (f)**). Therefore, the coordination between Li⁺ and the adsorbed TFSI⁻ on the gold surface is stronger than that in the bulk solution due to the chemisorption of TFSI⁻ on the gold surface. This discussion suggests that in an electrolyte within a concentration of 2.31 M, the chemisorbed TFSI⁻ on the gold substrate gradually coordinates with Li⁺ as the LITFSI concentration increases. With LITFSI concentrations higher than 2.31 M, chemisorbed TFSI⁻ on the gold surface is completely coordinated by Li⁺.

Figure 3-8 shows the comparison of Raman spectrum of LiNO₃-DMSO solutions

in bulk solution and gold surface in $\nu_s(\text{NO}_3^-)$ vibrational mode region. The behavior of $\nu_s(\text{NO}_3^-)$ peak position against LiNO_3 concentration is similar for both bulk solution and surface case. That is, peak position of $\nu_s(\text{NO}_3^-)$ remain constant at LiNO_3 concentration lower than 2.21 M, while blueshift was observed in electrolytes with concentration above 2.21 M (Figure 3-8(a) and (b)). This means the solvation structure of NO_3^- on gold surface is same as that in bulk solution.

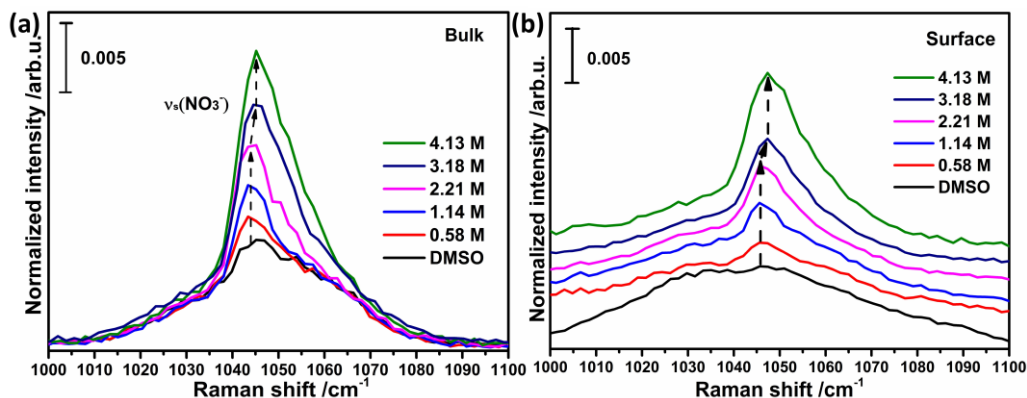
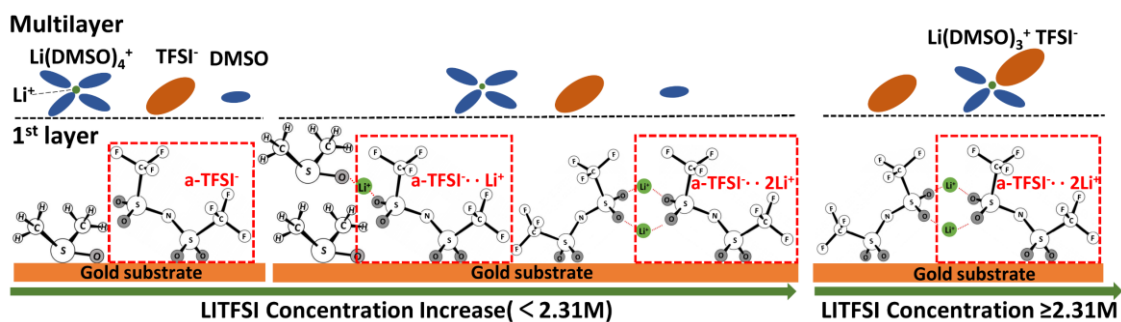


Figure 3-8. Raman spectra of LiNO_3 -DMSO electrolytes with various concentrations. (a) in the bulk solution and (b) at the gold surface. The regions correspond to $\nu_s(\text{NO}_3^-)\text{NO}_3^-$.

3.2.4 Proposed solvation structure at gold/LITFSI-DMSO and gold/ LiNO_3 -DMSO interface as a function of concentration

Based on the Raman results above, the proposed solvation structure of the LITFSI-DMSO solutions on the gold/electrolyte interface was summarized. Scheme of the proposed interfacial solvation structures in three concentration regimes, low concentration, high concentration (≤ 2.31 M), and ultra-high concentration (> 2.31 M), are shown in **Scheme 1**. At low concentrations, large amount of uncoordinated DMSO were chemisorbed on gold surface via Au-O and Au-S bond. Only small quantity of TFSI $^-$ are proposed to be interacting with the gold surface via O atoms. In addition, chemisorbed TFSI $^-$ at the gold surface did not coordinate with Li^+ in low concentration electrolytes. These chemisorbed DMSO and TFSI $^-$ form the first adsorption layer of the gold/LITFSI interface. Due to the existence of the adsorption layer, the solvation structure near the adsorption layer is no longer affected by gold. Thus, its solvation structure is consistent with that in bulk solution, mainly including TFSI $^-$, free DMSO and $\text{Li}(\text{DMSO})_4^+$.

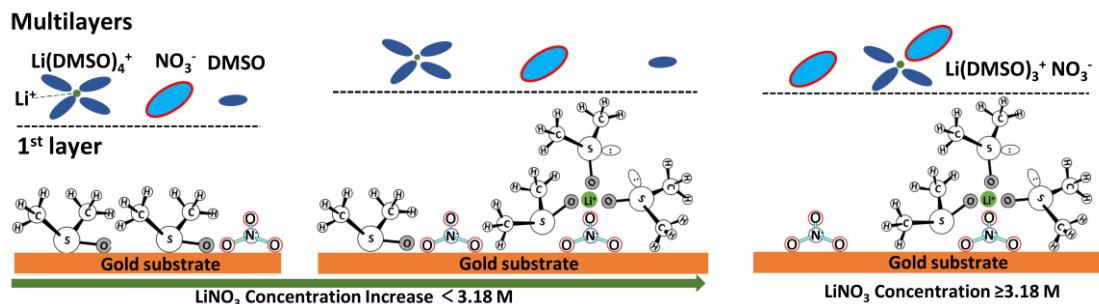


Scheme 1. Proposed scheme for electrolyte component adsorption on a gold substrate with an increase LITFSI concentration. Red dotted box in the scheme represent chemisorbed TFSI⁻ with different Li⁺ coordination. The solvation structure near the 1st layer (multilayers) is same as solvation structure in the corresponding bulk electrolytes. In multilayer, green, blue, brown colors represent Li⁺, free DMSO and free TFSI⁻, respectively.

When the concentration gradually increased below 2.31 M, chemisorbed DMSO still remained on the gold surface, but the number is reduced. Notedly, the chemisorbed TFSI⁻ start to gradually coordinate with Li⁺ by one or two S = O bonds. Further increase the concentration to above 2.31 M, chemisorbed DMSO is absent, instead chemisorbed TFSI⁻ become the dominant species. The chemisorbed TFSI⁻ are proposed to be coordinated with Li⁺ by two of its oxygen in such ultra-high concentration, making its coordination saturated. The solvation structure adjacent to the adsorption layer under ultra-high concentration is Li(DMSO)₃⁺TFSI⁻ and free TFSI⁻. Notedly, the proposed interfacial solvation model of present electrolytes is similar to the electric double layer model in electrochemistry. The chemisorbed TFSI⁻ and chemisorbed DMSO form inner Helmholtz layer, while the adjacent layer consists of free TFSI/DMSO and solvated TFSI/DMSO was outer Helmholtz layer. Therefore, when the electrolyte concentration changes, it is regulating the composition of the inner Helmholtz layer of the electric double layer.

Correspondingly, the concentration-dependence solvation structure of LiNO₃-DMSO solutions at gold/LiNO₃-DMSO interface was shown in **Scheme 2**. As LiNO₃ concentration less than 3.18 M, inner Helmholtz layer was dominant by NO₃⁻, chemisorbed DMSO and part of Li(DMSO)₃⁺NO₃⁻ complex. In addition, with LiNO₃ concentration increase, chemisorbed DMSO was gradually replaced by NO₃⁻ or

$\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ complex. In electrolyte with concentration above 3.18 M, gold surface was fully covered by NO_3^- and $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ complex.



Scheme 2. Proposed scheme for electrolyte component adsorption on a gold substrate with an increase LiNO_3 concentration. In multilayer, green, dark blue, light blue (with red) colors represent Li^+ , free DMSO and free NO_3^- , respectively.

By comparing the concentration-dependence of solvation structure at electrolyte/gold interface in LITFSI-DMSO and LiNO_3 -DMSO solutions, chemisorbed DMSO on the surface of gold electrode decrease with concentration in both electrolytes. Chemisorbed TFSI $^-$ was found to gradually increases in LITFSI-DMSO solution, while in LiNO_3 -DMSO solution, $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ and NO_3^- increase. It worth noting that, the component of adsorption layer in superconcentrated LiNO_3 -DMSO solution were $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ and NO_3^- , which is same as that in bulk solution. While the component of adsorption layer in superconcentrated LiNO_3 -DMSO solution is just Li^+ coordinated chemisorbed TFSI $^-$ which is different from that in bulk solution with TFSI $^-$ and $\text{Li}(\text{DMSO})_3^+\text{TFSI}^-$ as solvation component. The difference between LITFSI-DMSO and LiNO_3 -DMSO solution was proposed to relate to the adsorption strength of adsorbent.

According to SERS analysis, TFSI $^-$ is found to interact with gold by chemisorption via Au-O bond, while no chemical bond could be observed for NO_3^- , suggesting stronger adsorption strength of TFSI $^-$ than NO_3^- towards gold electrode. The adsorption strength of $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ and $\text{Li}(\text{DMSO})_3^+\text{TFSI}^-$ cluster were thought to even weaker because the electron-donating ability of DMSO, TFSI $^-$ and NO_3^- is neutralized by Li^+ solvation. Thus, the adsorption strength is possible to follow the order of $\text{TFSI}^- > \text{NO}_3^- \geq \text{Li}(\text{DMSO})_3^+\text{TFSI}^- \approx \text{Li}(\text{DMSO})_3^+\text{NO}_3^-$. Adsorbents with stronger adsorption strength will preferentially occupy the adsorption layer. Therefore, in LITFSI-DMSO solution, the stronger adsorption strength of TFSI $^-$ than $\text{Li}(\text{DMSO})_3^+\text{TFSI}^-$ makes

TFSI⁻ occupy the adsorption layer. In LiNO₃-DMSO solutions, the relatively equal adsorption strength of NO₃⁻ and Li(DMSO)₃⁺NO₃⁻ resulted in both species coexist in the adsorption layer. This may be the possible explanation.

Based on our model, it can be found that at superconcentrated LITFSI-DMSO and LiNO₃-DMSO electrolytes, chemisorbed DMSO are absent on the adsorption layer of gold surface, instead TFSI⁻, NO₃⁻ and Li(DMSO)₃⁺NO₃⁻ complex are fully adsorbed. To the best of our knowledge, the SEI derived from DMSO is unstable, whereas the SEI produced by LITFSI and LiNO₃ are much more stable due to the presence of LiF and Li₂O, respectively.^{11, 14} Therefore, the DMSO-free adsorption layer at superconcentrated LITFSI- and LiNO₃-based electrolytes help to form an uniform anion-derived SEI under electrical field, which contribute to improve the long-term cyclability of batteries. In addition, it should be note that preferentially decomposed electrolyte components will contribute to the main component of the SEI in a battery and the redox potential of an electrolyte component is dependent on its interfacial surroundings. According to our proposed model, chemisorbed TFSI⁻ on the gold surface gradually coordinates with Li⁺ as the LITFSI concentration increases, which results in chemisorbed TFSI⁻ with different electronic states. It will be interesting to investigate the redox potential of chemisorbed TFSI⁻ under different coordination states to understand the electroreduction stability of the electrolyte. The evolution of the solvation structure at the gold surface with a bias potential on the gold would also be worthy of investigation. Related research is thus ongoing.

3.3 Conclusion

Understanding of the solvation of electrolytes at the electrode/electrolyte interface between low- and high-concentration electrolytes is critical for the design of new electrolytes with longer-term stability and economy for LMBs. The solvation structure of LITFSI-DMSO and LiNO₃-DMSO solution at gold electrode surface was investigated by SERS measurement. Experimental analysis revealing that DMSO was adsorbed on the gold substrate via Au-S and Au-O bonds, while TFSI⁻ interacted with gold substrate by Au-O bonds. Chemisorbed TFSI⁻ was found to be uncoordinated with Li⁺ in a low-concentration electrolyte, while it became gradually coordinated with an increased LITFSI concentration. However, there is no indication that NO₃⁻ interacts with gold

through chemical adsorption. In a high concentration electrolyte, the adsorption layer on the gold surface is composed entirely of TFSI⁻ in LiTFSI-DMSO solution, while in LiNO₃-DMSO solution NO₃⁻ and Li(DMSO)₃⁺NO₃⁻ complex occupy adsorption layer, which may due to the stronger adsorption strength of TFSI⁻ than NO₃⁻ with gold substrate. The anion -riched adsorption layer was thus thought to promote the formation of lithium salt anion-derived SEI for batteries. In the future, measures could be taken such as: adding additives to enhanced the affinity of TFSI⁻ to the electrode surface, even at low concentrations.

References

- (1) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Wei, F.; Zhang, J. G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. *Adv. Sci.* **2016**, *3*.
- (2) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587-603.
- (3) Xu, W.; Wang, J. L.; Ding, F.; Chen, X. L.; Nasybutin, E.; Zhang, Y. H.; Zhang, J. G. Lithium Metal Anodes for Rechargeable Batteries. *Energy Environ. Sci.* **2014**, *7*, 513-537.
- (4) Peled, E.; Menkin, S. Review-Sei: Past, Present and Future. *J. Electrochem. Soc.* **2017**, *164*, A1703-A1719.
- (5) Chen, W., et al. Designing Safe Electrolyte Systems for a High-Stability Lithium-Sulfur Battery. *Adv. Energy Mater.* **2018**, *8*.
- (6) Trahan, M. J.; Mukerjee, S.; Plichta, E. J.; Hendrickson, M. A.; Abraham, K. M. Studies of Li-Air Cells Utilizing Dimethyl Sulfoxide-Based Electrolyte. *J. Electrochem. Soc.* **2013**, *160*, A259-A267.
- (7) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air Battery. *J. Phys. Chem. C* **2010**, *114*, 9178-9186.
- (8) Calvo, E. J.; Mozhzhukhina, N. A Rotating Ring Disk Electrode Study of the Oxygen Reduction Reaction in Lithium Containing Non Aqueous Electrolyte. *Electrochem. Commun.* **2013**, *31*, 56-58.
- (9) Xu, D.; Wang, Z. L.; Xu, J. J.; Zhang, L. L.; Zhang, X. B. Novel DmsO-Based Electrolyte for High Performance Rechargeable Li-O₂ Batteries. *Chem. Commun.* **2012**, *48*, 6948-6950.
- (10) Roberts, M.; Younesi, R.; Richardson, W.; Liu, J.; Gustafsson, T.; Zhu, J. F.; Edstrom, K. Increased Cycling Efficiency of Lithium Anodes in Dimethyl Sulfoxide Electrolytes for Use in Li-O₂ Batteries. *ECS Electrochem. Lett.* **2014**, *3*, A62-A65.
- (11) Liu, B.; Xu, W.; Yan, P. F.; Kim, S. T.; Engelhard, M. H.; Sun, X. L.; Mei, D. H.; Cho, J.; Wang, C. M.; Zhang, J. G. Stabilization of Li Metal Anode in DmsO-Based Electrolytes Via Optimization of Salt-Solvent Coordination for Li-O₂ Batteries. *Adv. Energy Mater.* **2017**, *7*.

- (12) Lu, Y. Y.; Tu, Z. Y.; Archer, L. A. Stable Lithium Electrodeposition in Liquid and Nanoporous Solid Electrolytes. *Nat. Mater.* **2014**, *13*, 961-969.
- (13) Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A. Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries. *JACS* **2014**, *136*, 5039-5046.
- (14) Yamada, Y.; Yaegashi, M.; Abe, T.; Yamada, A. A Superconcentrated Ether Electrolyte for Fast-Charging Li-Ion Batteries. *Chem. Commun.* **2013**, *49*, 11194-11196.
- (15) Fan, X. L., et al. Highly Fluorinated Interphases Enable High-Voltage Li-Metal Batteries. *Chem* **2018**, *4*, 174-185.
- (16) Suo, L. M.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X. L.; Luo, C.; Wang, C. S.; Xu, K. "Water-in-Salt" Electrolyte Enables High-Voltage Aqueous Lithium-Ion Chemistries. *Science* **2015**, *350*, 938-943.
- (17) Zhang, X. Q.; Chen, X.; Hou, L. P.; Li, B. Q.; Cheng, X. B.; Huang, J. Q.; Zhang, Q. Regulating Anions in the Solvation Sheath of Lithium Ions for Stable Lithium Metal Batteries. *ACS Energy Lett.* **2019**, *4*, 411-416.
- (18) Campion, A.; Kambhampati, P. Surface-Enhanced Raman Scattering. *Chem. Soc. Rev.* **1998**, *27*, 241-250.
- (19) Sharma, B.; Frontiera, R. R.; Henry, A. I.; Ringe, E.; Van Duyne, R. P. Sers: Materials, Applications, and the Future. *Mater. Today* **2012**, *15*, 16-25.
- (20) Ely, Y. E.; Aurbach, D. Identification of Surface-Films Formed on Active Metals and Nonactive Metal-Electrodes at Low Potentials in Methyl Formate Solutions. *Langmuir* **1992**, *8*, 1845-1850.
- (21) Aurbach, D.; Daroux, M.; Faguy, P.; Yeager, E. The Electrochemistry of Noble-Metal Electrodes in Aprotic Organic-Solvents Containing Lithium-Salts. *J. Electroanal. Chem.* **1991**, *297*, 225-244.
- (22) Aurbach, D.; Moshkovich, M.; Cohen, Y.; Schechter, A. The Study of Surface Film Formation on Noble-Metal Electrodes in Alkyl Carbonates/Li Salt Solutions, Using Simultaneous in Situ Afm, Eqcm, Ftir, and Eis. *Langmuir* **1999**, *15*, 2947-2960.
- (23) Martens, W. N.; Frost, R. L.; Kristof, J.; Klopogge, J. T. Raman Spectroscopy of Dimethyl Sulphoxide and Deuterated Dimethyl Sulphoxide at 298 and 77 K. *J. Raman. Spectrosc.* **2002**, *33*, 84-91.

- (24) Vlckova, B.; Matejka, P.; Vanoutersterp, J. W. M.; Snoeck, T. L.; Stufkens, D. J. Surface-Enhanced Raman-Scattering Spectroscopy of Organometallics in Systems with Aqueous Silver Colloids. *Inorg. Chem.* **1994**, *33*, 2132-2136.
- (25) Miller, R. E.; Getty, R. R.; Treuil, K. L.; Leroi, G. E. Raman Spectrum of Crystalline Lithium Nitrate. *J. Chem. Phys.* **1969**, *51*, 1385-+.
- (26) Shen, A. J.; Pemberton, J. E. Interfacial Structure of Dimethylsulfoxide at Ag Electrodes from Surface Enhanced Raman Scattering and Differential Capacitance. *J. Electroanal. Chem.* **1999**, *479*, 21-31.
- (27) Yamada, Y.; Takazawa, Y.; Miyazaki, K.; Abe, T. Electrochemical Lithium Intercalation into Graphite in Dimethyl Sulfoxide-Based Electrolytes: Effect of Solvation Structure of Lithium Ion. *J. Phys. Chem. C* **2010**, *114*, 11680-11685.
- (28) Xuan, X. P.; Wang, J. J.; Zhao, Y.; Zhu, J. J. Experimental and Computational Studies on the Solvation of Lithium Tetrafluoroborate in Dimethyl Sulfoxide. *J. Raman. Spectrosc.* **2007**, *38*, 865-872.
- (29) Rey, I.; Johansson, P.; Lindgren, J.; Lassegues, J. C.; Grondin, J.; Servant, L. Spectroscopic and Theoretical Study of (Cf3so2)(2)N- (Tfsi-) and (Cf3so2)(2)Nh (Htfsi). *J. Phys. Chem. A* **1998**, *102*, 3249-3258.
- (30) Rey, I.; Lassegues, J. C.; Grondin, J.; Servant, L. Infrared and Raman Study of the Peo-Litfsi Polymer Electrolyte. *Electrochim. Acta* **1998**, *43*, 1505-1510.
- (31) Parker, J. F.; Choi, J. P.; Wang, W.; Murray, R. W. Electron Self-Exchange Dynamics of the Nanoparticle Couple [Au-25(Sc2ph)(18)](0/1-) by Nuclear Magnetic Resonance Line-Broadening. *J. Phys. Chem. C* **2008**, *112*, 13976-13981.
- (32) Varnholt, B.; Oulevey, P.; Lubner, S.; Kumara, C.; Dass, A.; Burgi, T. Structural Information on the Au-S Interface of Thiolate-Protected Gold Clusters: A Raman Spectroscopy Study. *J. Phys. Chem. C* **2014**, *118*, 9604-9611.
- (33) Freeman, D. W.; Baglin, F. G. A Raman-Study of Gold Oxygen Bonds from Several Tetracoordinate Complexes in Aqueous-Solution. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 161-167.
- (34) Peng, Z. Q.; Freunberger, S. A.; Hardwick, L. J.; Chen, Y. H.; Giordani, V.; Barde, F.; Novak, P.; Graham, D.; Tarascon, J. M.; Bruce, P. G. Oxygen Reactions in a Non-Aqueous Li⁺ Electrolyte. *Angew. Chem. Int. Ed.* **2011**, *50*, 6351-6355.

- (35) Kim, J. W.; Gewirth, A. A. Mechanism of Oxygen Electroreduction on Gold Surfaces in Basic Media. *J. Phys. Chem. B* **2006**, *110*, 2565-2571.
- (36) Liu, J. C.; Ruffini, N.; Pollot, P.; Llopis-Mestre, V.; Dilek, C.; Eckert, C. A.; Liotta, C. L.; Roberts, C. B. More Benign Synthesis of Palladium Nanoparticles in Dimethyl Sulfoxide and Their Extraction into an Organic Phase. *Ind. Eng. Chem. Res.* **2010**, *49*, 8174-8179.
- (37) Schroter, C.; Roelfs, B.; Solomun, T. The Interaction of Dimethylsulfoxide with a Gold Surface. *Surf. Sci.* **1997**, *380*, L441-L445.
- (38) Feng, Z.; Velari, S.; Cossaro, A.; Castellarin-Cudia, C.; Verdini, A.; Vesselli, E.; Dri, C.; Peressi, M.; De Vita, A.; Comelli, G. Trapping of Charged Gold Adatoms by Dimethyl Sulfoxide on a Gold Surface. *Acs Nano* **2015**, *9*, 8697-8709.
- (39) Chen, Y. X.; Zou, S. Z.; Huang, K. Q.; Tian, Z. Q. Sers Studies of Electrode/Electrolyte Interfacial Water Part II - Librations of Water Correlated to Hydrogen Evolution Reaction. *J. Raman. Spectrosc.* **1998**, *29*, 749-756.
- (40) Murphy, P. J.; LaGrange, M. S. Raman Spectroscopy of Gold Chloro-Hydroxy Speciation in Fluids at Ambient Temperature and Pressure: A Re-Evaluation of the Effects of Ph and Chloride Concentration. *Geochim. Cosmochim. Acta* **1998**, *62*, 3515-3526.
- (41) Kondo, K.; Sano, M.; Hiwara, A.; Omi, T.; Fujita, M.; Kuwae, A.; Iida, M.; Mogi, K.; Yokoyama, H. Conductivity and Solvation of Li⁺ Ions of Lipf6 in Propylene Carbonate Solutions. *J. Phys. Chem. B* **2000**, *104*, 5040-5044.
- (42) Yamada, Y. Developing New Functionalities of Superconcentrated Electrolytes for Lithium-Ion Batteries. *Electrochemistry* **2017**, *85*, 559-565.
- (43) Younesi, R.; Veith, G. M.; Johansson, P.; Edstrom, K.; Vegge, T. Lithium Salts for Advanced Lithium Batteries: Li-Metal, Li-O₂, and Li-S. *Energy Environ. Sci.* **2015**, *8*, 1905-1922.
- (44) Nie, M.; Lucht, B. L. Role of Lithium Salt on Solid Electrolyte Interface (Sei) Formation and Structure in Lithium Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A1001-A1006.
- (45) Chen, Z. H.; Ren, Y.; Jansen, A. N.; Lin, C. K.; Weng, W.; Amine, K. New Class of Nonaqueous Electrolytes for Long-Life and Safe Lithium-Ion Batteries. *Nat. Commun.* **2013**, *4*.

- (46) Tatara, R., et al. Oxygen Reduction Reaction in Highly Concentrated Electrolyte Solutions of Lithium Bis(Trifluoromethanesulfonyl)Amide/Dimethyl Sulfoxide. *J. Phys. Chem. C* **2017**, *121*, 9162-9172.
- (47) Alia, J. M.; Edwards, H. G. M. Ion Solvation and Ion Association in Lithium Trifluoromethanesulfonate Solutions in Three Aprotic Solvents. An Ft-Raman Spectroscopic Study. *Vib. Spectrosc* **2000**, *24*, 185-200.
- (48) Fujii, K.; Wakamatsu, H.; Todorov, Y.; Yoshimoto, N.; Morita, M. Structural and Electrochemical Properties of Li Ion Solvation Complexes in the Salt-Concentrated Electrolytes Using an Aprotic Donor Solvent, N,N-Dimethylformamide. *J. Phys. Chem. C* **2016**, *120*, 17196-17204.
- (49) Yang, G.; Ivanov, I. N.; Ruther, R. E.; Sacci, R. L.; Subjakova, V.; Hallinan, D. T.; Nanda, J. Electrolyte Solvation Structure at Solid-Liquid Interface Probed by Nanogap Surface-Enhanced Raman Spectroscopy. *Acs Nano* **2018**, *12*, 10159-10170.
- (50) Linert, W.; Jameson, R. F.; Taha, A. Donor Numbers of Anions in Solution - the Use of Solvatochromic Lewis-Acid Base Indicators. *Dalton Trans.* **1993**, 3181-3186.
- (51) Togasaki, N.; Momma, T.; Osaka, T. Enhanced Cycling Performance of a Li Metal Anode in a Dimethylsulfoxide-Based Electrolyte Using Highly Concentrated Lithium Salt for a Lithium-Oxygen Battery. *J. Power Sources* **2016**, *307*, 98-104.
- (52) daCunha, M. C. P. M.; Weber, M.; Nart, F. C. On the Adsorption and Reduction of NO₃⁻ Ions at Au and Pt Electrodes Studied by in Situ Ftir Spectroscopy. *J. Electroanal. Chem.* **1996**, *414*, 163-170.
- (53) Marinkovic, N. S.; Calvente, J. J.; Kloss, A.; Kovacova, Z.; Fawcett, W. R. Sniftirs Studies of the Electrochemical Double Layer - Part II. Au(111) Electrode in Solutions with Specifically Adsorbed Nitrate Ions. *J. Electroanal. Chem.* **1999**, *467*, 325-334.
- (54) Nowinski, J. L.; Lightfoot, P.; Bruce, P. G. Structure of Lin(Cf₃so₂)₂, a Novel Salt for Electrochemistry. *J. Mater. Chem.* **1994**, *4*, 1579-1580.
- (55) Seo, D. M.; Boyle, P. D.; Sommer, R. D.; Daubert, J. S.; Borodin, O.; Henderson, W. A. Solvate Structures and Spectroscopic Characterization of Litfsi Electrolytes. *J. Phys. Chem. B* **2014**, *118*, 13601-13608.
- (56) Johansson, P.; Gejji, S. P.; Tegenfeldt, J.; Lindgren, J. The Imide Ion: Potential Energy Surface and Geometries. *Electrochim. Acta* **1998**, *43*, 1375-1379.

- (57) Umebayashi, Y.; Mitsugi, T.; Fukuda, S.; Fujimori, T.; Fujii, K.; Kanzaki, R.; Takeuchi, M.; Ishiguro, S. I. Lithium Ion Solvation in Room-Temperature Ionic Liquids Involving Bis(Trifluoromethanesulfonyl) Imide Anion Studied by Raman Spectroscopy and Dft Calculations. *J. Phys. Chem. B* **2007**, *111*, 13028-13032.
- (58) Upadhyay, G.; Devi, T. G. Raman Spectroscopic Study of Polar Aprotic Molecule and Its Molecular Associations with Chemical and Isotopic Solvents: Comparative Study with Quantum-Chemical Calculations. *J. Mol. Liq.* **2014**, *197*, 263-271.

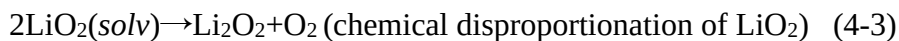
Chapter 4

Oxygen Reduction Reaction in High-concentrated Electrolyte of Lithium Nitrate-Dimethyl Sulfoxide

4.1 Introduction

With the development of the electric vehicle industry, lithium-air batteries have received widespread attention because of its extremely high theoretical specific capacity (3860 mAh g^{-1}).¹⁻³ Even though two decades of research have gone through since the concept of lithium-air battery was proposed¹, some obstacles still hinder its commercialization, mainly low round-trip energy efficiency⁴⁻⁶ and low practical areal capacity⁷⁻⁸. The low round-trip energy efficiency mainly arises from the instability of lithium anode, i.e., lithium dendrite formation,^{3, 9-10} while the low practical areal capacity is due to the passivation of air cathode by Li_2O_2 , the discharging product on air cathode.¹¹⁻¹³ The issue related to lithium dendrite formation on lithium anode is attributing to terrible SEI layer which composed of organic and inorganic degradation products of aprotic electrolyte with lithium salt.¹⁴⁻¹⁶ Thus, the composition and property of SEI could be modulated by adjusting electrolyte components such as, selection of proper solvent,¹⁷ lithium salt¹⁸⁻¹⁹ or additives^{3, 20-21}.

The cell capacity was widely believed to depends on electrolyte components as well. The oxygen reduction reaction (ORR) mechanism on air cathode in aprotic electrolyte was considered to depend mainly on the Gutmann acceptor number (AN) and donor number (DN) of electrolyte, instead of O_2 solubility, ionic conductivity and viscosity of electrolyte.²²⁻²⁵ The use of low DN solvents such as dimethoxyethane in commonly-used 1 M solution would induce surface reaction pathway, while high DN solvent such as DMSO lead to solution pathway. The surface pathway is that oxygen is converted to Li_2O_2 on electrode surface through a 2e^- oxygen reaction (reaction (4-1) and (4-4) as follow). The solution pathway could be divided into two steps to produce Li_2O_2 : (1) O_2 was reduced on electrode surface by 1e^- oxygen reduction and combine with one Li^+ into LiO_2 , and go to solution (reaction (4-1) and (4-2)); (2) The LiO_2 in solution was further converted into Li_2O_2 via chemical disproportionation of LiO_2 to Li_2O_2 (reaction (4-3)).^{22-24, 26-27} That is,



* represents intermediate on electrode surface, *solv* means in solution. The DN of lithium salt anion has also been shown to affect the reaction pathway of ORR. High DN of lithium salt was proven to enhance discharge capacity in low DN solvents by increasing the solubility of ORR intermediates, such as LiNO_3 in DME, whereas the enhancement could not be observed in high DN solvent like DMSO.¹²

Since DMSO was introduced to lithium-air batteries, as a representative of high DN solvents, it has received extensive attention from researchers due to achieved high capacity.^{13, 28-30} However, the SEI layer derived from DMSO was not a good passivator for lithium anode, which would be resulting low cycle performance of the battery.³¹⁻³³ In DMSO solution with Li salt, Li^+ is solvated by DMSO to form $\text{Li}(\text{DMSO})_4^+$ complex.³⁴⁻³⁶ Conventional 1 M DMSO-based electrolytes possess high proportion of free DMSO molecules. As the concentration of lithium salt increases, the free DMSO that is not involved in $\text{Li}(\text{DMSO})_4^+$ decreases.³⁷ Extremely, electrolytes with high lithium salt concentration was termed “superconcentrated electrolyte” that no or very little free DMSO exists in solution.³⁸⁻³⁹ The electrolyte with this unique property is reported to greatly improve the stability of lithium anode by forming an anion-derived SEI on lithium metal.^{31, 33, 40} However, the effect of lithium salt concentration on the ORR mechanism was limited. Tatara et al. shows that LiO_2 dissolution was prohibited by increasing LITFSI concentration over 2.3 mol L^{-1} owing to the lack of free DMSO in electrolyte by RRDE measurement in LITFSI-DMSO solutions.³⁷ Leverick et al. reported that increasing salt concentration would weaken Li^+ solvation, resulting in an increment of $\text{Li}^+ \text{-O}_2^-$ coupling strength and thus decrease soluble species during ORR.²⁶ Note that above conclusions are just drawn based on ex-situ method. As the ORR mechanism strongly dependence on the surroundings at electrode surface as well as working potential. Consequently, the use of in situ characterization method would disclose the actual surface electrochemistry more precisely.

In the present study, in situ surface enhanced Raman spectroscopy (SERS) and electrochemical quartz crystal microbalance (EQCM) measurements were used to monitor surface reaction on electrode surface in various concentration of LiNO₃-DMSO solutions, while rotating ring/disk electrodes (RRDE) were utilized to detect soluble reaction product. Gold was used as working electrode because it has been shown to produce less Li₂CO₃ and limit the decomposition of DMSO, thus enhancing the cycling performance of Li-O₂ battery,⁴¹⁻⁴³ b) the intrinsic ORR activity on gold electrode is much more active than glassy carbon during discharge.⁴⁴⁻⁴⁵ It turns out that the effect of LiNO₃ concentration on oxygen reduction mainly achieved by affecting the O₂⁻ adsorbed on the electrode surface and LiO₂ dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. It shows that the O₂⁻ adsorbed on electrode surface in low concentration is much higher than that in medium concentration, which allow for more O₂⁻ to be reduced into Li₂O₂ in low concentration. While in the high-concentration electrolyte, due to the high viscosity of the electrolyte, a large amount of O₂⁻ is concentrated on the electrode surface, eventually failed to form Li₂O₂.

4.2 Results and discussion

4.2.1 RRDE measurements

Linear sweep voltammograms (LSV) of oxygen reduction were obtained using RRDE measurement in O₂-saturated various concentrated LiNO₃-DMSO solutions on gold disk/ring electrode at 900 rpm to detect the formation of soluble reduction intermediates (**Figure 4-1(a)**). Cathodic current starts flow at ca. 2.8 V and a reduction peak was observed at around 2.4 V for all electrolytes, rather than a steady current, which can be attributed to that ORR kinetic under dynamic conditions are limited not by the constant mass transport, but rather electron transfer, such as through a growing layer of insulating Li₂O₂. With the increase of LiNO₃ concentration, the peak current density of the reduction reaction is reduced, means that the ORR is affected by LiNO₃ concentration. There is a positive ring current (E_{ring} is 3.5 V, which is enough to oxidize soluble oxidizable species in present study) during the ORR for all electrolytes which is consistent with the depletion of LiO₂ from the electrode surface during rotation. The peak current of ring electrode decreases with LiNO₃ concentration, which is coincided with the decrease

of peak current of disk electrode. The ratio of ring-disk charge ($Q_{\text{Ring}}/Q_{\text{Disk}}$), against LiNO_3 concentration was calculated in **Figure 4-1(b)** based on Figure 4-1(a), representing quantitative comparison of LiO_2 dissolution from disk electrode to ring electrode. Theoretic collection efficiency (N_k) value of 0.23 was obtained experimentally in the O_2 -saturated NBu_4NO_3 -DMSO solution at potentials more negative than 2.5 V, where O_2^- is generated with 100% current efficiency at the disk electrode. Figure 4-1(b) shows that as the concentration of LiNO_3 increases from 0.58 to 2.21 M, the ratio slightly decreases from ca. 0.19 to 0.17, while as concentration higher than 2.21 M, it significantly decreases to ca. 0.09 at 4.13 M. This observation shows that, as LiNO_3 concentration lower than 2.21 M, it has little effect on the dissolution of LiO_2 , as the concentration higher than 2.21 M, the dissolution of LiO_2 gradually decreases. Note that even the maximum $Q_{\text{Ring}}/Q_{\text{disk}}$ ratio is less than collection efficiency of the RRDE (0.23), this is attributed to the passivation of disk electrode by insulating Li_2O_2 .

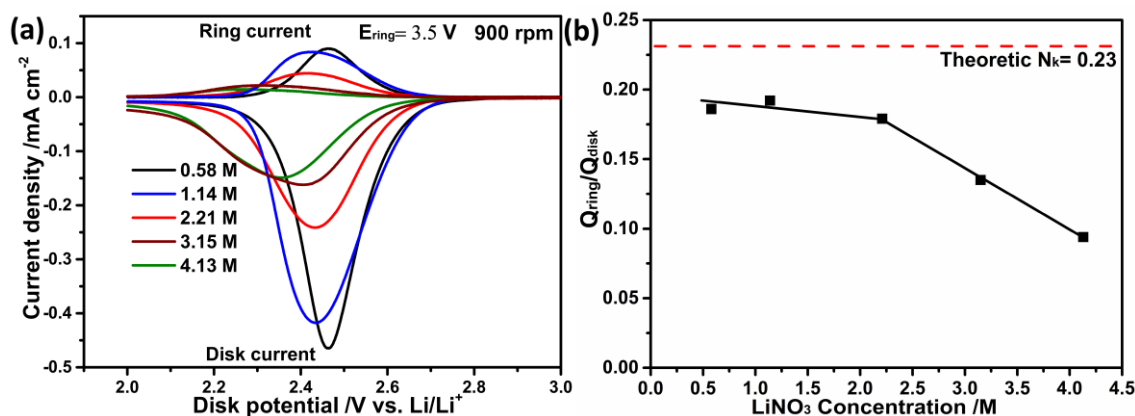


Figure 4-1. (a) Current response of ORR at 10 mV s^{-1} in O_2 -saturated 0.58, 2.21 and 4.13 M LiNO_3 -DMSO solutions on gold electrode at 900 rpm showing disk (cathodic current) and ring current (anodic current) densities. The ring was held at 3.5 V vs Li/Li^+ . (b) Concentration-dependence of ring-disk charge ratio. Red dash line represent the theoretic N_k determined by O_2/O_2^- redox reaction. The line in (b) is just guide for eyes.

To systematically investigate the effect of applied discharge potential on the amount of LiO_2 , potentiostatic ORR measurements were carried out at a rotation of 900 rpm. 0.58, 2.21 and 4.13 M LiNO_3 -DMSO solutions was used represent low, medium and high concentration electrolytes, respectively. The potential of disk was step from OCP (ca. 3.2 V) to investigated potentials between 3.0 and 2.0 V, while the potential of ring

was step from OCP (ca. 3.2V) to 3.5 V (**Figure 4-2**). In 0.58 M solution, both disk and ring current responses are constant at 2.6 V, which can be attributed to steady-state production of soluble LiO_2 with minimal Li_2O_2 formation on disk electrode (**Figure 4-2(a) and (b)**). In contrast, disk/ring currents response at higher overpotentials (defined as the difference between the applied potential and reversible potential of 2.96 V vs $\text{Li}/\text{Li}^{+44}$) decay with time, where both of them decay faster and faster with increasing overpotential, which might be resulting from the passivation of the disk by solid Li_2O_2 with potential.

In 2.21 M solution, the disk and ring current is not constant as that in 0.58 M solution which shows slightly decrease with time even though at 2.7 V, suggesting that the passivation of disk electrode is occurred at lower overpotential than in 0.58 M solution (**Figure 4-2(c) and (d)**). At higher overpotential, both disk and ring current decay with time, representing the passivation of disk electrode at high overpotential. In 4.13 M, the disk current shows constant at 2.5 and 2.6 V, and slightly decay at higher potential, while the ring current at investigated four potentials, i.e. 2.5, 2.4, 2.3 and 2.2 V are all constant (**Figure 4-2(e) and (f)**). This observation shows that the steady-state production of soluble LiO_2 could be achieved not only at low overpotential but also high overpotential in high concentration solution, which further suggest that in contrast to low- and medium concentration, the passivation of disk electrode is weaker in high overpotential.

The $Q_{\text{ring}}/Q_{\text{disk}}$ ratio versus applied disk potential was shown in **Figure 4-2(g)**. The $Q_{\text{ring}}/Q_{\text{disk}}$ ratio was calculated based on potentiostatic current response on ring and disk electrode shown in Figure 4-2(a) to (f). It can be found that this ratio decreases as potential become negative for both 0.58 and 2.21 M solutions, indicating that increasing the overpotential tend to transform LiO_2 to insoluble Li_2O_2 on electrode. In addition, the $Q_{\text{ring}}/Q_{\text{disk}}$ ratio for 2.21 M solution is lower than that in 0.58 M solution at the same potential. This means higher proportion of charge was consumed for Li_2O_2 formation in 2.21 M solution compared with 0.58 M, instead of soluble LiO_2 . However, the ratio for 4.13 M solution is remarkably lower than that in 0.58 and 2.21 M solutions, which is due to low LiO_2 diffusion rate hindered by high electrolyte viscosity, as is confirmed later. In addition, $Q_{\text{ring}}/Q_{\text{disk}}$ ratio at high overpotential is higher than low overpotential, which is opposite to the tendency in 0.58 and 2.21 M solution, suggesting more LiO_2 was generated at higher overpotential. It worth noting that, even at potential where steady-state production of soluble LiO_2 such as 2.6 V in 0.58 M solution, the ring-disk charge ratio is

smaller than the theoretic N_k (0.23). This indicates that even at the highest LiO_2 solubilities, LiO_2 generated at the disk electrode can be partially converted to insoluble Li_2O_2 before transport to the ring can occur.

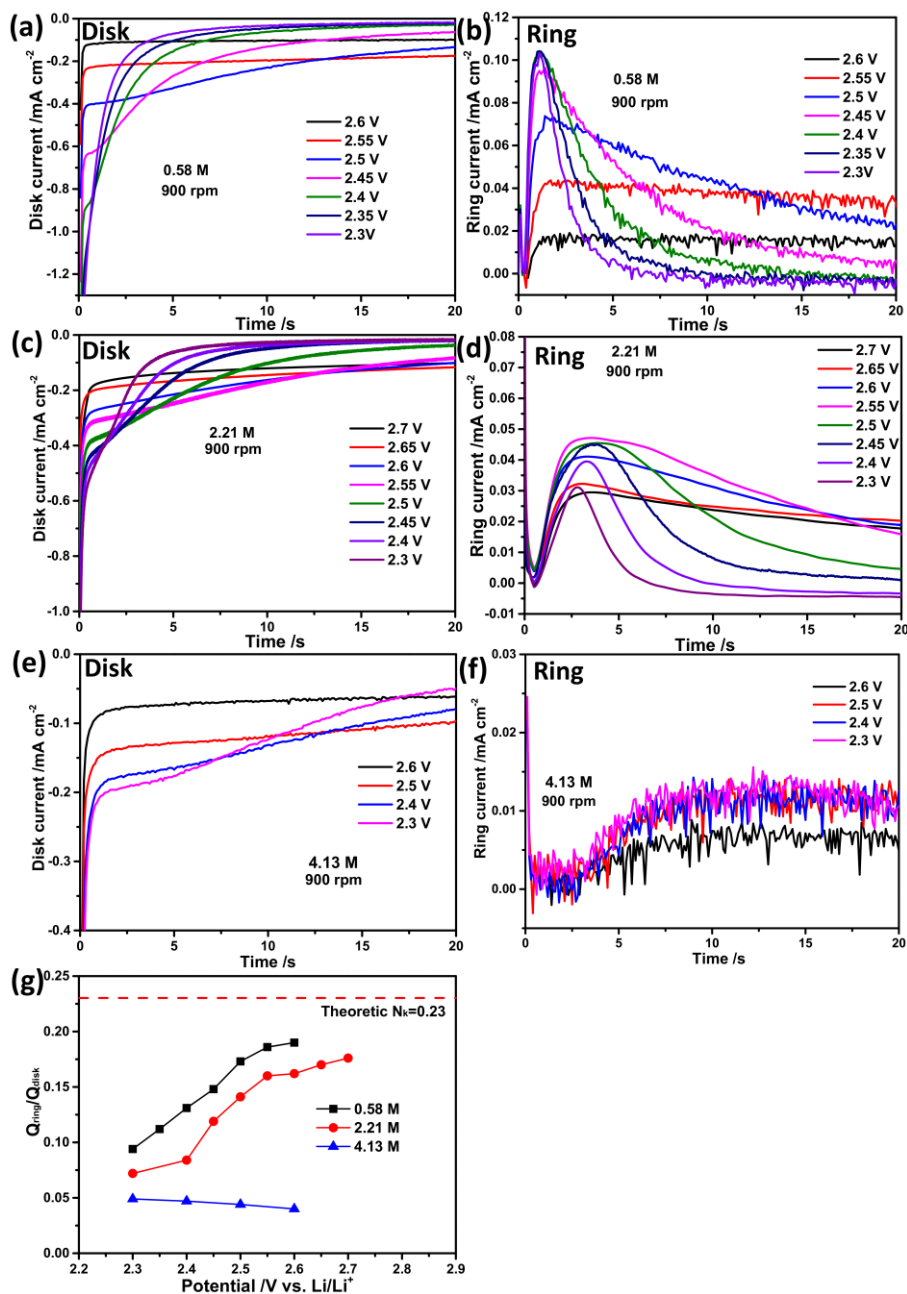


Figure 4-2. First 20 s of ring and disk current response in O_2 -saturated (a, b) 0.58, (c, d) 2.21 and (e, f) 4.13 M LiNO_3 -DMSO solutions with the ring held at 3.5 V vs Li/Li^+ . The potential applied on disk electrode was shown in the figure. (g) $Q_{\text{ring}}/Q_{\text{disk}}$ ratio versus applied disk potential in above three electrolytes. The lines in the (g) just guide for eyes.

4.2.2 In situ SERS measurements

As RRDE measurement is sensitive to the formation of soluble specie during ORR, in order to further confirm the interfacial species, in situ SERS measurement was carried out. As shown in **Figure 4-3 (a) to (c)**, peaks in the frequency of 630~750 cm^{-1} , 930~990 cm^{-1} and 990 ~ 1090 cm^{-1} are assigned as C-S-C stretching, CH_3 rocking and S = O stretching modes of DMSO, respectively.⁴⁶⁻⁴⁷ The sharp peak observed at 1043 cm^{-1} is due to stretching vibration modes of NO_3^- .⁴⁸ Weak features observed at 459 cm^{-1} and 1120 cm^{-1} are due to stretching mode ($\nu(\text{Au-O})$) of chemisorbed DMSO on gold and adsorbed O_2 .⁴⁹⁻⁵¹ In addition, three peaks related to oxygen reduction products could be observed in the low overpotential region. The peak at 490 cm^{-1} is ascribed to Au-O stretching mode ($\nu(\text{Au-O})$) of chemisorbed O_2^- on gold and peak at 789 cm^{-1} is assigned to O-O stretching mode of Li_2O_2 ($\nu(\text{Li}_2\text{O}_2)$), while 1110 cm^{-1} is due to stretching mode of O_2^- ($\nu(\text{O}_2^-)$).^{28, 52} **Figure 4-3 (d) to (f)** show potential dependence of current and integrate intensity at 490 cm^{-1} , 789 cm^{-1} and 1110 cm^{-1} in three different electrolytes

In 0.58 M solution (**Figure 4-3(a) and (d)**), the integrate intensity of peaks at 490 cm^{-1} and 1110 cm^{-1} due to $\nu(\text{Au-O})$ and $\nu(\text{O}_2^-)$ start to increase as potential negative than 2.8 V. Before decreasing to 0 at ca. 2.3 V, both peaks reach to maximum at ca. 2.7 V. Just at the potential where above two peaks decrease, i.e. 2.7 V, $\nu(\text{Li}_2\text{O}_2)$ increased significantly and reached a maximum at 2.6 V, then its intensity gradually decreased as the potential became negative. Thus, the decreasing of $\nu(\text{Au-O})$ and $\nu(\text{O}_2^-)$ peak might contribute to the formation of Li_2O_2 on electrode surface. The above observation shows that as the potential is higher than 2.7 V, ORR relate to one electron oxygen reduction (reaction (4-1)) on electrode surface. While at potential from 2.7 to 2.3 V, adsorbed O_2^- on electrode surface was further reduced into Li_2O_2 . The O_2 was directly convert to Li_2O_2 by surface $2e^-$ reaction as the potential negative than 2.3 V.

In 2.21 M solution (**Figure 4-3(b)**), $\nu(\text{Au-O})$ and $\nu(\text{O}_2^-)$ peak could hardly be observed in the entire investigated potential area, only $\nu(\text{Li}_2\text{O}_2)$ peak shows potential dependence. This peak start at ca. 2.7 V and increase sharply to 2.6 V, then decreased as potential became more negative. It worth noting that at potential region from 2.8 to 2.7 V, ORR current was continuously flowing. However, ORR related products were not detected. Interestingly, in 4.13 M solution (**Figure 4-3(c)**), the peak intensity of $\nu(\text{Au-O})$

and $\nu(\text{O}_2^-)$ start at ca. 2.8 V and gradually increase until 2.0 V, which is not consistent with current response. Noting that in the three investigated electrolytes, the Raman peak of solid LiO_2 was not observed in the corresponding SERS spectra (ca. 1130 cm^{-1}), excluded the presence of solid LiO_2 on the electrode surface.²³ In the three investigated electrolytes, the behavior of Li_2O_2 intensity against potential show almost similar profile as current response. However, the behavior of O_2^- is quite different. The detailed explanation will be discussed in a later section.

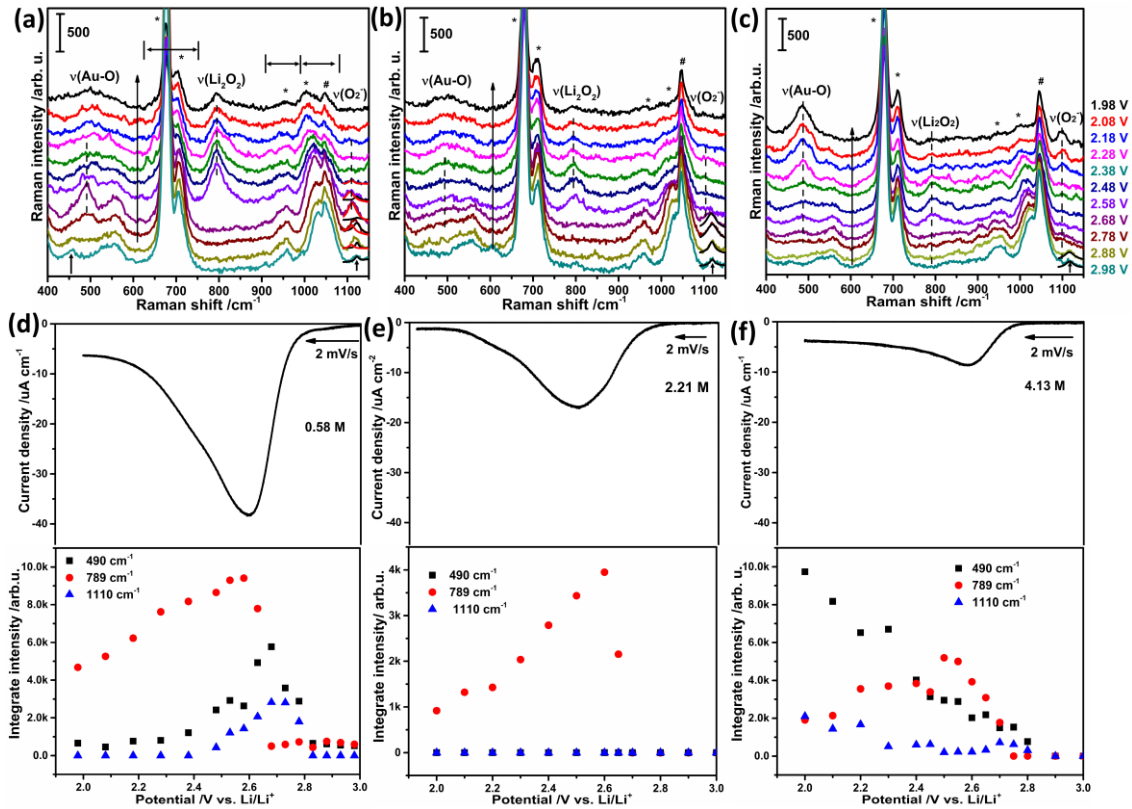


Figure 4-3. In situ SERS measurement recorded in different potential at a scan rate of 2 mV s^{-1} in (a) 0.58, (b) 2.21 and (c) 4.13 M LiNO_3 -DMSO solutions. * and # represent vibrational mode from DMSO and LiNO_3 , respectively. potential dependence of current (top panel) and integrate SERS intensity (bottom panel) for $\nu(\text{Au-O})$, $\nu(\text{Li}_2\text{O}_2)$ and $\nu(\text{O}_2^-)$ during scanning in (d) 0.58, (e) 2.21 and (f) 4.13 M solutions.

4.2.3 In situ EQCM measurements

EQCM measurements was carried out to further confirm above insights, which are sensitive to the deposition of solid species. **Figure 4-4(a) and (b)** shows the current

and frequency shift (ΔF) as function of potential recorded simultaneously on Au QCM electrode at 2 mV s^{-1} in 0.58, 2.21 and 4.13 M LiNO_3 -DMSO solutions. As can be seen, the current start to flow for all three solutions at ca. 2.8 V, whereas the onset of frequency change is more negative compared with the onset of current (ca. 100 mV for 0.58 M solution and ca. 200 mV for the rest two solutions). In other words, at the beginning of ORR (ca. 2.8~2.7 V for 0.58 M solution, ca. 2.8~2.6 V for 2.21 and 4.13 M solutions), the consumption of electrons was not contribute to mass change on electrode surface, which might relate to one electron oxygen reduction (reaction (1) in Table 1), where mass change is zero.⁵³ As the current continues to flow, the corresponding frequency change gradually increases, confirmed the indication by RRDE measurement that increasing overpotential would result in more amounts of insoluble Li_2O_2 on electrode. In addition, the frequency decrease in 0.58 M solution (ca. 780 Hz) until 2 V is significantly higher than that in 2.21 M (ca. 95 Hz) and 4.13 M solutions (ca. 200 Hz) (Figure 4-4(b)).

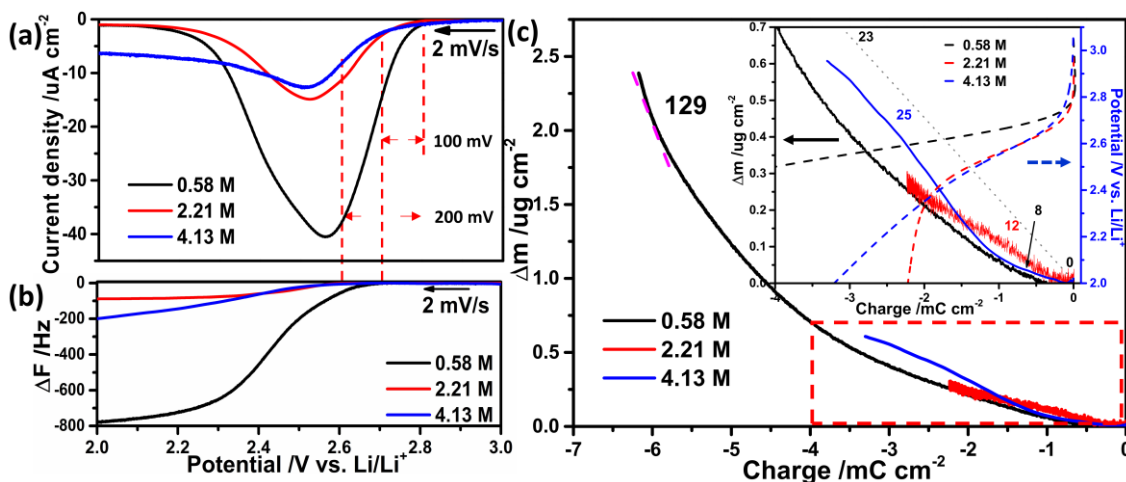


Figure 4-4. Potential dependencies of current (a) and corresponding frequency change (b) at a scan rate of 2 mV s^{-1} , (c) mass change as a function of charge in 0.58, 2.21 and 4.13 M LiNO_3 -DMSO solutions. Inset is the enlarged area marked by red dash rectangle. left Y-axis is mass change and right Y-axis potential. Solid lines and long dotted lines represent mass change and potential, respectively. Short dotted lines show Δm -charge relation for mpe of 7 and 23 $\text{g mol}^{-1}\text{-e}^{-1}$, corresponding to atomic weight of Li, half of molecular weight of Li_2O_2 , respectively.

Figure 4-4(c) and inset shows the mass change, which is calculated based on frequency change by considering viscoelastic change as a function of the integrate

charge.⁵⁴ The initial slope, i.e., mass change per electron (mpe) in three solutions was 0 when charge up to -0.5 mC cm^{-2} , representing reaction (1) ($\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solution})$, $0 \text{ g mol}^{-1} \cdot \text{e}^{-1}$) in Table 1, which is consistent with the frequency delay described previously. Detailed mpe and corresponding information in specific potential range was shown in **Figure 4-5** based on Figure 4-4(c). In 0.58 M solution, mpe slightly increase to $8 \text{ g mol}^{-1} \cdot \text{e}^{-1}$ at potential range from ca. 2.7 to 2.6 V. Although this value is very close to the mpe of $7 \text{ g mol}^{-1} \cdot \text{e}^{-1}$ for reaction (2) and (3), it cannot represent these two reactions is occurring because both reactions need LiO_2 or Li_2O_2 as a reactant, which is excluded by in situ SERS measurement in section 4.2.2. According to in situ SERS result in 0.58 M solution, O_2^- was found to chemisorbed on electrode surface at this potential region. Considering that O_2^- adsorbed on the electrode surface can easily combine with Li^+ to form highly soluble LiO_2 and leave electrode surface, $8 \text{ g mol}^{-1} \cdot \text{e}^{-1}$ might correspond to the average combination of generating soluble LiO_2 (reaction (1), $\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solution})$, $0 \text{ g mol}^{-1} \cdot \text{e}^{-1}$, 75%) and chemisorbed O_2^- (reaction (6), $\text{O}_2 + \text{e}^- \leftrightarrow \text{O}_2^-(\text{electrode})$, $32 \text{ g mol}^{-1} \cdot \text{e}^{-1}$, 25%). The ratio in brackets was calculated based on the charge balance and mass balance on the basis of above two reactions, which finally contribute to $8 \text{ g mol}^{-1} \cdot \text{e}^{-1}$. In fact, according to the results of in situ SERS measurement in 2.21 and 4.13 M solution, $8 \text{ g mol}^{-1} \cdot \text{e}^{-1}$ was not observed in 2.21 M solution where O_2^- was not detected, while this value is present in 4.13 M solution where O_2^- was detected. The above results further indicate $8 \text{ g mol}^{-1} \cdot \text{e}^{-1}$ represents the average combination of generating soluble LiO_2 and chemisorbed O_2^- .

Table 1. Possible reaction during ORR and corresponding mpe.

	Reaction	mpe ($\text{g mol}^{-1} \cdot \text{e}^{-1}$)
(1)	$\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solution})$	0
(2)	$\text{LiO}_2(\text{solid}) + \text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}_2\text{O}_2(\text{solid})$	7
(3)	$\text{Li}_2\text{O}_2(\text{solid}) + 2\text{e}^- + 2\text{Li}^+ \leftrightarrow \text{Li}_2\text{O}(\text{solid})$	7
(4)	$\text{O}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Li}_2\text{O}(\text{solid})$	15
(5)	$\text{O}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2(\text{solid})$	23
(6)	$\text{O}_2 + \text{e}^- \leftrightarrow \text{O}_2^-(\text{electrode})$	32
(7)	$\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solid})$	39
(8)	$\text{LiO}_2(\text{solution}) + \text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}_2\text{O}_2(\text{solid})$	46
(9)	$2\text{LiO}_2(\text{solution}) \leftrightarrow \text{Li}_2\text{O}_2(\text{solid}) + \text{O}_2$	∞

As the potential increase to peak potential (ca. 2.5 V), mpe gradually increased to $23 \text{ g mol}^{-1} \cdot \text{e}^{-1}$, represent that ORR was gradually dominated by surface-mediated 2e^- reduction (reaction(5), $\text{O}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2(\text{solid})$, $23 \text{ g mol}^{-1} \cdot \text{e}^{-1}$). As potential sweep from peak potential to 2 V, the mpe increase to $129 \text{ g mol}^{-1} \cdot \text{e}^{-1}$, which is much higher than the

mpe for possible ORR reaction in Table (1). Such high mpe is also observed in other works where DMSO was used as solvent. The co-deposition of the solvent (DMSO) with Li_2O_2 arise from strong interaction between Li^+ and DMSO was thought to contribute to the high mpe.⁵⁵⁻⁵⁶ The above analysis shows that O_2 was converted to O_2^- at low overpotential and electrochemical reduce to Li_2O_2 at high overpotential in low LiNO_3 concentration.

In 2.21 M solution, a mpe value of 0 was observed from ca. 2.8 to 2.6 V, reflecting one electron reduction of oxygen (reaction (1), $\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solution})$, $0 \text{ g mol}^{-1} \text{e}^{-1}$). At potential below 2.6 V, the mpe is almost constant at $12 \text{ g mol}^{-1} \text{e}^{-1}$ which is close to reaction (4) ($\text{O}_2 + 4\text{Li}^+ + 4\text{e}^- \leftrightarrow \text{Li}_2\text{O}(\text{solid})$, $15 \text{ g mol}^{-1} \text{e}^{-1}$). However, Li_2O related vibrational peak was not observed by in situ SERS measurement, only Li_2O_2 could be detected. Thus, the mpe of $12 \text{ g mol}^{-1} \text{e}^{-1}$ is likely representing that 48% charge was consumed for reaction (1) ($\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_2(\text{solution})$, $0 \text{ g mol}^{-1} \text{e}^{-1}$) and 52% charge for reaction (5) ($\text{O}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2(\text{solid})$, $23 \text{ g mol}^{-1} \text{e}^{-1}$).

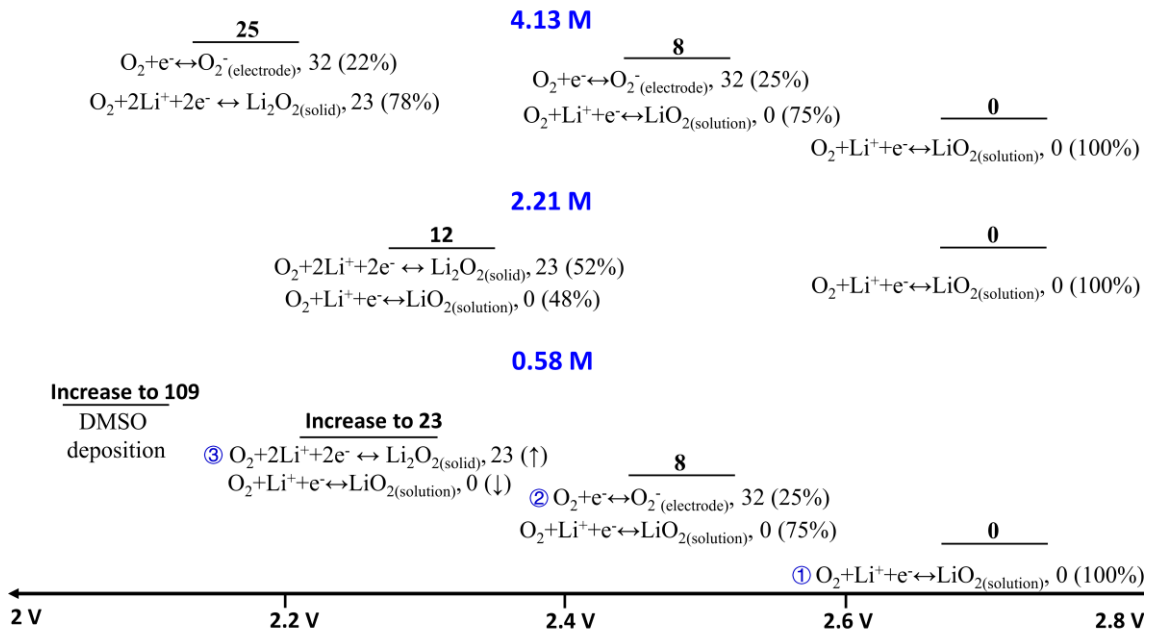


Figure 4-5. Summary of reaction occurred in 0.58, 2.21 and 4.13 M solution with potential. The bold number on solid line represent mpe number. The percentage in brackets represent the reaction that contribute to overall mpe on solid line. ↑ and ↓ represent percentage increase and decrease, respectively. The blue ①, ② and ③ is used in Scheme 1 to illustrate occurred reaction.

In a high-concentrated electrolyte of 4.13 M solution, the potential could be divided into three part according to the mpe value. That is ca. 2.8-2.6V, ca. 2.6-2.5 V and ca. 2.5-2.0 V, corresponding to mpe of 0, 8 and 25 g mol⁻¹-e⁻¹, respectively. The mpe of 0 and 8 g mol⁻¹-e⁻¹ reflect same process as in low concentration, while 25 g mol⁻¹-e⁻¹ is little bit higher than that of reaction (5) ($\text{O}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_{2(\text{solid})}$, 23 g mol⁻¹-e⁻¹, 78%), which might involve small amount of chemisorbed O₂⁻ (reaction (6), $\text{O}_2 + \text{e}^- \leftrightarrow \text{O}_{2(\text{electrode})}^-$, 32 g mol⁻¹-e⁻¹, 22%). However, in situ SERS measurements has ruled out the existence of LiO₂. The increment in this value thus could be originated from the chemisorption of some O₂⁻ on electrode surface as is confirmed by in situ SERS measurement.

Therefore, combining the analysis of SERS and EQCM measurement, it can be found that electrochemical reduction of O₂ was occurred firstly by one electron reduction from O₂ to LiO₂ and dissolve in electrolyte at low overpotential for all concentration region. As potential shift to more negative, O₂⁻ was found to capable of chemisorbed on electrode surface and show different behavior as a function of LiNO₃ concentration. At low concentration, O₂⁻ was detected on electrode surface at low overpotential, while the presence of O₂⁻ on electrode was not observed in medium concentration. In high concentration, O₂⁻ was found to detected on electrode surface from low overpotential to high overpotential. The detailed explanation of its origin would be discussed in next section. At higher overpotential, most of O₂ was converted into Li₂O₂ by surface-mediated 2e⁻ reduction, i.e. surface pathway for electrolytes. At the same time, part of O₂ was reduced to LiO₂ and dissolve into the electrolyte for both 0.58 and 2.21 M solution, while in 4.13 M solution, O₂⁻ generation was occurred instead of LiO₂ formation. In addition, in 0.58 M solution, the proportion of LiO₂ dissolution decrease with potential increase, which is consistent with the RRDE measurement results.

Regarding to solution pathway, direct evidence was not observed in the present study. To data, little direct evidence exists during cell discharge. The observation of toroidal Li₂O₂ particles after discharging was thought to the most direct indication of solution pathway.^{22, 57} However, limited by low discharge capacity during CV, the toroidal Li₂O₂ particles of nuclear growth is too small to be observed at present. A recent study shows that the addition of Li⁺ into KO₂-saturated DMSO would generate Li₂O₂ with morphologies closely to toroidal particles observed in Li-O₂ battery, proved the disproportionation of LiO₂ to Li₂O₂.⁵⁸ Considering the high solubility of LiO₂ in DMSO

solution by RRDE measurement, solution pathway should also be considered, especially at low overpotential where more LiO_2 was dissolved.

4.2.4 The behavior of LiO_2 dissolution against LiNO_3 concentration and its role in affecting oxygen reduction reaction.

According to above analysis, it will be interesting to understand the origin of LiO_2 dissolution and its role in affecting oxygen reduction reaction against LiNO_3 concentration. RRDE measurement in section 4.2.1 shows that the ratio of $Q_{\text{ring}}/Q_{\text{disk}}$ decreases with the increase of LiNO_3 concentration, indicating that the ratio of LiO_2 diffuse from disk electrode to the ring electrode decreases. This ratio depends on the solubility of LiO_2 on the one hand, and the diffusion rate of LiO_2 on the other hand. The diffusion of an ion is usually affected by viscosity of electrolyte, because high viscosity electrolyte usually leads to a higher diffusion resistance. **Figure 4-6(a)** shows the concentration-dependence of kinematic viscosity in various concentration of LiNO_3 -DMSO solutions at 25°C. The viscosity increases exponentially with LiNO_3 concentration increase, which can be correlated with the solvation structure change of electrolyte with LiNO_3 concentration. As discussed in Chapter 3, as the concentration of LiNO_3 increases, free DMSO and NO_3^- gradually coordinates with Li^+ to form $\text{Li}(\text{DMSO})_4^+$ and $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ cluster. The larger hydrodynamic radius of $\text{Li}(\text{DMSO})_4^+$ and $\text{Li}(\text{DMSO})_3^+\text{NO}_3^-$ in the solution was thought to contribute to the increasement of viscosity. Concentration-dependence of $Q_{\text{ring}}/Q_{\text{disk}}$ ratio in Figure 4-1(b) shows inverse tendency to viscosity that electrolyte viscosity increases with $Q_{\text{ring}}/Q_{\text{disk}}$ ratio decrease. It seems the viscosity and $Q_{\text{ring}}/Q_{\text{disk}}$ ratio correlate with each other. Note that RRDE measurement in 0.58 M solution with higher rotation speed (1600 rpm) shows increasing disk/ring currents but same $Q_{\text{ring}}/Q_{\text{disk}}$ ratio of 0.185 as that at 900 rpm (**Figure 4-6(a)**). This suggests that the viscosity is not the major factor to determine LiO_2 dissolution from disk electrode to ring electrode at low concentration. However, in 4.13 M solution, the $Q_{\text{ring}}/Q_{\text{disk}}$ ratio is 0.098 at 1600 rpm, which is higher than that in 900 rpm with $Q_{\text{ring}}/Q_{\text{disk}}$ ratio of 0.084, indicating that the effect of viscosity should not be neglected.

Since the viscosity is not the major factor to affect LiO_2 dissolution in low concentration, then LiO_2 solubility might contribute. Considering that Li^+ is a hard acid

and DMSO molecule has high electron-donor ability, it can be reasonably assumed that the Li^+ of LiO_2 should be well-solvated by free DMSO for dissolution of LiO_2 to occur. Raman spectroscopy measurements in chapter 3 revealed that free DMSO decrease with LiNO_3 concentration increase, which is coincide with the trend of concentration-dependence of $Q_{\text{ring}}/Q_{\text{disk}}$. Thus, the solubility of LiO_2 was hypothesized that decreased with increasing concentration of LiNO_3 because amount of the free DMSO, which can contribute to the solvation of LiO_2 , decreased. Actually, this phenomenon was observed in concentration-dependence LITFSI-DMSO solutions as well. The solubility of LiO_2 was negligible in the extremely concentrated 3 M solution, where free DMSO is not present in electrolyte solution.³⁷

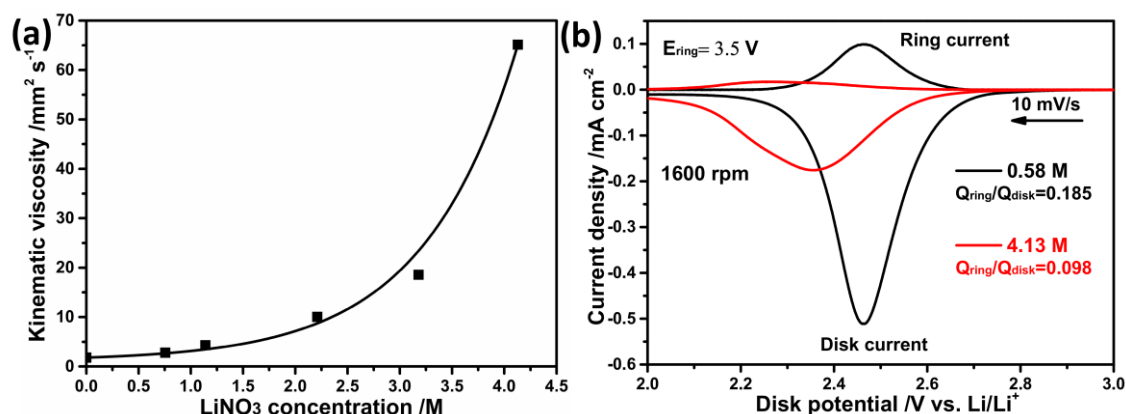


Figure 4-6 (a) Concentration dependence of kinematic viscosity, (b) current response of ORR at 10 mV s⁻¹ in O₂-saturated 0.58 M LiNO₃-DMSO solutions on gold electrode at 1600 rpm showing disk and ring current densities. The ring was held at 3.5 V vs Li/Li⁺. The line in (a) is just guide for eyes.

Regarding the effect of LiNO_3 on the oxygen reduction reaction, a major difference is the behavior of O_2^- chemisorbed on the electrode surface. O_2^- was detected in 0.58 M solution at low overpotential and 4.13 M solutions at both low and high overpotential, but not detected at 2.21 M solution. This suggest the amount of O_2^- on electrode surface in 0.58 M at low overpotential and 4.13 M solution at low and high overpotential is higher than that in 2.21 M solution. In order to confirm the above assumption, CV measurements were carried out at lower limit potential where O_2^- generate at a scan rate of 2 mV s⁻¹(**Figure 4-7(a)**). The big reduction current at around

2.7 V for three electrolytes are due to O_2^- generation (reaction (4-1)), while the broad oxidation current at 2.8 V is attributed to the oxidation of O_2^- .⁵⁹ It can be found that the O_2^- oxidation current is smaller than that of O_2 reduction. It is proposed that only O_2^- stay on electrode surface would be oxidized due to the high solubility of LiO_2 in Li^+ -DMSO solutions. The amount of O_2^- on electrode surface was thus calculated based on the charge of O_2^- oxidation current. 0.67, 0.085 and 0.01 mC cm^{-2} was calculated for 0.58, 2.21 and 4.13 M solutions, corresponding to 6.24×10^{15} , 5.3×10^{14} and 6.2×10^{12} O_2^- molecule on per square centimeter electrode surface, respectively, showing that the amount of O_2^- on electrode surface decrease with LiNO_3 concentration which confirm the above assumption. The ratio of O_2^- oxidation charge to O_2 reduction charge was calculated for three electrolytes in low overpotential region (> 2.65 V) and was shown in the inset of Figure 4-6(b). It shows that this ratio decreases from 0.33 to 0.05 as LiNO_3 concentration increase from 0.58 to 4.13 M. In other words, the amount of generated O_2^- that go to solution increase with LiNO_3 concentration. Considering that O_2^- is a moderate Lewis acid,^{29, 60} it either goes to solution by coordination with one Li^+ or stay on electrode surface by chemisorption which is determined by Li^+ concentration and solubility of LiO_2 . In the 0.58 M solution, although Li^+ solubility is high, the low Li^+ concentration limits the O_2^- that can go into the solution, resulting in some O_2^- chemisorb on the electrode surface. In contrast to 0.58 M, the solubility of LiO_2 is slightly lower in 2.21 M solution, but with higher Li^+ concentration, the proportion of LiO_2 that go to solution tend to increase, leaving small amount of O_2^- on electrode surface. In 4.13 M solution, the solubility of LiO_2 is limited, even though Li^+ concentration is high, most of O_2^- thus prefer to stay on electrode surface. However, question remain is that why O_2^- present at high overpotential (< 2.3 V) in 4.13 M solution rather than in 0.58 and 2.21 M solutions.

Actually, in addition to the influence of Li^+ concentration, the viscosity of electrolyte should also be taken into consideration. High-viscosity electrolyte slows ion diffusion rate due to high diffusion resistance by the Stokes-Einstein equation.⁶¹ The LiO_2 diffusion coefficient was measured by RRDE measurement based on diffusion time of LiO_2 from disk electrode to ring electrode at varied rotation speed. The potential on disk electrode was set at 2.5 V for producing LiO_2 , while the potential on ring electrode was stepped from OCP at ca. 3.2 V to 3.5 V to oxidize LiO_2 from disk electrode. The diffusion time was calculated based on following expression,⁶²⁻⁶³

$$T_s = K \left(\frac{\nu}{D} \right)^{\frac{1}{3}} \omega^{-1} \quad (4-5)$$

where K is a geometric constant, ν is the kinematic viscosity, D is the diffusion coefficient and ω is the rotation rate. **Figure 4-7(b)** shows potential and current response of ring electrode against in O_2 -saturated $LiNO_3$ -DMSO solutions with various $LiNO_3$ concentration (also shown in Figure 2). The potential on disk electrode quickly step from 0 to 3.5 V. Before anodic current increases, there is a current plateau close 0 mA, whose duration time is called “diffusion time” from disk to ring. It can be found that the diffusion time increase with $LiNO_3$ concentration.

The diffusion time at different rotation speed is also investigated in **Figure 4-7(c)**. The slower rotation speed resulting longer diffusion time. The diffusion time of LiO_2 increases almost linearly with $LiNO_3$ concentration, as $LiNO_3$ concentration lower than 2.87 M. When $LiNO_3$ concentration reaches 4.13 M, the diffusion time is 9, 10 and 16 times longer than that of in 0.58 M at 900, 620 and 400 rpm, respectively. The tendency of concentration dependence of diffusion time is very similar as concentration dependence-viscosity, showing that solution viscosity does play an important role in controlling the diffusion of LiO_2 . **Figure 4-6(d)** shows LiO_2 diffusion coefficient in $LiNO_3$ -DMSO solutions against $LiNO_3$ concentration based on reaction (4-5). LiO_2 diffusion coefficient decreasing almost linearly as $LiNO_3$ concentration increase below 2.87 M. It worth noting that the LiO_2 diffusion coefficient is in the same order of magnitude at 10^{-7} in $LiNO_3$ -DMSO solutions with concentration lower than 2.21 M, while this value for 4.13 M solution reach 10^{-9} . This means LiO_2 diffuses much faster in 0.58 and 2.21 M solutions than that in 4.13 M solutions. As current continues to flow in high $LiNO_3$ concentration electrolyte, the generated LiO_2 (reaction (4-1) and (4-2)) would accumulate in electrolyte near electrode surface due to extremely low LiO_2 diffusion coefficient. On the one hand, the accumulation consumes the Li^+ on the electrode surface, on the other hand, the Li^+ cannot be supplied immediately due to high diffusion resistance, resulting the continuously decrease of Li^+ concentration on electrode surface. With the potential shift to more negative, more O_2^- would produce on the electrode surface. However, step that O_2^- combine with Li^+ and leave electrode surface is suppressed due to extremely low Li^+ concentration on electrode surface. Therefore, O_2^- is accumulating on electrode surface with potential.

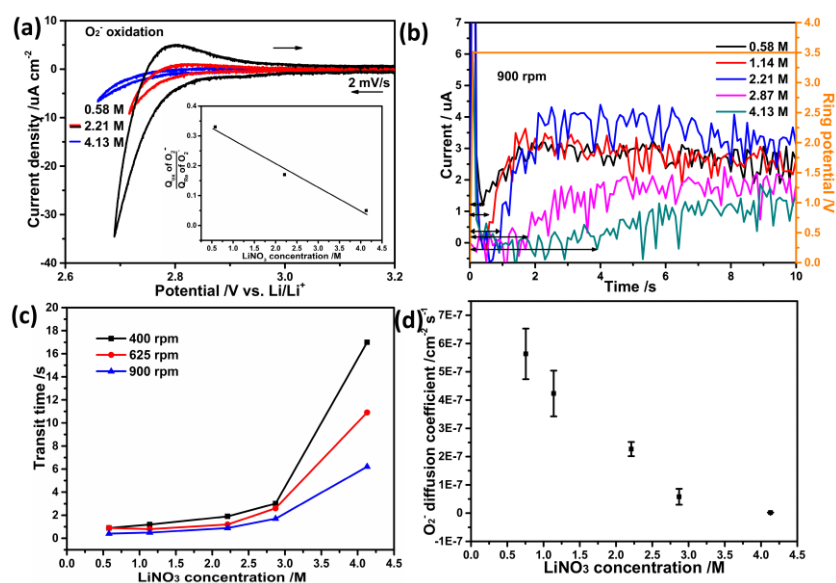


Figure 4-7. (a) CVs recorded at lower limit potential around 2.6 V in 0.58, 2.21 and 4.13 M solutions with scan rate of 2 mV s^{-1} , inset is concentration dependence of charge ratio of O_2^- oxidation to O_2 reduction. (b) potential applied on ring electrode versus time (right Y-axis) corresponding ring current (left Y-axis) recorded at 900 rpm in various $LiNO_3$ concentration, (c) concentration dependence of diffusion time measured by RRDE measurement in different rotation speed. (d) calculated LiO_2 diffusion coefficient against $LiNO_3$ concentration, the error bars represent standard deviation of calculated solvation number based on three different rotation rates at the same electrolyte. The lines in the inset of (a) and (c) just guide for eyes.

Therefore, whether O_2^- was chemisorbed on electrode at low overpotential depends on the LiO_2 dissolution reaction (reaction (4-2)), which is affected by Li^+ concentration, LiO_2 solubility and viscosity of electrolyte. The produced O_2^- prefer to stay on the electrode surface by chemisorption (reaction (4-1)) or either dissolve into solution by combining one Li^+ near electrode surface (reaction (4-2)). In low concentration at low overpotential, reaction (4-2) is limited due to the lower Li^+ concentration, which allows more O_2^- to chemisorb on the electrode surface, while in medium concentration at low overpotential, reaction (4-2) become dominant due to higher Li^+ concentration, leaving small amount of O_2^- chemisorb on electrode surface. In high concentration, reaction (4-2) is dominant at low overpotential. LiO_2 accumulates near the electrode surface due to the high viscosity of the electrolyte and resulted in the decreasing of Li^+ concentration. With

the potential move negatively, LiO_2 dissolution is suppressed and O_2^- was accumulated on electrode surface.

Actually, the effect of LiNO_3 on LiO_2 dissolution reaction (reaction (4-2), $\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_{2(\text{solution})}$) not only affect O_2^- adsorption, but also Li_2O_2 formation at higher overpotential. Since the surface pathway is proceeding via a two-step electron reduction reaction (reaction (4-1) and (4-4)) with O_2^- as intermediate. In 0.58 M solution, as potential shift to higher overpotential, chemisorbed O_2^- on electrode surface gradually converted to Li_2O_2 by consuming one electron and two Li^+ on electrode surface. In the meantime, LiO_2 dissolution reaction was suppressed with potential due to lower Li^+ concentration compare to low overpotential, which explain the gradually increased mpe in 0.58 M solution. For comparison, in 2.21 M solution, the LiO_2 dissolution reaction seems not affected by potential with fixed reaction between LiO_2 dissolution reaction ($\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_{2(\text{solution})}$, 48%) and Li_2O_2 formation ($\text{O}_2 + \text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2$, 52%). This may be resulting from the abundant Li^+ to fully promote the formation of soluble LiO_2 that makes the electrochemical production of Li_2O_2 and the LiO_2 dissolution reaction reach a proportional balance. In 4.13 M solution, at high overpotential, Li^+ on the electrode surface are consumed and cannot be supplied soon due to high electrolyte viscosity, so that the generated O_2^- was failed to converted into Li_2O_2 and accumulate on the electrode surface. It is worth noting that the O_2^- accumulated on the electrode surface in the high concentration electrolyte does not generate Li_2O_2 , which is a loss of battery capacity to some extent.

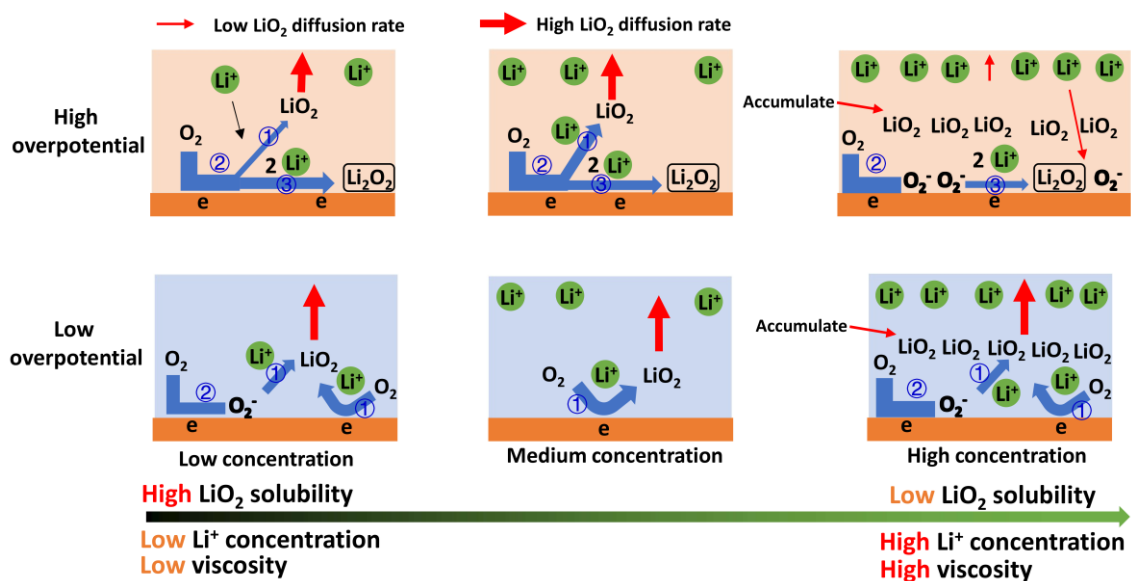
4.2.5 Proposed concentration-dependence of electrochemical reduction of O_2 in various LiNO_3 -DMSO solutions.

In short, the proposed model for electrochemical reduction of O_2 in various LiNO_3 -DMSO solutions was drawn in the **Scheme 1**. The oxygen was electrochemically reduced into LiO_2 on electrode surface and dissolve in electrolyte at initial low overpotential as the first step in all concentration ranges. After that, O_2^- was found to be chemisorbed on the electrode surface in low and high concentration, together with LiO_2 dissolution, while O_2^- was not chemisorbed on electrode in medium concentration. The different behavior of O_2^- was found to related to the formation of LiO_2 process ($\text{Li}^+ + \text{O}_2^- \rightarrow \text{LiO}_{2(\text{solution})}$) and its dissolution. The produced O_2^- on electrode surface would either

stay on electrode surface by chemisorption or goes to solution by coordination with one Li^+ to form LiO_2 , which is affected by Li^+ concentration, solubility of LiO_2 and viscosity of electrolyte. In low concentration, although the solubility of LiO_2 is high, due to the relatively low Li^+ concentration, the adsorption of O_2^- on the electrode will be relatively high. Compared with low concentration, LiO_2 solubility decreases but the concentration of Li^+ increases in medium concentration, this result in more LiO_2 dissolute in solution and less O_2^- stay on electrode surface. The influence of viscosity is negligible for both low and medium concentration due to minor difference. However, the effect of viscosity should not be ignored in high concentrations. Limited by the low LiO_2 solubility and the low LiO_2 diffusion coefficient caused by the high viscosity of the electrolyte, LiO_2 tends to accumulate near the electrode surface. The formation of LiO_2 consumes the Li^+ on the electrode surface, and the Li^+ on the electrode surface cannot be supplied immediately under high viscosity conditions, which greatly reduces the Li^+ concentration on the electrode surface. So that O_2^- was not capable of converting to LiO_2 and would stay on the electrode surface.

At high overpotential, the ORR against LiNO_3 concentration also shows concentration-dependence. In low and medium concentration, O_2 was mainly converted to Li_2O_2 by surface $2e^-$ reduction, together with LiO_2 dissolute into solution at high overpotential. However, the LiO_2 dissolution in medium concentration is higher than that in low concentration due to higher Li^+ concentration which is benefit for the formation of LiO_2 and its dissolution. In high concentration, a large amount of LiO_2 produced at low overpotential accumulates near the surface of the electrode, due to the high viscosity of the electrolyte. Some part of O_2 was electrochemically reduced in to Li_2O_2 , whereas the rest could only reduce to O_2^- due to the extremely low Li^+ concentration on the electrode surface.

Therefore, the effect of LiNO_3 concentration on the oxygen reduction reaction is mainly achieved by affecting the O_2^- adsorbed on the electrode surface and LiO_2 dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. Respecting to solution pathway, given the high solubility of LiO_2 in DMSO and the fact that LiO_2 can readily disproportionate into Li_2O_2 ,^{23, 58} the disproportionate reaction is highly possible in low and medium concentration where LiO_2 was largely detected (not shown in scheme).



Scheme 1. Proposed electrochemical reduction of O_2 in low, medium and high concentrated $LiNO_3$ -DMSO solutions. The red arrow represents diffusion rate of LiO_2 into bulk electrolytes. Thick and thin red arrow means low- and high- diffusion rate, respectively. Blue arrows represent the direction of molecular transformation. The thickness of the arrow represents the conversion ratio over the oxygen involved in the reaction or the generated O_2^- in this step. The blue ①, ② and ③ refers to the reaction in Figure 4-5.

4.3 Conclusion

The influence of $LiNO_3$ concentration on electrochemical reduction of O_2 in $LiNO_3$ -DMSO solutions were investigated by in situ SERS, EQCM and RRDE measurements. It turns out that the effect of $LiNO_3$ concentration on oxygen reduction mainly achieved by affecting the O_2^- adsorbed on the electrode surface and LiO_2 dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. At low concentration, due to the low Li^+ concentration, the LiO_2 dissolution is small, so that most of the O_2 is electrochemically converted into Li_2O_2 . At medium concentration, due to the higher Li^+ concentration, LiO_2 dissolves more, so that less O_2 is electrochemically converted into Li_2O_2 . At high concentrations, due to the high viscosity of electrolyte, O_2^- tends to be adsorbed on the electrode surface, resulting more O_2 to be electrochemically converted into Li_2O_2 .

References

- (1) Abraham, K. M.; Jiang, Z. A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery. *J. Electrochem. Soc.* **1996**, *143*, 1-5.
- (2) Bruce, P. G.; Hardwick, L. J.; Abraham, K. M. Lithium-Air and Lithium-Sulfur Batteries. *MRS Bull.* **2011**, *36*, 506-512.
- (3) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Wei, F.; Zhang, J. G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. *Adv. Sci.* **2016**, *3*.
- (4) Feng, N. N.; Mu, X. W.; Zhang, X. P.; He, P.; Zhou, H. S. Intensive Study on the Catalytical Behavior of N-Methylphenothiazine as a Soluble Mediator to Oxidize the Li₂O₂ Cathode of the Li-O₂ Battery. *Acs Applied Materials & Interfaces* **2017**, *9*, 3733-3739.
- (5) Elia, G. A., et al. An Advanced Lithium-Air Battery Exploiting an Ionic Liquid-Based Electrolyte. *Nano Lett.* **2014**, *14*, 6572-6577.
- (6) Zhang, T.; Zhou, H. S. From Li-O₂ to Li-Air Batteries: Carbon Nanotubes/Ionic Liquid Gels with a Tricontinuous Passage of Electrons, Ions, and Oxygen. *Angew. Chem. Int. Ed.* **2012**, *51*, 11062-11067.
- (7) Jung, H. G.; Hassoun, J.; Park, J. B.; Sun, Y. K.; Scrosati, B. An Improved High-Performance Lithium-Air Battery. *Nature Chemistry* **2012**, *4*, 579-585.
- (8) Gao, X. W.; Chen, Y. H.; Johnson, L. R.; Jovanov, Z. P.; Bruce, P. G. A Rechargeable Lithium-Oxygen Battery with Dual Mediators Stabilizing the Carbon Cathode. *Nature Energy* **2017**, *2*.
- (9) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587-603.
- (10) Shui, J. L.; Okasinski, J. S.; Kenesei, P.; Dobbs, H. A.; Zhao, D.; Almer, J. D.; Liu, D. J. Reversibility of Anodic Lithium in Rechargeable Lithium-Oxygen Batteries. *Nat. Commun.* **2013**, *4*.
- (11) Meini, S.; Piana, M.; Tsiouvaras, N.; Garsuch, A.; Gasteiger, H. A. The Effect of Water on the Discharge Capacity of a Non-Catalyzed Carbon Cathode for Li-O₂ Batteries. *Electrochemical and Solid State Letters* **2012**, *15*, A45-A48.
- (12) Burke, C. M.; Pande, V.; Khetan, A.; Viswanathan, V.; McCloskey, B. D. Enhancing Electrochemical Intermediate Solvation through Electrolyte Anion Selection to Increase

Nonaqueous Li-O-2 Battery Capacity. *Proceedings of the National Academy of Sciences of the United States of America* **2015**, *112*, 9293-9298.

(13) Xu, D.; Wang, Z. L.; Xu, J. J.; Zhang, L. L.; Zhang, X. B. Novel Dmso-Based Electrolyte for High Performance Rechargeable Li-O-2 Batteries. *Chem. Commun.* **2012**, *48*, 6948-6950.

(14) Ely, Y. E.; Aurbach, D. Identification of Surface-Films Formed on Active Metals and Nonactive Metal-Electrodes at Low Potentials in Methyl Formate Solutions. *Langmuir* **1992**, *8*, 1845-1850.

(15) Naoi, K.; Mori, M.; Naruoka, Y.; Lamanna, W. M.; Atanasoski, R. The Surface Film Formed on a Lithium Metal Electrode in a New Imide Electrolyte, Lithium Bis(Perfluoroethylsulfonylimide) [Li(C₂F₅SO₂)(2)]. *J. Electrochem. Soc.* **1999**, *146*, 462-469.

(16) Peled, E.; Menkin, S. Review-Sei: Past, Present and Future. *J. Electrochem. Soc.* **2017**, *164*, A1703-A1719.

(17) Bryantsev, V. S.; Giordani, V.; Walker, W.; Uddin, J.; Lee, I.; van Duin, A. C. T.; Chase, G. V.; Addison, D. Investigation of Fluorinated Amides for Solid-Electrolyte Interphase Stabilization in Li-O-2 Batteries Using Amide-Based Electrolytes. *J. Phys. Chem. C* **2013**, *117*, 11977-11988.

(18) Tong, B.; Huang, J.; Zhou, Z. B.; Peng, Z. Q. The Salt Matters: Enhanced Reversibility of Li-O-2 Batteries with a Li[(C₆F₅SO₂)(N-C₄F₉SO₂)N]-Based Electrolyte. *Adv. Mater.* **2018**, *30*.

(19) Miao, R. R.; Yang, J.; Feng, X. J.; Jia, H.; Wang, J. L.; Nuli, Y. N. Novel Dual-Salts Electrolyte Solution for Dendrite-Free Lithium-Metal Based Rechargeable Batteries with High Cycle Reversibility. *J. Power Sources* **2014**, *271*, 291-297.

(20) Guo, J.; Wen, Z. Y.; Wu, M. F.; Jin, J.; Liu, Y. Vinylene Carbonate-LiNO₃: A Hybrid Additive in Carbonic Ester Electrolytes for SEI Modification on Li Metal Anode. *Electrochem. Commun.* **2015**, *51*, 59-63.

(21) Zhang, H.; Eshetu, G. G.; Judez, X.; Li, C. M.; Rodriguez-Martinez, L. M.; Armand, M. Electrolyte Additives for Lithium Metal Anodes and Rechargeable Lithium Metal Batteries: Progress and Perspectives. *Angew. Chem. Int. Ed.* **2018**, *57*, 15002-15027.

- (22) Aetukuri, N. B.; McCloskey, B. D.; Garcia, J. M.; Krupp, L. E.; Viswanathan, V.; Luntz, A. C. Solvating Additives Drive Solution-Mediated Electrochemistry and Enhance Toroid Growth in Non-Aqueous Li-O₂ Batteries. *Nature Chemistry* **2015**, *7*, 50-56.
- (23) Johnson, L.; Li, C. M.; Liu, Z.; Chen, Y. H.; Freunberger, S. A.; Ashok, P. C.; Praveen, B. B.; Dholakia, K.; Tarascon, J. M.; Bruce, P. G. The Role of LiO₂ Solubility in O₂ Reduction in Aprotic Solvents and Its Consequences for Li-O₂ Batteries. *Nature Chemistry* **2014**, *6*, 1091-1099.
- (24) Lim, H. D.; Lee, B.; Bae, Y.; Park, H.; Ko, Y.; Kim, H.; Kim, J.; Kang, K. Reaction Chemistry in Rechargeable Li-O₂ Batteries. *Chem. Soc. Rev.* **2017**, *46*, 2873-2888.
- (25) Sharon, D.; Hirsberg, D.; Salama, M.; Afri, M.; Frimer, A. A.; Noked, M.; Kwak, W.; Sun, Y. K.; Aurbach, D. Mechanistic Role of Li⁺ Dissociation Level in Aprotic Li-O₂ Battery. *Acs Applied Materials & Interfaces* **2016**, *8*, 5300-5307.
- (26) Leverick, G.; Tatara, R.; Feng, S. T.; Crabb, E.; France-Lanord, A.; Tulodziecki, M.; Lopez, J.; Stephens, R. M.; Grossman, J. C.; Shao-Horn, Y. Solvent- and Anion-Dependent Li⁺-O₂(-) Coupling Strength and Implications on the Thermodynamics and Kinetics of Li-O₂ Batteries. *J. Phys. Chem. C* **2020**, *124*, 4953-4967.
- (27) Viswanathan, V.; Thygesen, K. S.; Hummelshoj, J. S.; Norskov, J. K.; Girishkumar, G.; McCloskey, B. D.; Luntz, A. C. Electrical Conductivity in Li₂O₂ and Its Role in Determining Capacity Limitations in Non-Aqueous Li-O₂ Batteries. *J. Chem. Phys.* **2011**, *135*.
- (28) Qiao, Y.; Ye, S. Spectroscopic Investigation for Oxygen Reduction and Evolution Reactions with Tetrathiafulvalene as a Redox Mediator in Li-O₂ Battery. *J. Phys. Chem. C* **2016**, *120*, 15830-15845.
- (29) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air Battery. *J. Phys. Chem. C* **2010**, *114*, 9178-9186.
- (30) Trahan, M. J.; Mukerjee, S.; Plichta, E. J.; Hendrickson, M. A.; Abraham, K. M. Studies of Li-Air Cells Utilizing Dimethyl Sulfoxide-Based Electrolyte. *J. Electrochem. Soc.* **2013**, *160*, A259-A267.
- (31) Togasaki, N.; Momma, T.; Osaka, T. Enhanced Cycling Performance of a Li Metal Anode in a Dimethylsulfoxide-Based Electrolyte Using Highly Concentrated Lithium Salt for a Lithium-Oxygen Battery. *J. Power Sources* **2016**, *307*, 98-104.

- (32) Togasaki, N.; Momma, T.; Osaka, T. Role of the Solid Electrolyte Interphase on a Li Metal Anode in a Dimethylsulfoxide-Based Electrolyte for a Lithium-Oxygen Battery. *J. Power Sources* **2015**, *294*, 588-592.
- (33) Liu, B.; Xu, W.; Yan, P. F.; Kim, S. T.; Engelhard, M. H.; Sun, X. L.; Mei, D. H.; Cho, J.; Wang, C. M.; Zhang, J. G. Stabilization of Li Metal Anode in DmsO-Based Electrolytes Via Optimization of Salt-Solvent Coordination for Li-O₂ Batteries. *Adv. Energy Mater.* **2017**, *7*.
- (34) Xuan, X. P.; Wang, J. J.; Zhao, Y.; Zhu, J. J. Experimental and Computational Studies on the Solvation of Lithium Tetrafluoroborate in Dimethyl Sulfoxide. *J. Raman. Spectrosc.* **2007**, *38*, 865-872.
- (35) Yamada, Y.; Takazawa, Y.; Miyazaki, K.; Abe, T. Electrochemical Lithium Intercalation into Graphite in Dimethyl Sulfoxide-Based Electrolytes: Effect of Solvation Structure of Lithium Ion. *J. Phys. Chem. C* **2010**, *114*, 11680-11685.
- (36) Alia, J. M.; Edwards, H. G. M. Ion Solvation and Ion Association in Lithium Trifluoromethanesulfonate Solutions in Three Aprotic Solvents. An Ft-Raman Spectroscopic Study. *Vib. Spectrosc* **2000**, *24*, 185-200.
- (37) Tatara, R., et al. Oxygen Reduction Reaction in Highly Concentrated Electrolyte Solutions of Lithium Bis(Trifluoromethanesulfonyl)Amide/Dimethyl Sulfoxide. *J. Phys. Chem. C* **2017**, *121*, 9162-9172.
- (38) Yamada, Y.; Yamada, A. Review-Superconcentrated Electrolytes for Lithium Batteries. *J. Electrochem. Soc.* **2015**, *162*, A2406-A2423.
- (39) Suo, L. M.; Hu, Y. S.; Li, H.; Armand, M.; Chen, L. Q. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* **2013**, *4*.
- (40) Sun, B.; Huang, X. D.; Chen, S. Q.; Zhang, J. Q.; Wang, G. X. An Optimized Lino₃/DmsO Electrolyte for High-Performance Rechargeable Li-O₂ Batteries. *Rsc Advances* **2014**, *4*, 11115-11120.
- (41) Sharon, D.; Afri, M.; Noked, M.; Garsuch, A.; Frimer, A. A.; Aurbach, D. Oxidation of Dimethyl Sulfoxide Solutions by Electrochemical Reduction of Oxygen. *Journal of Physical Chemistry Letters* **2013**, *4*, 3115-3119.
- (42) Peng, Z. Q.; Freunberger, S. A.; Chen, Y. H.; Bruce, P. G. A Reversible and Higher-Rate Li-O₂ Battery. *Science* **2012**, *337*, 563-566.

- (43) Chen, Y. H.; Freunberger, S. A.; Peng, Z. Q.; Fontaine, O.; Bruce, P. G. Charging a Li-O₂ Battery Using a Redox Mediator. *Nature Chemistry* **2013**, *5*, 489-494.
- (44) Lu, Y. C.; Gasteiger, H. A.; Crumlin, E.; McGuire, R.; Shao-Horn, Y. Electrocatalytic Activity Studies of Select Metal Surfaces and Implications in Li-Air Batteries. *J. Electrochem. Soc.* **2010**, *157*, A1016-A1025.
- (45) Lu, Y. C.; Gasteiger, H. A.; Shao-Horn, Y. Catalytic Activity Trends of Oxygen Reduction Reaction for Nonaqueous Li-Air Batteries. *JACS* **2011**, *133*, 19048-19051.
- (46) Shen, A. J.; Pemberton, J. E. Interfacial Structure of Dimethylsulfoxide at Ag Electrodes from Surface Enhanced Raman Scattering and Differential Capacitance. *J. Electroanal. Chem.* **1999**, *479*, 21-31.
- (47) Martens, W. N.; Frost, R. L.; Kristof, J.; Klopogge, J. T. Raman Spectroscopy of Dimethyl Sulphoxide and Deuterated Dimethyl Sulphoxide at 298 and 77 K. *J. Raman. Spectrosc.* **2002**, *33*, 84-91.
- (48) Miller, R. E.; Getty, R. R.; Treuil, K. L.; Leroi, G. E. Raman Spectrum of Crystalline Lithium Nitrate. *J. Chem. Phys.* **1969**, *51*, 1385-+.
- (49) Freeman, D. W.; Baglin, F. G. A Raman-Study of Gold Oxygen Bonds from Several Tetracoordinate Complexes in Aqueous-Solution. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 161-167.
- (50) Schroter, C.; Roelfs, B.; Solomun, T. The Interaction of Dimethylsulfoxide with a Gold Surface. *Surf. Sci.* **1997**, *380*, L441-L445.
- (51) Nicolai, S. H. A.; Rubim, J. C. Effect of Molecular-Oxygen on the Surface-Enhanced Raman Intensity of Adsorbed Molecules on Silver, Copper and Gold Electrodes. *Vib. Spectrosc* **1994**, *7*, 175-183.
- (52) Peng, Z. Q.; Freunberger, S. A.; Hardwick, L. J.; Chen, Y. H.; Giordani, V.; Barde, F.; Novak, P.; Graham, D.; Tarascon, J. M.; Bruce, P. G. Oxygen Reactions in a Non-Aqueous Li⁺ Electrolyte. *Angew. Chem. Int. Ed.* **2011**, *50*, 6351-6355.
- (53) Kwabi, D. G.; Tulodziecki, M.; Pour, N.; Itkis, D. M.; Thompson, C. V.; Shao-Horn, Y. Controlling Solution-Mediated Reaction Mechanisms of Oxygen Reduction Using Potential and Solvent for Aprotic Lithium-Oxygen Batteries. *Journal of Physical Chemistry Letters* **2016**, *7*, 1204-1212.

- (54) Serizawa, N.; Katayama, Y.; Miura, T. Eqcm Measurement of Ag(I)/Ag Reaction in an Amide-Type Room-Temperature Ionic Liquid. *J. Electrochem. Soc.* **2009**, *156*, D503-D507.
- (55) Torres, W. R.; Tesio, A. Y.; Calvo, E. J. Solvent Co-Deposition During Oxygen Reduction on Au in Dmsolipf6. *Electrochem. Commun.* **2014**, *49*, 38-41.
- (56) Marchini, F.; Herrera, S.; Torres, W.; Tesio, A. Y.; Williams, F. J.; Calvo, E. J. Surface Study of Lithium-Air Battery Oxygen Cathodes in Different Solvent-Electrolyte Pairs. *Langmuir* **2015**, *31*, 9236-9245.
- (57) Zhai, D. Y., et al. Raman Evidence for Late Stage Disproportionation in a Li-O-2 Battery. *Journal of Physical Chemistry Letters* **2014**, *5*, 2705-2710.
- (58) Zakharchenko, T. K.; Kozmenkova, A. Y.; Itkis, D. M.; Goodilin, E. A. Lithium Peroxide Crystal Clusters as a Natural Growth Feature of Discharge Products in Li-O-2 Cells. *Beilstein Journal of Nanotechnology* **2013**, *4*, 758-762.
- (59) Yu, Q.; Ye, S. In Situ Study of Oxygen Reduction in Dimethyl Sulfoxide (Dmsol) Solution: A Fundamental Study for Development of the Lithium-Oxygen Battery. *J. Phys. Chem. C* **2015**, *119*, 12236-12250.
- (60) Smirnov, V. S.; Kislenko, S. A. Effect of Solvents on the Behavior of Lithium and Superoxide Ions in Lithium-Oxygen Battery Electrolytes. *Chemphyschem* **2018**, *19*, 75-81.
- (61) Hiss, T. G.; Cussler, E. L. Diffusion in High-Viscosity Liquids. *AIChE J.* **1973**, *19*, 698-703.
- (62) Gan, F.; Chin, D. T. Determination of Diffusivity and Solubility of Oxygen in Phosphoric-Acid Using a Transit-Time on a Rotating Ring-Disc Electrode. *J. Appl. Electrochem.* **1993**, *23*, 452-455.
- (63) Gittleson, F. S.; Jones, R. E.; Ward, D. K.; Foster, M. E. Oxygen Solubility and Transport in Li-Air Battery Electrolytes: Establishing Criteria and Strategies for Electrolyte Design. *Energy Environ. Sci.* **2017**, *10*, 1167-1179.

Chapter 5

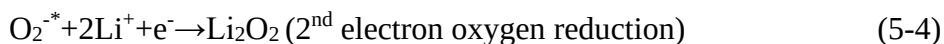
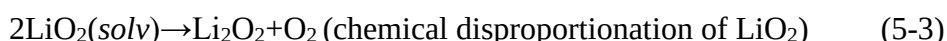
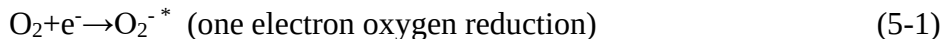
Electrochemical Reduction of Oxygen in LiNO₃-TEGDME Solutions: The Effect of LiNO₃ Concentration

5.1 Introduction

Although some electric vehicles that use LIBs have been commercialized, new secondary batteries with higher energy density and low cost are required for further driving range. Recently, non-aqueous lithium-oxygen (Li-O₂) batteries have emerged due to their extremely high theoretical specific capacity (3505 Wh kg⁻¹ calculated based on lithium metal) which is four to six times larger than those of Li ion batteries.¹⁻³ A typical Li-O₂ battery includes a lithium metal anode, a porous carbon-air electrode and an electrolyte containing a lithium salt and an aprotic solvent. As an emerging energy storage system, its commercialization is still inhibited by the low cycle performance and capacity fading.⁴⁻⁶ These two flaws of Li-O₂ battery are mainly caused by lithium anode instability and blockage of air electrode by electrolyte decomposition products on air cathode.^{4, 6-7} The stability of the lithium anode depends on the characteristics of the SEI on the anode surface, which is an inorganic and organic film from electrolyte degradation when in contact with active lithium anode.⁸⁻⁹ The electrolyte decomposition on air electrode is arising from the attack by reduced oxygen species (O₂⁻, Li₂O₂ and singlet oxygen, etc.)¹⁰⁻¹² Therefore, various combination of solvents and lithium salts are design of new stable electrolyte compositions that can withstand both anode and cathode chemistries.

Polyethers like tetraglyme (TEGDME) are considered as good candidates as solvent for aprotic Li-O₂ battery since they are less reactivity with superoxide species than typical carbonates solvent and stable to lithium anode. However, the application of TEGDME is limited by its low discharge capacity on air cathode. The oxygen reduction on air cathode was though to strongly dependence on the donor number (DN) of solvent.¹³⁻¹⁵ The use of high donor number solvent like DMSO (DN = 30) would drive solution pathway (reaction (5-1), (5-2) and (5-3) shown as follow), while low donor number solvent such as TEGDME (DN = 16) would induce surface pathway (reaction (5-1) and (5-4)).¹⁶⁻¹⁹ The solution pathway in high DN solvents would lead to the growth of large Li₂O₂ particle and result in larger discharge capacity, while surface pathway would

grow film-like Li_2O_2 with low discharge capacity.²⁰⁻²² Electrolyte with high donor number lithium salt dissolved in low donor number solvent such as 1M LiNO_3/DME has also been shown to affect the reaction pathway of ORR by increasing the solubility of ORR intermediates, whereas the enhancement could not be observed in high DN solvent like DMSO.^{14, 17}



* represents intermediate on electrode surface, *solv* means in solution.

High salt concentration in TEGDME was recently reported to improved stability with lithium metal during cell operations, thereby improving the cycle life of Li-O₂ batteries.²³⁻²⁶ Molecular dynamics simulations suggested that changes to the solvation shell around cations in the electrolyte can help reduce their overall reactivity, thus stabilizing the electrode.²⁶⁻²⁷ However, there are few studies on the influence of lithium salt concentration on the air electrode reaction in TEGDME solution. Liu et al. investigated the effect of salt concentration on the capacity of Li-O₂ battery in LITFSI-TEGDME solutions.²⁸ They found that the capacity is much higher in high-concentration electrolyte (2-3 M) than those using low concentration electrolyte (1 M or less), but without detailed explanation for the reason. Recently, a high-concentration electrolyte of LiNO_3 has also been reported to improve the stability of lithium anodes.²⁹⁻³¹ However, the effect of LiNO_3 concentration on the oxygen reduction reaction of the cathode is still unclear.

In present study, the effect of LiNO_3 concentration in TEGDME solutions was investigated by EQCM and RRDE measurements. Gold electrode was used as model electrode for present study with the same reason as Chapter 4. RRDE measurement shows that the dissolution of LiO_2 from disk electrode decrease as LiNO_3 concentration increase, which is due to the decrease of free TEGDME with concentration. EQCM measurement shows that, the concentration of LiNO_3 has almost no effect on the solid species deposition on electrode surface during ORR in LiNO_3 -TEGDME solution. At low

overpotential, O_2 was electrochemically reduced into LiO_2 and dissolve into solution immediately for three concentrated electrolytes. At medium overpotential, O_2 is mainly converted to Li_2O_2 through surface two-electron reduction pathway, together with small part of LiO_2 dissolve into electrolyte. At high overpotential, electrode surface was covered by conducting Li_2O_2 . The electron could still penetrate through Li_2O_2 and reduce O_2 into LiO_2 .

5.2 Results and discussion

5.2.1 RRDE and Raman measurements

Oxygen reduction in O_2 -saturated $LiNO_3$ -TEGDME solutions with various molar concentration were investigated using RRDE measurement by linear sweep voltammograms (LSV) on gold disk/ring electrode at 900 rpm to detect the formation of soluble reduction intermediates (**Figure 5-1(a)**). Ag/Ag^+ electrode and Pt wire were used as reference and counter electrode in this study, respectively. As can be seen in Figure 5-1(a), cathodic current starts flow at ca. -0.6 V and a reduction peak was observed at around -1.6, -1.35 and -1.3 V for $LiNO_3$ -TEGDME solutions with concentration of 0.19, 0.73 and 1.4 M, which can be attributed to the fact that ORR kinetic under dynamic conditions are limited by electron transfer, in this case is the growth of insulating Li_2O_2 . In addition, the peak current density of the reduction reaction increases with $LiNO_3$ concentration increasing, means that less oxygen was reduced with $LiNO_3$ concentration increase. An anodic ring current (E_{ring} is 0.3 V) during the ORR for all investigated electrolytes could be observed which is consistent with the oxidation of LiO_2 from the disk electrode surface during rotation. We assess the solubility of LiO_2 using the fraction of ORR charge composed of soluble LiO_2 , which we estimate using the ring charge/disk charge ratio during ORR, Q_{ring}/Q_{disk} (**Figure 5-1(b)**). Theoretic collection efficiency (N_k) value of 0.23 was determined experimentally in the O_2 -saturated NBu_4NO_3 -DMSO solution. As the molar concentration of $LiNO_3$ increases from 0.19 to 1.4 M, the Q_{Ring}/Q_{Disk} ratio decreases from ca. 0.22 to 0.14, which shows that the solubility of LiO_2 decrease as concentration increase. Tatara et al reported that the LiO_2 dissolution was relating to the presence of free DMSO in LITFSI-DMSO solution.²⁴ Inspired by this work, the solvation structure of $LiNO_3$ -TEGDME solution was investigated.

Raman measurement was carried out to evaluate the solvation structure of LiNO_3 -TEGDME solutions with different LiNO_3 concentrations, because the solvation structure should vary significantly in the salt-concentrated solution. **Figure 5-1(c)** shows the Raman spectra of pure TEGDME, 0.19, 0.78 and 1.4 M LiNO_3 -TEGDME solutions in a range of $760\text{--}920\text{ cm}^{-1}$. The Raman spectrum of pure TEGDME shows two bands at 812 and 856 cm^{-1} , which were assigned to the $\nu_{\text{as}}(\text{COC})$ and $\gamma(\text{CH}_2)$ vibration modes of TEGDME molecules, respectively.^{18, 32} The later band was reported to be sensitive to Li^+ coordination.³³⁻³⁴ In the Raman spectra of 0.19, 0.78 and 1.4 M LiNO_3 -TEGDME solutions, these two bands were not change too much, instead a weak shoulder band at ca. 880 cm^{-1} appears. This band was attributed to $\gamma(\text{CH}_2)$ vibration modes of Li^+ solvated TEGDME.³⁴ Compared with $\gamma(\text{CH}_2)$ of free TEGDME, the intensity of $\gamma(\text{CH}_2)$ of Li^+ solvated TEGDME is very weak, indicating that Li^+ could hardly coordinate with TEGDME even at high LiNO_3 concentration.

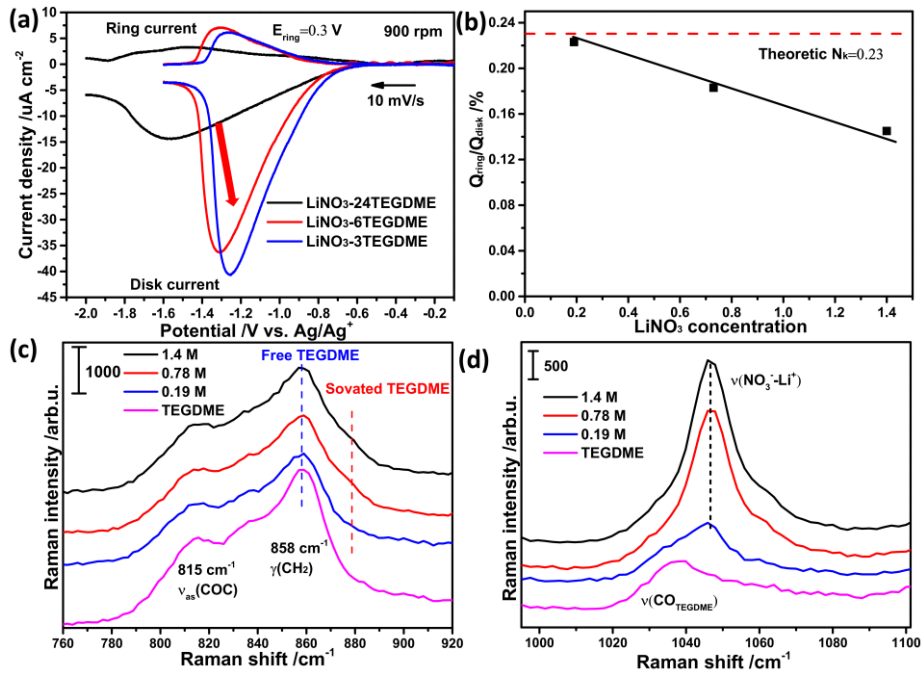


Figure 5-1. Current response of ORR at 10 mV s^{-1} in O_2 -saturated (a) 0.19, 0.73 and 1.4 M LiNO_3 -TEGDME on gold electrode at 900 rpm showing disk (cathodic current) and ring current (anodic current) densities. The ring was held at 0.3 V. (b) Concentration-dependence of ring-disk charge ratio. Red dash line represents the theoretic N_k . The solid line in (b) is just guide for eyes. Concentration-dependence of Raman spectra of LiNO_3 -TEGDME bulk solutions in vibration region of (a) $\gamma(\text{CH}_2)_{\text{TEGDME}}$ and $\nu(\text{NO}_3^-\text{-Li}^+)$.

Another band appeared at ca. 1047 cm^{-1} in **Figure 5-1(d)**, which might relate to vibration mode of NO_3^- or Li^+ solvated NO_3^- .³⁵ Considering the donor number of NO_3^- (DN = 21) is lower than that of TEGDME (DN = 16), Li^+ is prefer to coordinate with NO_3^- . The band at 1047 cm^{-1} was attributed to Li^+ solvated NO_3^- . Therefore, in LiNO_3 -TEGDME solutions, Li^+ was coordinated with NO_3^- as $\text{Li}^+\text{-NO}_3^-$ complex and TEGDME was presence as free molecule. In addition, $\text{Li}^+\text{-NO}_3^-$ increase with free TEGDME decrease as LiNO_3 concentration increasing. As a strong Lewis acid, Li^+ tends to coordinate with molecules with Lewis base properties. In the current solution, both NO_3^- and TEGDME have the properties of Lewis base, but free NO_3^- is not exist while TEGDME is abundant. We have reason to believe that free TEGDME can coordinate with the Li^+ of $\text{Li}^+\text{-O}_2^-$ and promote its dissolution. Thus, the decrease of LiO_2 dissolution against LiNO_3 concentration was due to the decrease of free TEGDME with LiNO_3 concentration increase.

5.2.2 In situ EQCM measurements

As RRDE measurement is to the formation of soluble species during ORR, EQCM measurements, which is sensitive to the deposition of solid species, was carried out to further confirm above observation. **Figure 5-2(a)** shows the current and frequency change (ΔF) as a function of potential recorded simultaneously on Au QCM electrode at 2 mV s^{-1} in three different concentration LiNO_3 -TEGDME solutions. As can be seen in Figure 5-2(a), the current start to flow for all three solutions at ca. -0.5 V, whereas the onset of frequency change is more negative compared with the onset of current (ca. 700 mV, 400 mV and 200 mV for 0.19, 0.73 and 1.4 M LiNO_3 -TEGDME solutions, respectively). This means the charge flow was not contribute to mass increase on electrode surface, which is attributing to one electron oxygen reduction (reaction (1) in Table 1 of Chapter 4, $\text{O}_2 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiO}_{2(\text{solution})}$, $0 \text{ g mol}^{-1}\text{-e}^{-1}$) with zero mass change.³⁶ The frequency change gradually increases with potential sweep to more negative, indicating that increasing overpotential would result in more amounts of insoluble deposits on electrode. It worth noting that as the potential sweep negative than peak potential in each electrolyte, even though current keeps flowing, the mass change is negligible. This might be related to reaction (1) in Table 1 (NOTE: The reactions quoted below refer to the reactions in Table 1 in chapter 4 if not mention). In addition, the frequency change in three investigated

solutions until -1.6 V shows increase with LiNO₃ concentration.

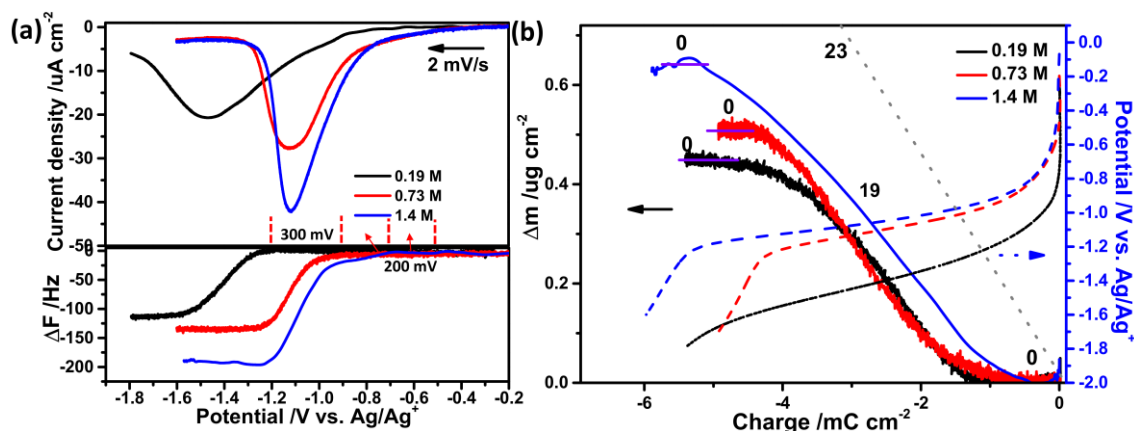


Figure 5-2. (a) Potential dependencies of current (up panel) and corresponding frequency change (bottom panel) at a scan rate of 2 mV s⁻¹, (b) mass change as a function of charge in O₂-saturated LiNO₃-TEGDME with molar concentration of 0.19, 0.73 and 1.4 M. In figure (b) left Y-axis is mass change and right Y-axis potential. Solid lines and long dotted lines represent mass change and potential, respectively. Short dotted lines show Δm -charge relation for mpe of 23 g mol⁻¹-e⁻¹, corresponding to half of molecular weight of Li₂O₂.

Figure 5-2(b) shows the mass change, which is calculated based on frequency change by considering viscoelastic change as a function of the integrate charge.³⁷ Detailed mpe and corresponding reaction information in specific potential range was shown in **Figure 5-3** based on Figure 5-2(b). The initial mpe in three solutions was 0 g mol⁻¹-e⁻¹, representing reaction (1), which is consistent with the frequency delay described previously. In 0.19 M solution, mpe gradually increase from 0 to 19 g mol⁻¹-e⁻¹ at potential range from ca. -1.2 to -1.3 V and keep constant until ca. -1.5 V. 19 g mol⁻¹-e⁻¹ is very close to the mpe of 23 g mol⁻¹-e⁻¹ for reaction (5) (O₂+2Li⁺+2e⁻ ↔ Li₂O₂(solid), 23 g mol⁻¹-e⁻¹), it's proposed as an average result of reaction (5) and reaction (1) (O₂+Li⁺+e⁻ ↔ LiO₂(solution), 0 g mol⁻¹-e⁻¹). In addition, 83% of reaction (5) and 17% reaction (1) contribute to 19 g mol⁻¹-e⁻¹, indicating that surface pathway is dominant at potential region from ca. -1.2 to -1.5 V. This means that while Li₂O₂ is electrochemically formed, part of the LiO₂ is dissolute from the electrode surface and enters the electrolyte. Further sweep potential to ca. -1.6 V, the mpe decrease to 0 g mol⁻¹-e⁻¹, which is corresponding to reaction (1). Since Li₂O₂ has been deposited on the electrode surface at potential

between ca. -1.2 and -1.5 V, it is indicated that O₂ was reduced on the surface of Li₂O₂ as potential higher than -1.5 V. In 0.73 and 1.4 M solution, similar mpe tendency was observed, i.e. increase from 0 to 19 g mol⁻¹-e⁻¹, then decrease to 0 g mol⁻¹-e⁻¹. This indicates that the concentration of LiNO₃ has little effect on the deposition of solid Li₂O₂ on the electrode surface. According to the discussion in chapter 4, the effect of LiNO₃ concentration on ORR in LiNO₃-DMSO solution is achieved by affecting the LiO₂ dissolution in the solution. However, the LiO₂ dissolution is not affecting too much in TEGDME solution based on EQCM results. It is proposed that the Li⁺-NO₃⁻ complex in solution would promote surface reaction because it is easier to extract Li⁺ from Li⁺-NO₃⁻ complex than Li(DMSO)₄⁺, where Li⁺ is closely surrounded by four DMSO molecules. Therefore, the contribution of LiO₂ dissolution reaction (O₂+Li⁺+e⁻↔LiO_{2(solution)}) would be weak.

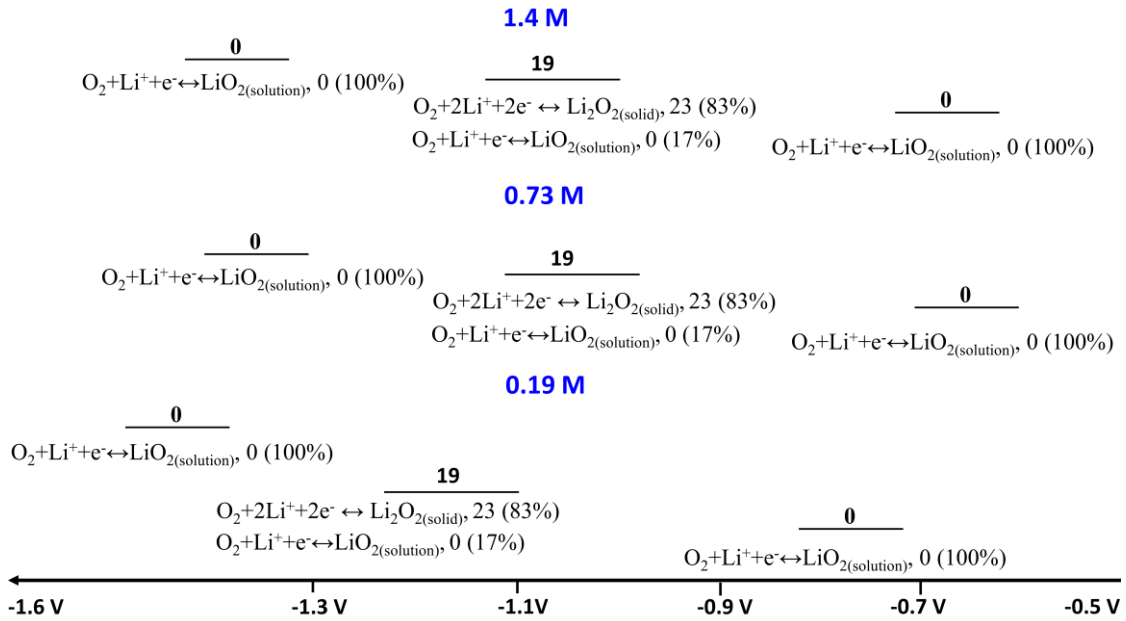
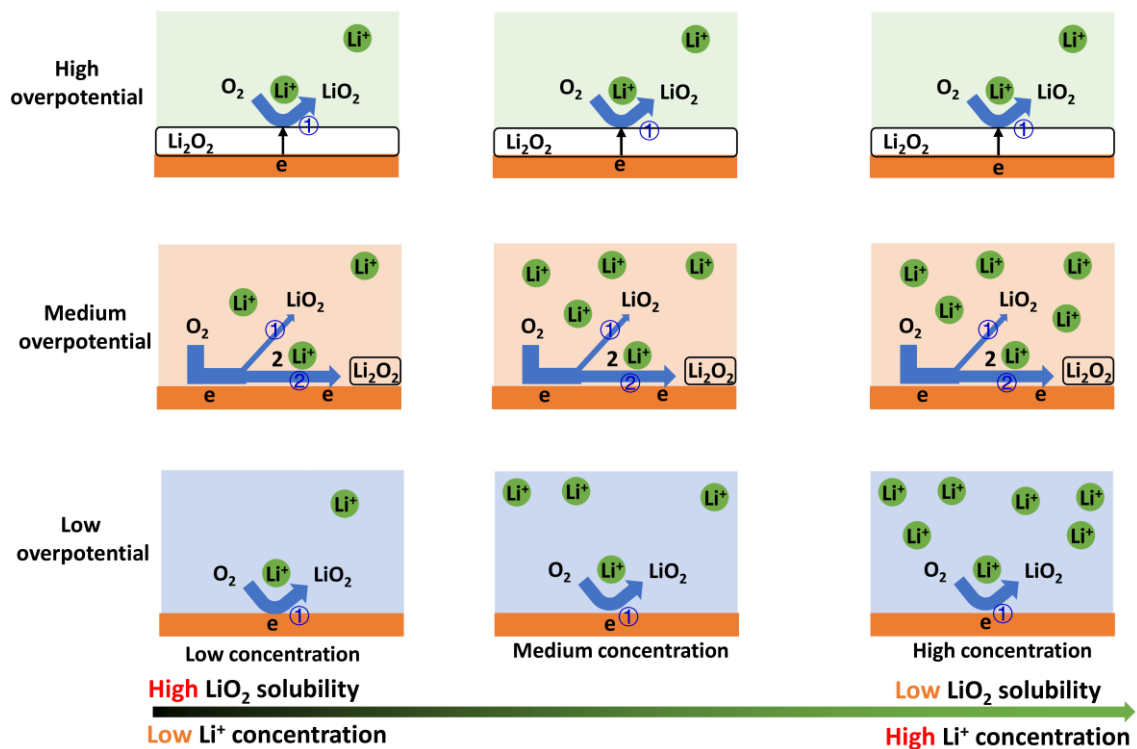


Figure 5-3. The calculated mpe at designate potential regions for three electrolytes based on the data in Figure 5-2(b).

Scheme 1 shows the proposed electrochemical reduction of O₂ model in low, medium and high concentrated LiNO₃-TEGDME solutions with potential. The oxygen reduction reaction did not show obvious concentration independence. At low overpotential, O₂ was electrochemically reduced into LiO₂ and dissolute into solution immediately for three concentrated electrolytes. In medium overpotential, most of O₂ was

electrochemically converted into Li_2O_2 , leaving small amount of LiO_2 go to solution. At high overpotential, electrode surface was covered by conducting Li_2O_2 . The electron could still penetrate through Li_2O_2 and reduce O_2 into LiO_2 .



Scheme 1. Proposed electrochemical reduction of O_2 in low, medium and high concentrated LiNO_3 -TEGDME solutions. Thick and thin red arrow means low- and high-diffusion rate, respectively. Blue arrows represent the direction of molecular transformation. The thickness of the arrow represents the conversion ratio over the oxygen involved in the reaction or the generated O_2^- in this step.

5.3 Conclusion

The effect of LiNO_3 concentration on electrochemical reduction of oxygen in Li^+ -TEGDME solutions was investigated by RRDE and EQCM measurements. It turns out that the LiO_2 solubility decrease with LiNO_3 concentration, which is relate to free TEGDME in the solution. EQCM measurements shows that LiNO_3 concentration has almost no effect on the surface electrode reaction. O_2 was firstly electrochemically reduced into LiO_2 and leave electrode surface at low overpotential. At medium overpotential, O_2 is mainly converted to Li_2O_2 through surface two-electron reduction

pathway, together with small part of LiO_2 dissolve into electrolyte. At high overpotential, oxygen is found to be reduced into LiO_2 on the surface of Li_2O_2 .

References

- (1) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. Li-O-2 and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19-29.
- (2) Peng, Z. Q.; Freunberger, S. A.; Chen, Y. H.; Bruce, P. G. A Reversible and Higher-Rate Li-O-2 Battery. *Science* **2012**, *337*, 563-566.
- (3) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Applications. *J. Phys. Chem. C* **2009**, *113*, 20127-20134.
- (4) Yang, S. X.; He, P.; Zhou, H. S. Research Progresses on Materials and Electrode Design Towards Key Challenges of Li-Air Batteries. *Energy Storage Materials* **2018**, *13*, 29-48.
- (5) Asadi, M., et al. A Lithium-Oxygen Battery with a Long Cycle Life in an Air-Like Atmosphere. *Nature* **2018**, *555*, 502-+.
- (6) Thotiyl, M. M. O.; Freunberger, S. A.; Peng, Z. Q.; Bruce, P. G. The Carbon Electrode in Nonaqueous Li-O-2 Cells. *JACS* **2013**, *135*, 494-500.
- (7) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Wei, F.; Zhang, J. G.; Zhang, Q. A Review of Solid Electrolyte Interphases on Lithium Metal Anode. *Adv. Sci.* **2016**, *3*.
- (8) Zhang, X. Q.; Chen, X.; Hou, L. P.; Li, B. Q.; Cheng, X. B.; Huang, J. Q.; Zhang, Q. Regulating Anions in the Solvation Sheath of Lithium Ions for Stable Lithium Metal Batteries. *ACS Energy Lett.* **2019**, *4*, 411-416.
- (9) Wang, A. P.; Kadam, S.; Li, H.; Shi, S. Q.; Qi, Y. Review on Modeling of the Anode Solid Electrolyte Interphase (Sei) for Lithium-Ion Batteries. *Npj Computational Materials* **2018**, *4*.
- (10) Houchins, G.; Pande, V.; Viswanathan, V. Mechanism for Singlet Oxygen Production in Li-Ion and Metal-Air Batteries. *ACS Energy Lett.* **2020**, *5*, 1893-1899.
- (11) Chen, X.; Li, H. R.; Shen, X.; Zhang, Q. The Origin of the Reduced Reductive Stability of Ion-Solvent Complexes on Alkali and Alkaline Earth Metal Anodes. *Angew. Chem. Int. Ed.* **2018**, *57*, 16643-16647.
- (12) Mahne, N., et al. Singlet Oxygen Generation as a Major Cause for Parasitic Reactions During Cycling of Aprotic Lithium-Oxygen Batteries. *Nature Energy* **2017**, *2*.

- (13) Smirnov, V. S.; Kislenko, S. A. Effect of Solvents on the Behavior of Lithium and Superoxide Ions in Lithium-Oxygen Battery Electrolytes. *Chemphyschem* **2018**, *19*, 75-81.
- (14) Sharon, D.; Hirsberg, D.; Salama, M.; Afri, M.; Frimer, A. A.; Noked, M.; Kwak, W.; Sun, Y. K.; Aurbach, D. Mechanistic Role of Li⁺ Dissociation Level in Aprotic Li-O₂ Battery. *Acs Applied Materials & Interfaces* **2016**, *8*, 5300-5307.
- (15) Johnson, L.; Li, C. M.; Liu, Z.; Chen, Y. H.; Freunberger, S. A.; Ashok, P. C.; Praveen, B. B.; Dholakia, K.; Tarascon, J. M.; Bruce, P. G. The Role of LiO₂ Solubility in O₂ Reduction in Aprotic Solvents and Its Consequences for Li-O₂ Batteries. *Nature Chemistry* **2014**, *6*, 1091-1099.
- (16) Gallant, B. M.; Kwabi, D. G.; Mitchell, R. R.; Zhou, J. G.; Thompson, C. V.; Shao-Horn, Y. Influence of Li₂O₂ Morphology on Oxygen Reduction and Evolution Kinetics in Li-O₂ Batteries. *Energy Environ. Sci.* **2013**, *6*, 2518-2528.
- (17) Burke, C. M.; Pande, V.; Khetan, A.; Viswanathan, V.; McCloskey, B. D. Enhancing Electrochemical Intermediate Solvation through Electrolyte Anion Selection to Increase Nonaqueous Li-O₂ Battery Capacity. *Proceedings of the National Academy of Sciences of the United States of America* **2015**, *112*, 9293-9298.
- (18) Qiao, Y.; Wu, S. C.; Yi, J.; Sun, Y.; Guo, S. H.; Yang, S. X.; He, P.; Zhou, H. S. From O₂(-) to HO₂⁻ : Reducing by-Products and Overpotential in Li-O₂ Batteries by Water Addition. *Angew. Chem. Int. Ed.* **2017**, *56*, 4960-4964.
- (19) Adams, B. D.; Radtke, C.; Black, R.; Trudeau, M. L.; Zaghib, K.; Nazar, L. F. Current Density Dependence of Peroxide Formation in the Li-O₂ Battery and Its Effect on Charge. *Energy Environ. Sci.* **2013**, *6*, 1772-1778.
- (20) Aetukuri, N. B.; McCloskey, B. D.; Garcia, J. M.; Krupp, L. E.; Viswanathan, V.; Luntz, A. C. Solvating Additives Drive Solution-Mediated Electrochemistry and Enhance Toroid Growth in Non-Aqueous Li-O₂ Batteries. *Nature Chemistry* **2015**, *7*, 50-56.
- (21) Knudsen, K. B.; Vegge, T.; McCloskey, B. D.; Hjelm, J. An Electrochemical Impedance Spectroscopy Study on the Effects of the Surface- and Solution-Based Mechanisms in Li-O₂ Cells. *J. Electrochem. Soc.* **2016**, *163*, A2065-A2071.
- (22) Lim, H. D.; Lee, B.; Bae, Y.; Park, H.; Ko, Y.; Kim, H.; Kim, J.; Kang, K. Reaction Chemistry in Rechargeable Li-O₂ Batteries. *Chem. Soc. Rev.* **2017**, *46*, 2873-2888.

- (23) Kottam, P. K. R.; Kalkan, D.; Wohlfahrt-Mehrens, M.; Marinaro, M. Influence of Li-Salt Concentration on Redox Potential of Lithium Metal and Electrochemistry of Ferrocene in Dmso-Based Electrolytes. *J. Electrochem. Soc.* **2019**, *166*, A1574-A1579.
- (24) Tatara, R., et al. Oxygen Reduction Reaction in Highly Concentrated Electrolyte Solutions of Lithium Bis(Trifluoromethanesulfonyl)Amide/Dimethyl Sulfoxide. *J. Phys. Chem. C* **2017**, *121*, 9162-9172.
- (25) Li, F. J.; Zhang, T.; Yamada, Y.; Yamada, A.; Zhou, H. S. Enhanced Cycling Performance of Li-O₂ Batteries by the Optimized Electrolyte Concentration of Litfsa in Glymes. *Adv. Energy Mater.* **2013**, *3*, 532-538.
- (26) Suo, L. M.; Hu, Y. S.; Li, H.; Armand, M.; Chen, L. Q. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* **2013**, *4*.
- (27) Qian, J. F.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J. G. High Rate and Stable Cycling of Lithium Metal Anode. *Nat. Commun.* **2015**, *6*.
- (28) Liu, Y.; Suo, L.; Lin, H.; Yang, W.; Fang, Y.; Liu, X.; Wang, D.; Hu, Y. S.; Han, W.; Chen, L. Novel Approach for a High-Energy-Density Li-Air Battery: Tri-Dimensional Growth of Li₂O₂ Crystals Tailored by Electrolyte Li⁺ Ion Concentrations. *Journal of Materials Chemistry A* **2014**, *2*, 9020-9024.
- (29) Walker, W.; Giordani, V.; Uddin, J.; Bryantsev, V. S.; Chase, G. V.; Addison, D. A Rechargeable Li-O₂ Battery Using a Lithium Nitrate/N,N-Dimethylacetamide Electrolyte. *JACS* **2013**, *135*, 2076-2079.
- (30) Sun, B.; Huang, X. D.; Chen, S. Q.; Zhang, J. Q.; Wang, G. X. An Optimized Lino3/Dmso Electrolyte for High-Performance Rechargeable Li-O₂ Batteries. *Rsc Advances* **2014**, *4*, 11115-11120.
- (31) Togasaki, N.; Momma, T.; Osaka, T. Enhanced Cycling Performance of a Li Metal Anode in a Dimethylsulfoxide-Based Electrolyte Using Highly Concentrated Lithium Salt for a Lithium-Oxygen Battery. *J. Power Sources* **2016**, *307*, 98-104.
- (32) Qiao, Y.; Wu, S. C.; Sun, Y.; Guo, S. H.; Yi, J.; He, P.; Zhou, H. S. Unraveling the Complex Role of Iodide Additives in Li-O₂ Batteries. *ACS Energy Lett.* **2017**, *2*, 1869-1878.

- (33) Yang, H. C.; Yin, L. C.; Shi, H. F.; He, K.; Cheng, H. M.; Li, F. Suppressing Lithium Dendrite Formation by Slowing Its Desolvation Kinetics. *Chem. Commun.* **2019**, 55, 13211-13214.
- (34) Brouillette, D.; Irish, D. E.; Taylor, N. J.; Perron, G.; Odziemkowski, M.; Desnoyers, J. E. Stable Solvates in Solution of Lithium Bis(Trifluoromethylsulfone)Imide in Glymes and Other Aprotic Solvents: Phase Diagrams, Crystallography and Raman Spectroscopy. *PCCP* **2002**, 4, 6063-6071.
- (35) Miller, R. E.; Getty, R. R.; Treuil, K. L.; Leroi, G. E. Raman Spectrum of Crystalline Lithium Nitrate. *J. Chem. Phys.* **1969**, 51, 1385-+.
- (36) Kwabi, D. G.; Tulodziecki, M.; Pour, N.; Itkis, D. M.; Thompson, C. V.; Shao-Horn, Y. Controlling Solution-Mediated Reaction Mechanisms of Oxygen Reduction Using Potential and Solvent for Aprotic Lithium-Oxygen Batteries. *Journal of Physical Chemistry Letters* **2016**, 7, 1204-1212.
- (37) Serizawa, N.; Katayama, Y.; Miura, T. Eqcm Measurement of Ag(I)/Ag Reaction in an Amide-Type Room-Temperature Ionic Liquid. *J. Electrochem. Soc.* **2009**, 156, D503-D507.

Chapter 6

General Conclusion and Future Prospects

6.1 General conclusion

In the present thesis, the concentration-dependence of solvation structure at gold/electrolyte interface were investigated in LITFSI-DMSO and LiNO₃-DMSO electrolytes using surface enhanced Raman spectroscopy (SERS). In addition, the oxygen reduction mechanism on gold model cathode affected by lithium salt concentration in DMSO and TEGDME solution was studied as well by in situ SERS, electrochemical quartz crystal microbalance (EQCM) and rotating ring/disk electrodes (RRDE) measurements.

In Chapter 3, SERS measurement was used to detect solvation structure at the electrode/electrolyte interface in LiNO₃-DMSO and LITFSI-DMSO solutions with various lithium salt concentrations. DMSO molecules were found to interact with the gold substrate and form Au-O and Au-S bonds, while TFSI⁻ was adsorbed by the formation of Au-O bonds. However, there is no indication that NO₃⁻ interacts with gold through chemical adsorption. In the superconcentrated LITFSI-DMSO electrolytes, chemisorbed TFSI⁻ is the only species on the gold surface, while NO₃⁻ and Li(DMSO)₃⁺NO₃⁻ complex is dominant in superconcentrated LiNO₃-DMSO solutions, which may due to the stronger adsorption strength of TFSI⁻ than NO₃⁻ with gold substrate. High proportion of salt anion (TFSI⁻ and NO₃⁻) dominant gold surface in superconcentrated DMSO electrolytes might benefit for the formation of SEI-derived from salt anion, which is the reason for good battery cycle performance.

In Chapter 4, The influence of LiNO₃ concentration on electrochemical reduction of O₂ in LiNO₃-DMSO solutions were investigated by in situ SERS, EQCM and RRDE measurements. It turns out that the effect of LiNO₃ concentration on oxygen reduction mainly achieved by affecting the O₂⁻ adsorbed on the electrode surface and LiO₂ dissolution into bulk electrolyte, which is the intermediate for surface and solution pathway, respectively. At low concentration, due to the low Li⁺ concentration, the LiO₂ dissolution is small, so that most of the O₂ is electrochemically converted into Li₂O₂. At medium concentration, due to the higher Li⁺ concentration, LiO₂ dissolves more, less O₂

is electrochemically converted into Li_2O_2 . At high concentrations, O_2^- tends to be adsorbed on the electrode surface due to the high viscosity of electrolyte, resulting more O_2 to be electrochemically converted into Li_2O_2 .

In Chapter 5, the effect of LiNO_3 concentration on electrochemical reduction of oxygen in Li^+ -TEGDME solutions was investigated by RRDE and EQCM measurements. It turns out that the LiO_2 solubility decrease with LiNO_3 concentration, which is relate to free TEGDME in the solution. EQCM measurements shows that LiNO_3 concentration has almost no effect on the surface electrode reaction. O_2 was firstly electrochemically reduced into LiO_2 and leave electrode surface at low overpotential. At medium overpotential, O_2 is mainly converted to Li_2O_2 through surface two-electron reduction pathway, together with small part of LiO_2 dissolute into electrolyte. At high overpotential, oxygen is found to be reduced into LiO_2 on the surface of Li_2O_2 .

In this thesis, surface solvation structure affected by lithium salt concertation was revealed by SERS measurement. A series of surface-sensitive characterization methods, including in situ SERS, EQCM and RRDE measurements are used to study the oxygen reduction reaction mechanism on gold in different concentrated DMSO and TEGDME solutions for Li- O_2 battery. The high concentration electrolyte stabilizes the lithium anode is due to the anion-rich adsorption layer is formed on the surface of the electrode, which is good for creating uniformly solid electrolyte interface at lithium anode. While on cathode part, the high viscosity of electrolyte was proved to decrease the diffusion of LiO_2 , and eventually cause O_2^- to accumulate on the electrode surface and render O_2 to convert into Li_2O_2 by surface reaction.

6.2 Future Prospects

Although the superconcentrated electrolyte can effectively stabilize the lithium anode, the effect of electrolyte concentration on the oxygen reduction reaction on cathode is independent of the solvent property. In the future, it can be considered to develop more lithium salt and solvent combination for superconcentrated electrolytes to apply to Li- O_2 battery, in order to achieve the goal of high cycle stability and high capacity. In addition, in-depth understanding of the reaction mechanism by different in situ techniques should be used as well.