Lithium-Sulfur Batteries Employing Hybrid-electrolyte Structure with Li$_7$La$_3$Zr$_2$O$_{12}$ at Middle Operating Temperature: Effect of Li Salts Concentration on Electrochemical Performance

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ABSTRACT

All solid state Lithium-Sulfur batteries can effectively solve the problem of the conventional Li-S batteries with a liquid electrolyte. However, they still do not achieve sufficient cycle stability and rate capability because of high interfacial resistance between the electrode and the solid electrolyte. Hybrid-electrolyte structure using a liquid electrolyte and a solid electrolyte can efficiently solve the interfacial problem. Here, we demonstrate the effect of Li salt concentration in the liquid electrolyte between the sulfur cathode and the solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) on the electrochemical properties in Lithium-Sulfur batteries employing hybrid-electrolyte structure. Furthermore, the interfacial reactivity between the liquid electrolyte and LLZ is investigated. With increasing Li salt concentration, the electrochemical performances including the utilization of sulfur, the cycle stability and coulombic efficiency are improved because the dissolution of lithium polysulfides during cycle into the liquid electrolyte at cathode side is inhibited. The interfacial layer is formed on LLZ surface during discharge-charge cycle by a contact of the liquid electrolyte with LLZ, leading to increasing the interfacial resistance. We believe that this study helps to improve the electrochemical properties of Lithium-Sulfur batteries with hybrid electrolyte concepts.

Keywords: Lithium-Sulfur Battery, Hybrid-electrolyte Structure, Garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$

1. Introduction

Renewable energy has been introduced actively to prevent the energy shortage and environmental pollution issues. At the same time, energy storage with highly efficiency has been studied by many researchers worldwide. Li-ion batteries have applied with various devices such as portable electrical device and electric vehicle. However, in recent years, Li-ion battery technologies including energy density, cost and safety are currently approaching their limits. Therefore, developments for post-Li ion battery are needed.

Lithium sulfur (Li-S) batteries have attracted much attention as one of the candidates for post-Li ion batteries due to high theoretical energy density (2600 Wh kg$^{-1}$ based on Li$_2$S), low material cost and environmental-friendly.$^2$ A typical Li-S battery consists of S cathode (which has a theoretical capacity of 1675 mAh g$^{-1}$), Li metal anode (which has a theoretical capacity of 3680 mAh g$^{-1}$ and the lowest electrochemical reductive potential of $\sim$3.040 V vs. SHE) and a separator containing an organic liquid electrolyte.$^3$ Despite lots of advantages, conventional Li-S batteries are facing some critical technical problems. Lithium polysulfides (Li$_{2-x}$S$_x$, $4 \leq x \leq 8$) easily dissolve into a liquid electrolyte during charge-discharge cycling process. The polysulfide anion (S$_2^{x-}$) migrates through a liquid electrolyte and reacts with Li metal anode during charge, causing to low coulombic efficiency, poor rate capability and short cycle-life. This behavior is well known as “redox shuttle.”$^4$–6 Therefore, designs of advanced cathode structure$^7$–$^8$ and novel electrolytes$^9$–$^{11}$ are necessary.
have been demonstrated to solve this problem. The use of highly concentrated liquid electrolyte can effectively inhibit the redox shuttle behavior. For instance, Y. Ishino, et al. reported that nonequimolar (highly Li salt concentration) lithium bis (trifluoro-methanesulfonyl) imide (LiTFSI)/Triglyme (G3) electrolytes suppressed the dissolution of lithium polysulfides and provided to improve the discharge-charge performance of Li-S cell. A new design of “soil in salt” electrolyte with ultra-high salt concentration has shown high cycle stability and high rate performance, because it inhibits not only the dissolution of lithium polysulfides but also the formation of lithium dendrites. Nevertheless, the redox shuttle cannot be completely avoided with conventional Li-S battery structure.

The application of a tightly packed (dense) solid electrolyte can block the redox shuttle physically and effectively solves the problem of the conventional Li-S batteries. All solid state Li-S batteries have been demonstrated by some researchers. However, they still do not achieve sufficient cycle stability and rate capability because of high interfacial resistance between the electrode and the solid electrolyte at both S cathode and Li anode sides. A hybrid-electrolyte structure using a liquid-based electrolyte and a solid electrolyte has been suggested to solve the interfacial problem. The introduction of the liquid-based electrolyte interlayer between the electrode and the solid electrolyte can reduce the interfacial resistance because of excellent contact at the interface. Several researchers have reported about electrochemical performances of Li-S battery employing hybrid-electrolyte structure. For example, Q. Wang, et al. have demonstrated stable cycle stability with excellent coulombic efficiency of ca. 100% in hybrid-structure Li-S battery using an organic liquid electrolyte, which consists of 1 mol dm⁻³ LiTFSI in 1,3-dioxolane (DOL) and 1,2-dimethoxy-ethane (DME) (1:1, v/v), between S cathode and a solid electrolyte.7 However, there is no report on an effect of Li salt concentration in the liquid electrolyte at cathode side on an electrochemical performance of Li-S battery with hybrid-electrolyte structure.

In this study, we investigated electrochemical performance of Li-S batteries with hybrid-electrolyte structure with increasing Li salt concentration. Garnet-type Li₇La₃Zr₂O₁₂ (LLZ) was selected as a solid electrolyte because it has a high Li-ionic conductivity (≥10⁻³ S cm⁻¹ at room temperature). Our battery system was operated at 120 °C which was almost the melting point of sulfur. When sulfur active material is applied as a liquid (i.e. catholyte), the S/KB interface can be changed from solid–solid contact to solid–liquid contact, expecting to reduce the S/KB interfacial resistance. Furthermore, we investigated a mechanism of capacity fading caused by an interfacial reactivity between the liquid electrolyte and LLZ.

2. Experimental

2.1 S/KB composite cathode

The Sulfur (S, 99.99%, Wako)/Ketjen black (KB, EC600JD, Lion Co.) composite cathode was prepared by a typical melt-diffusion strategy. Elemental S and KB in a weight ratio of 77 : 23 were mixed and then heated at 155°C for 12 h to incorporate S into KB. The weight ratio of S in the S/KB composite was determined 77% by thermogravimetric analysis (TGA) as shown in Fig. S1. S/KB composite, KB and Carbosymethyl cellulose (CMC, MAC350HC, Nippon Paper Industries Co., Ltd.) in a weight ratio of 80 : 10 : 10 were mixed with deionized water. The obtained slurry was coated on carbon-coated aluminum foil and dried at 60°C under vacuum to remove water. The S/KB composite cathode was compressed and cut in a circular pattern of 9 mm diameter. The mass of S per unit area was ca. 1.5 mg cm⁻².

![Figure 1](image-url)  
**Figure 1.** Schematic diagram of Li-S battery with hybrid-electrolyte structure.

2.2 Assembly of S/KB/LLZ/Li cell

Li-S batteries with hybrid-electrolyte structure (S/KB/LLZ/Li) were assembled with 2032-type coin cell (Hosen Co., Ltd.) using the S/KB composite cathode, LLZ pellet and Li foil anode (thickness of 600 μm and diameter of 15 mm, Honjo Metal Co., Ltd.) in a glove box with argon atmosphere, as shown in Fig. 1. The LLZ pellet was purchased from Japan Fine Ceramics Co., Ltd. The LLZ pellet, with the thickness of 500 μm and the diameter of 14.4 mm, has a Li-ion conductivity of ≥10⁻³ S cm⁻¹ at 120°C. The relative density was more than 97%, which is sufficient to prevent the permeation of the liquid electrolyte. The surface of the LLZ pellets was polished by emery paper (grit number 400) before the assembly of the cell. The liquid electrolyte of LiTFSI/G4 (15–20 μL mg⁻¹–sulfur weight) was injected into a glass separator between the S/KB composite cathode and LLZ. LiTFSI and G4 were purchased from Kishida Chemical. The liquid electrolytes were prepared by dissolving LiTFSI into G4 with different molar ratios of 1/1, 1.5/1, 2/1, and 2.5/1 (= LiTFSI/G4) and were stirred at 80°C for overnight in a glove box filled with argon gas. Three dimensionally ordered macro-porous polyimide separator (3DOM PI separator) filled with the LiTFSI/G4 1/1 solution was introduced between LLZ and Li anode. Figure S2 shows the schematic diagram of 3DOM PI separator.

2.3 Assembly of CC/LLZ/CC symmetric cell

S/KB/LLZ/Li cell has many resistance factors including S/KB cathode, Li anode, a liquid electrolytes, LLZ, and a liquid electrolyte/LLZ interface at cathode/anode side. A symmetric cell can simplify their resistance factors. Symmetric cells (CC/LLZ/CC) using carbon cloth electrolyte (CC, EC-CC1-060, Toray Co., Ltd.) filled with different solutions (the LiTFSI/G4 1/1 solution with/without ca. 10 wt% Li₂S₄) were fabricated in order to study interfacial reactivity between the liquid electrolytes and LLZ. Li₂S₄ was synthesized by mixing sulfur and lithium sulfide (Li₂S, %, Sigma-Aldrich) at molar ratio of 7 : 8, referring to previous report.

2.4 Electrochemical measurement

All electrochemical measurements were conducted at operating temperature of 120°C. The galvanostatic charge and discharge test was conducted by TOCAT-3000U (Toyo System Co. Ltd.) to investigate cycle performance. Internal resistance was measured by electrochemical impedance spectroscopy (EIS, SP-200, Bio-Logic Sci. Inst.) in a frequency range from 3 MHz to 100 mHz with an amplitude of 10 mV.

2.5 Surface characterization of LLZ

In order to identify the chemical components of the LLZ surface, the LLZ pellet was analyzed by X-ray photoelectron spectroscopy.
the liquid electrolytes with low salt concentration, the discharge capacity retentions were 14.9% and 17.9% in the LiTFSI/G4 1/1 and 1.5/1, respectively. In contrast, in the liquid electrolytes with high salt concentration (i.e. LiTFSI/G4 2/1 and 2.5/1), the discharge capacity retentions at 100th cycle were 26.7% and 35.3% in the LiTFSI/G4 2/1 and 2.5/1, respectively. At the 100th cycle, LiTFSI/G4 2.5/1 showed the discharge capacity of 348 mAh g\(^{-1}\), which was twice larger discharge capacity than that in LiTFSI/G4 1/1.

3.2 Electrochemical impedance spectroscopy analysis

In section 3.1, we demonstrate that the application of highly concentrated liquid electrolyte provides to improve electrochemical performances in Li-S battery with hybrid-electrolyte structure. However, it is noted that capacity dramatically reduces at the initial cycle term (1st-10th cycles) even when using highly concentrated liquid electrolyte. For instance, the discharge capacity in the LiTFSI/G4 2.5/1 liquid electrolyte decreased after 10 cycles from 985 mAh g\(^{-1}\) to 762 mAh g\(^{-1}\), as shown in Fig. 3d. In contrast, the discharge capacity decreased from 1007 mAh g\(^{-1}\) to 550 mAh g\(^{-1}\) in the case of the LiTFSI/G4 1/1 liquid electrolyte, as shown in Fig. 3a.

Therefore, it is important to further understand a mechanism of the capacity fading at the initial cycle. In order to investigate the mechanism of the capacity fading, the internal resistances during discharge-charge cycle (at the current density of 0.22 mA cm\(^{-2}\)) in S/KB/LLZ/Li cell using the LiTFSI/G4 2.5/1 liquid electrolyte was measured by EIS analysis. Figure 4a shows Nyquist plots before cycle and after charge at 2nd-10th cycles. The internal resistance increased with increasing cycle number. The plots were analyzed using an equivalent circuit model composing of two resistances (R\(_{\text{int}}\)) and two constant phase elements (CPE), as shown in Fig. S3. An intersection of a semi-circle with the real axis at high frequency was assigned to the sum of the liquid electrolyte resistance and the solid electrolyte resistance (R\(_{\text{int}}\)). A depressed semi-circle in middle and high-frequency regions was assigned to the interfacial resistance between the liquid electrolyte and the solid electrolyte (R\(_{\text{int}}\)).

In order to clarify the reason of the increase in R\(_{\text{int}}\), EIS for symmetric cells with different solutions were measured. The LiTFSI/G4 electrolyte was well used in LiTFSI/G4 1/1 liquid electrolyte was dark brown (Fig. S5). In addition, the saturation solubility of lithium polysulfides in the Li plating/stripping test using Li/Li symmetric cell (Fig. S4), the cell voltage was nearly unchanged for 150 hour, meaning that the increase in the internal resistance at Li anode side is much small. Therefore, the internal resistance increase in Fig. 4a is likely attributed to the S/KB cathode and the liquid electrolyte-Li interface at cathode side. In Fig. 4b, R\(_{\text{int}}\) decreased after 10 cycles from 13.5 \(\Omega\) to 15.3 \(\Omega\). Interestingly, R\(_{\text{int}}\) increased after 10 cycles from 3.87 \(\Omega\) to 9.04 \(\Omega\), suggesting the formation of the interfacial layer on LLZ surface due to a chemical reaction between the liquid electrolyte and LLZ during cycle. Figure 4c shows photograph of the glass separator obtained from S/KB/LLZ/Li cell after cycle. It is confirmed that the color of the glass separator was light brown. This result can be ascribed to the dissolution of lithium polysulfide to the liquid electrolyte, indicating that lithium polysulfides cannot be trapped within carbon matrix during cycle. In comparison, the color of the glass separator in the dilute liquid electrolyte (LiTFSI/G4 1/1) was dark brown (Fig. S5). In addition, the saturation solubility of lithium polysulfides (Li\(_2\)S\(_x\) in this study) increased with decreasing LiTFSI salt concentration (Fig. S6). From these results, it can be considered that the dissolution of lithium polysulfides into the liquid electrolyte during cycle is inhibited with using highly concentrated liquid electrolyte, leading to improve the cycle performance as mentioned in Fig. 3.

In order to clarify the reason of the increase in R\(_{\text{int}}\), EIS for CC/LLZ/CC symmetric cells with different solutions were measured. The LiTFSI/G4 solutions with/witout lithium polysulfide
In comparison, RInt in the LiTFSI solution and the resistance change with standing time. The plots contacted with the liquid electrolytes, we analyzed by X-ray lithophyrosul (Li2S8 in this study) were used. Figures 5a–5b and 5c–5d show Nyquist plot and the resistance change with standing time. The plots were fitted using equivalent circuit model as shown in Fig. S3. The LiTFSI/G4 solution showed a slight increase in R_{L/S} and R_{int}. In comparison, R_{int} in the LiTFSI/G4 solution containing Li2S8 significantly increased from 2.23 Ω to 20.5 Ω. Moreover, R_{L/S} also increased from 9.00 Ω to 23.3 Ω. From these results, it can be said that the increase in R_{int} is caused by contact of the liquid electrolyte with LLZ, especially the liquid electrolyte containing lithium polysulfide (i.e. Li2S8 in this study).

### 3.3 X-ray photoelectron spectroscopy analysis

To clarify the chemical compositions of the LLZ pellet surfaces contacted with the liquid electrolytes, we analyzed by X-ray photoelectron spectroscopy (XPS). Figure 6 shows XPS spectra for LLZ pellet prepared from the CC/LLZ/CC symmetric cells using LiTFSI/G4 with Li2S8. Zr 3d spectra assigned to LLZ were not detected in LLZ surface, suggesting that the thick interfacial layer existed on LLZ surface.\(^{15,29,32}\) In S 2p spectra, the broad peak in binding energy region between 164 and 159 eV was observed. These peaks at 160.2 eV and 161.9 eV are assigned to Li2S and Li2S2, which were attributed to the reactive products between Li2S8 and LLZ, according to previous reports.\(^{15,30}\) On the other hand, these S 2p peaks were not observed in the case of LiTFSI/G4, as shown in Fig. S7. F 1s spectra attributable to -CF, species (ca. 688 eV) and LiF (685 eV) also were observed in the LLZ surface, which were attributed to the reactive products from LiTFSI.\(^{26,31,34}\) Moreover, for the LLZ pellet contacted with LiTFSI/G4 containing Li2S8, depth

Figure 3. Discharge-charge profiles of S/KB/LLZ/Li cells using different LiTFSI/G4 liquid electrolytes with different ratios of LiTFSI to G4. (a) 1/1, (b) 1.5/1, (c) 2/1, and (d) 2.5/1. (e) Cycle performance and (f) Coulometric efficiency during cycling. Discharge-charge test was conducted at current densities of 0.86 mA cm\(^{-2}\) (0.5 C) at potential range between 1.5 V and 2.8 V.
analysis was conducted using an Ar⁺-ion sputter etching for 20, 40 and 100 sec. The sputtering rate was calibrated to be 0.7 nm sec⁻¹.

Zr 3d peak assigned to LLZ was observed after the sputter etching and the intensity increased with increasing the sputter etching time. It should be noted that the S 2p and F 1s peaks attributed to the reactive products between the liquid electrolyte (i.e. LiTFSI and Li₂S₈) and LLZ were detected after the sputter etching, suggesting that the interfacial layer was formed at LLZ bulk near surface. The thickness of the interfacial layer was estimated to be more than 70 nm in this study. The formation of the interfacial layer may lead to both increase of the interfacial resistance and the resistance of LLZ surface.

4. Conclusions

In summary, we studied the effect of Li salt concentration in the liquid electrolyte on electrochemical performance of Li-S batteries employing hybrid-electrolyte structure with LLZ at 120 °C. The application of highly concentrated liquid electrolyte in hybrid-electrolyte structure provides higher electrochemical performances due to the suppression of dissolving lithium polysulfides, relative to the dilute liquid electrolyte. However, it’s not enough to achieve sufficient electrochemical performances by only the use of highly concentrated liquid electrolyte for hybrid structure Li-S batteries. In order to further improve them, the effective strategy to inhibit the dissolution of lithium polysulfides is needed. Moreover, the dissolved lithium polysulfide contacted with LLZ during cycle, leading to the formation of the interfacial layer on LLZ. The formation of the interfacial layer contributed to not only the interfacial resistance increase and also the resistance increase of LLZ surface.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00160.

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Figure 5. Time-dependent Nyquist plots of CC[LLZ]CC symmetric cells with (a) LiTFSI/G4 and (b) LiTFSI/G4 containing Li2S8. The resistances plotted with standing time in the CC[LLZ]CC symmetric cells with (c) LiTFSI/G4 and (d) LiTFSI/G4 containing Li2S8. The internal resistance was measured by EIS in the frequency range of 3 MHz to 0.1 Hz with the amplitude of 10 mV at 120 °C.

Figure 6. XPS spectra of F1s, Zr3d, and S2p of LLZ pellet surface prepared from CC[LLZ]CC symmetric cell using LiTFSI/G4 containing Li2S8. CC[LLZ]CC symmetric cell was maintained for 60 h at 120 °C. The XPS spectra were recorded after 0, 20, 40, 100 sec of Ar⁺-ion sputter etching. The sputtering rate was calibrated 0.7 nm sec⁻¹.
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