Lithium metal as an anode has the potential to achieve high energy density in the field of storage batteries. The lithium oxygen battery or lithium sulfur battery with metallic lithium anodes are examples of batteries with higher theoretical energy density than conventional lithium ion batteries. The application of these batteries requires improvement of the lithium electrode; however, practical cycle performance has not yet been achieved, even with decades of research on lithium metal. This is due to the dendritic growth of lithium metal, which causes internal short-circuiting between electrodes. Another reason is the much lower coulombic efficiency of lithium metal anodes in organic electrolytes than that of graphite anodes. These issues are caused by the unstable and non-uniform solid electrolyte interphase (SEI) formed on lithium metal. The SEI is formed from the reduction products of chemical species contained in the electrolyte solution, and its nature has a strong influence on the performance of the lithium metal anode. Various solvents, salts, and additives have been studied to chemically control the state of the SEI.

Ether solvents are often chosen for studies on metallic lithium because ether bonds are relatively stable against reduction. For example, lithium bis(2-ethylhexyl)sulfonate (LiFSI) in 1,2-dimethoxyethane (DME) was reported to show high rate and stable cycling of the lithium metal anode.\textsuperscript{12} 1,3-Dioxolane (DOL) is often used as the co-solvent for these electrolytes,\textsuperscript{13} while LiClO\textsubscript{4} in a DOL single solvent has previously been reported to produce organic components and LiCl in the SEI.\textsuperscript{5}

The concept of a highly concentrated electrolyte is effective to enlarge the stable potential range of the electrolyte. In a reductive atmosphere, salt decomposition becomes predominant to give a stable inorganic SEI.\textsuperscript{6,8} A small ether molecule-lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) equimolar complex is known as a solvate ionic liquid that has no free solvent molecules. The known as a solvate ionic liquid that has no free solvent molecules bis(trifluoromethanesulfonyl)imide (LiTFSI) equimolar complex is formed in the electrolyte solution to investigate the structures and compositions that are developed with these compositions. We also intend to clarify the roles that decomposition species from each salt anion play in the SEI. Here, DMSO as a solvent is adopted because it is a highly polar solvent and can dissolve solutes over a wide concentration range. This is a property necessary for investigation of the effect of salt compositions.

These previous works have suggested that a stable and dendrite-suppressing SEI was formed by an increase in inorganic components. However, the electrochemical role of individual inorganic components has yet to be clarified. A significant challenge remains to establish clear guidance as to the type of electrolyte materials that should be selected to form an SEI that provides practical cycle performance of the lithium metal electrode. This is due to the difficulties in obtaining quantitative information on the thin surface SEI film and electrode performance that appear as a total expression of the properties of these components.

In this study, two different electrolyte salts were mixed at a given ratio in one electrolyte solution to investigate the structures and compositions that are developed with these compositions. We also intend to clarify the roles that decomposition species from each salt anion play in the SEI. Here, DMSO as a solvent is adopted because it is a highly polar solvent and can dissolve solutes over a wide concentration range. This is a property necessary for investigation of the effect of salt compositions.

XPS is a powerful tool to elucidate the compositions of thin surface films. Chemical characterization of an SEI on the lithium electrode surface is thus often performed by XPS analysis.\textsuperscript{17} XPS measurements were also attempted to obtain information on the decomposition products that compose the SEI that are produced without the deposition of lithium metal by controlling the potential of the copper electrode. These results and the lithium plating/stripping performance are correlated to determine the role of each SEI component, and their effect is reported for other concentrated solutions using propylene carbonate (PC) and dimethyl sulfoxide (DMSO).\textsuperscript{14,15}

Some inorganic additives are also effective to suppress dendrite growth. Kanamura et al. reported that the surface film formed on lithium in a carbonate-based electrolyte by the addition of hydrogen fluoride (HF) solution consisted of a LiF/Li2O bilayer, based on X-ray photoelectron spectroscopy (XPS) measurements.\textsuperscript{16} Aurbach et al. reported the surface chemistry of lithium in an electrolyte with added LiNO\textsubscript{3} in Li-S cells, and showed the formation of Li\textsubscript{2}O and Li\textsubscript{2}SO\textsubscript{4} species.\textsuperscript{17} Other studies have shown that the concentration of these additives has an influence on the morphology of the lithium metal deposits.\textsuperscript{18} Lithium difluorophosphate (LiPO\textsubscript{2}F\textsubscript{2}) is used to inhibit lithium dendrite growth by the formation of a stable SEI comprised of LiF and P-O moieties.\textsuperscript{19} Zhang and colleagues reported that Cs\textsuperscript{+} ion adsorption onto a lithium surface leads to the suppression of lithium dendritic growth.\textsuperscript{20-22}

JES FOCUS ISSUE OF SELECTED PAPERS FROM IMLB 2018

Solid Electrolyte Interphase Film on Lithium Metal Anode in Mixed-Salt System

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The effect of electrolyte salt on the solid electrolyte interphase (SEI) is discussed with respect to improvement of the lithium metal anode. Lithium bis(2-ethylhexyl)sulfonate (LiFSI) and lithium nitrate (LiNO\textsubscript{3}) were dissolved together in dimethyl sulfoxide (DMSO), in which the ratio of LiNO\textsubscript{3} to LiFSI (x:100-x mol%) was in the range of 0 < x < 100. Electrochemical lithium plating/stripping was tested for various x-values. A LiNO\textsubscript{3} single salt electrolyte yielded small polarizations in the initial cycles; however, the polarization became larger with the cycle number. A LiFSI single salt electrolyte showed larger polarizations, but maintained an almost constant magnitude during all cycles. LiNO\textsubscript{3} and LiFSI salt-mixtures gave better cycle performance with low and stable polarizations compared to the single salt electrolytes. X-ray photoelectron spectroscopy (XPS) analyses revealed that LiNO\textsubscript{3} gave a Li2O-rich SEI membrane, while LiFSI gave a LiF-rich membrane. For LiNO\textsubscript{3} and LiFSI salt-mixtures, the ratio of these components changed according to the x value. The use of multiple lithium salts is thus an effective way to control the SEI properties and improve the cycle performance of a lithium metal anode.

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also discussed. Based on these analyses, we attempt to obtain guidelines to determine the type of SEI composition that is suitable to achieve a lithium metal electrode with high coulombic efficiency and cycle life.

**Experimental**

**Electrolytes.**—Electrolyte solutions were prepared using the following lithium salts: LiFSI (lithium battery grade, Kishida Chemical Co., Ltd.), LiTFSI (lithium battery grade; Kishida Chemical Co., Ltd.), lithium bis(tetrafluoroethanesulfonyl)imide (LiBETI; lithium battery grade, Kishida Chemical Co., Ltd.), lithium tetrafluoroborate (LiBF₄; lithium battery grade, Kishida Chemical Co., Ltd.), lithium perchlorate (LiClO₄; ≥99.9%, Sigma-Aldrich), lithium hexafluorophosphate (LiPF₆; lithium battery grade, Kishida Chemical Co., Ltd.), lithium iodide (LiI; Kojundo Chemical Laboratory Co., Ltd.), and lithium nitrate (LiNO₃; ≥99.9%, Wako Pure Chemical Industries Co., Ltd.). LiNO₃ was vacuum-dried overnight at room temperature. These lithium salts were dissolved in DMSO (lithium battery grade, Kishida Chemical Co., Ltd.). The water contents of the prepared electrolyte solutions were evaluated by the Karl Fischer method and fell within 2–50 ppm.

**Charge-discharge test.**—Lithium was plated/stripped using a 2025 type coin cell. Lithium metal (15 mm diameter, 0.2 mm thick, ≥99%, Honjo Metal Co., Ltd.) was used as the counter electrode, and copper foil (19 mm diameter, Thank-Metal Co., Ltd.) was used as the working electrode. The volume of electrolyte was 75 μL. A 260 μm thick glass fiber separator with an air permeability of 4.3 s/(100 mL inch⁻²) was adopted because it can be sufficiently soaked with the highly concentrated viscous electrolytes. This separator with high porosity does not block dendrite penetration; therefore, the glass fiber separator is a suitable choice to observe the deterioration of the lithium metal anode.²⁴ The coin cell was assembled in a glove box under a dry argon atmosphere.

The charge/discharge measurement was conducted using a charge/discharge test system (TOSCAT-3100, Toyo System Co., Ltd.) with a current density of 0.2 mA cm⁻² and a capacity of 0.2 mAh cm⁻². The cutoff voltage during the lithium stripping process was 1.5 V. The coulombic efficiency for stripping/plating was estimated using:

\[
\text{Coulombic efficiency (\%)} = \frac{Q_{\text{stripped}}}{Q_{\text{plated}}} \times 100 \quad [1]
\]

where \(Q_{\text{plated}}\) and \(Q_{\text{stripped}}\) are the amount of charge passed during each charge and discharge process, respectively.

**X-ray photoelectron spectroscopy.**—XPS measurements were conducted to analyze the compositions of SEI membranes. Samples were prepared by potentiostatic charging at an applied voltage of 0.02 V for 2 h. After formation of the SEI film, the cell was disassembled and the copper foil was rinsed with anhydrous DME to remove the electrolyte salts. The rinsed copper foil was dried under vacuum overnight at room temperature. The XPS apparatus (ESCA-3400, Shimadzu Corp.) was equipped with Mg Kα (1150 eV) X-ray anodes (acceleration voltage 10 kV, emission current 20 mA) and an argon sputtering gun. Argon sputtering of the sample was performed to obtain depth information on the SEI film. Sample installation into the apparatus was conducted using a transfer vessel, which allowed the copper foil sample to be inserted into the measurement system without exposure to the air.

**Impedance spectroscopy.**—Electrochemical impedance spectroscopy (EIS) measurements were conducted using a three-electrode cell with copper foil, lithium metal, and lithium wire as the working, counter, and reference electrodes, respectively. Plating and stripping of lithium were performed repeatedly under the same conditions as those for the coin cell test. EIS measurements were performed with the cell open-circuited each time when the charging process ends. All spectra were collected in the frequency range of 0.1 Hz to 1 MHz with an applied voltage of 10 mV at room temperature (1260 and 1287, Solartron group Ltd.).

**Results and Discussion**

**Electrochemical characterization of electrolytes.**—Figure 1 shows the coulombic efficiencies of lithium metal anodes during cycling in DMSO-based electrolytes with various lithium salts at 0.2 mA cm⁻². an applied voltage of 10 mV at room temperature (1260 and 1287, Solartron group Ltd.).

**Scanning electron microscopy.**—The obtained electrode was sealed in an airtight sample holder and transferred for surface morphology observations using scanning electron microscopy (SEM; S-4800, Hitachi). Samples for observation were prepared by galvanostatic lithium deposition on copper foil with the time control mode. After 0.2 mA cm⁻² of electrodeposition, the cell was disassembled and the copper foil was given the same washing and drying treatment as that for XPS measurements.

![Figure 1. Coulombic efficiencies of lithium metal anodes during cycling in DMSO-based electrolytes with various lithium salts at 0.2 mA cm⁻².](link_to_image)
Figure 2. Electrochemical performance of lithium metal plating/stripping on a copper working electrode in 4 M LiNO$_3$:LiFSI (x:100-x mol%)/DMSO at 0.2 mA cm$^{-2}$. Coulombic efficiency for (a) $x = 100$ and (c) $x = 90$, and lithium plating/stripping curves for (b) $x = 100$ and (d) $x = 90$.

Figure 3. Electrochemical performance of lithium metal plating/stripping on a copper working electrode in 4 M LiNO$_3$:LiFSI (x:100-x mol%)/DMSO at 0.2 mA cm$^{-2}$. Coulombic efficiency for (a) $x = 50$ and (c) $x = 40$, and lithium plating/stripping curves for (b) $x = 50$ and (d) $x = 40$. 
Figure 4. Electrochemical performance of lithium metal plating/striping on a copper working electrode in 4 M LiNO₃:LiFSI (x:100-x mol%)/DMSO at 0.2 mA cm⁻². Coulombic efficiency for (a) x = 10 and (c) x = 0, and lithium plating/stripping curves for (b) x = 10 and (d) x = 0.

showed an average coulombic efficiency of 90.6%, and 141 cycles of lithium plating/striping on the electrode. Both parameters were improved from those for the LiNO₃-rich electrolyte solutions discussed in Fig. 2. This tendency was maintained to 40% LiNO₃-60% LiFSI, which showed an average coulombic efficiency of 92.0% and 150 cycles. The improved efficiency data confirm that LiFSI enhances the passivation ability of the SEI formed in the LiNO₃ single salt electrolyte. The SEI formed in the mixed electrolyte solution is also considered to extend the cycle life by suppressing dendrite formation.

Figure 4 shows the data for LiFSI-rich electrolytes containing (a,b) 10% LiNO₃-90% LiFSI and (c,d) 100% LiFSI. The 10% LiNO₃ electrolyte showed a coulombic efficiency of 87.6% and a lifetime of 50 cycles. The LiFSI single salt electrolyte showed 90.5% coulombic efficiency and only 21 cycles, although the cell was cycled with stable voltage profiles. The lifetimes of these cells were significantly shorter than those obtained for the equimolar mixtures shown in Fig. 3. These data suggest that an excess amount of LiFSI promotes dendritic growth of lithium metal and quick short-circuiting. Another notable feature of these LiFSI-rich electrolytes is the polarization voltage, which gradually increases with the elapse time of the charge or discharge process. The increased polarization immediately decreased to its original magnitude when switching to the next discharge or charge process. The polarization behavior and the quick short-circuit are considered to correlate with each other in terms of the particular SEI formed in these LiFSI-rich electrolytes.

Figure 5 summarizes the coulombic efficiencies and cycle numbers as a function of the LiNO₃ ratio in the salt-mixture. Both parameters have maximum values in the middle concentration region and monotonically decrease as the ratio approaches toward each end composition. Consequently, the solution of 40% LiNO₃-60% LiFSI gives the best performance under the conditions used in this study. The arch-shaped data profiles suggest that the SEI properties systematically change based on the ratios of the two different lithium salts. The inorganic component of the SEI has a strong influence on the coulombic efficiency and cycle lifetime; therefore, the composition of the SEI is discussed in the next section. The data for both end compositions show some deviation from the general tendency. Other
parameters such as the aggregate structure of components should also be taken into consideration in these single-salt electrolytes.

**Surface film analysis by XPS.**—To further characterize the SEI membranes, the surface and interior part were analyzed using XPS with an argon ion etching technique. It is important to determine the substances each lithium salt produces and the reason why the 40% LiNO$_3$-60% LiFSI electrolyte solution exhibits better performance than the other compositions. Each SEI was formed on a copper electrode by potentiostatic charging at 0.02 V vs. lithium metal. Copper was used instead of lithium, so that the contamination of materials from the lithium metal surface could be avoided and only the membrane originally formed on the copper could be analyzed. The potential was set to 0.02 V, at which Li deposition did not occur, although the same SEI was expected on lithium metal. This was to avoid the influence of morphological change of the lithium metal on the SEI membrane and the XPS results.

Figures 6a and 6b show Li 1s and O 1s XPS spectra of the SEI formed on the copper electrode in 100% LiNO$_3$ and 100% LiFSI electrolyte solutions after argon ion etching for various durations. The electrolytes used are denoted as LiNO$_3$ and LiFSI on the top of each set of spectra. The Li 1s spectrum for the LiNO$_3$ electrolyte in Fig. 6a was mainly fitted to Li$_2$O (54.5 eV). The outermost surface at 0 s etching is attributed to lithium of Li$_2$CO$_3$ (55.5 eV), although Li$_2$O is the main component in the bulk of the membrane. Li 1s spectra for the LiFSI electrolyte was fitted to LiF (57.0 eV),$^{25,26}$ which is a decomposition product of the LiFSI salt. Trace amounts of lithium in Li$_2$S, Li$_2$S$_2$O$_4$ and Li$_2$SO$_3$ were also included here, as shown later in the S 2p XPS spectra.

The O 1s spectra for LiNO$_3$ electrolyte in Fig. 6b show two peaks that are attributed to oxygen in Li$_2$CO$_3$ (532.0 eV)$^{27}$ and Li$_2$O (529.5 eV). The relative peak intensity of Li$_2$O became larger from the surface to the deeper part of the membrane. On the other hand, in the SEI film formed in the LiFSI electrolyte, the main peak around 532 eV was assigned to Li$_2$S$_2$O$_4$ and/or Li$_2$SO$_3$, but no Li$_2$O was present. These XPS data indicate that Li$_2$O is formed by decomposition of the LiNO$_3$ electrolyte, while the LiFSI electrolyte does not yield Li$_2$O by decomposition.

Figures 7a and 7b show F 1s and S 2p XPS spectra for samples from the 100% LiNO$_3$ and 100% LiFSI electrolyte solutions. In Fig. 7a, the strong F 1s peak of the LiFSI electrolyte is assigned to LiF (686.7 eV). The spectrum at 0 s etching shows another small peak located at 170.5 eV, which is considered to be LiFSI salt remaining on the sample, even after solvent-washing. XPS spectra of the LiNO$_3$ electrolyte show no F-containing species, because there are no fluorine sources in this system. Figure 7b shows S 2p spectra of the LiFSI electrolyte with several sulfur-derived materials, such as Li$_2$S$_2$O$_4$ (169.3 eV), Li$_2$SO$_3$ (167.5 eV) and Li$_2$S (161.8 eV).$^{1,12}$ On the other hand, the LiNO$_3$ electrolyte gives only a very small S 2p peak located around 161 eV, which can be assigned to Li$_2$S. This is considered to be due to decomposition of the DMSO solvent. F 1s and S 2p XPS data indicate that the LiFSI electrolyte decomposes to LiF and some sulfur containing compounds, while the LiNO$_3$ electrolyte yields the least amount of these materials. Figure 7e shows XPS C 1s spectra of the LiNO$_3$ electrolyte with the appearance of carbonate species. However, Fig. 7f shows the carbonate peak does not appear in the LiFSI electrolyte. From these C 1s spectra, Li$_2$CO$_3$ of the LiNO$_3$ electrolyte was probably formed due to the reaction of oxygen from LiNO$_3$ and carbon from the DMSO solvent. Figure 8 shows XPS spectra of the copper electrode surface in the LiNO$_3$-LiFSI (40:60 mol%) electrolyte which showed the best electrode performance among all the compositions. The peaks appear with a broader shape compared to those with the end compositions, and are assigned to Li$_2$O, LiF and Li$_2$S$_2$O$_4$ formed in the SEI by...
Figure 7. XPS spectra for the copper working electrode after formation of the SEI film by potentiostatic charging at an applied voltage of 20 mV for 2 h; (a) F 1s, (c) S 2p, and (e) C 1s in 4 M LiNO₃/DMSO, and (b) F 1s, (d) S 2p, and (f) C 1s in 4 M LiFSI/DMSO.

Figure 8. XPS spectra for the copper working electrode after formation of the SEI film by potentiostatic charging at an applied voltage of 20 mV for 2 h; (a) Li 1s, (b) O 1s, (c) F 1s, (d) S 2p, and (e) C 1s in 4 M LiNO₃:LiFSI (40:60 mol%)/DMSO.
decomposition of the salt-mixture. Spectral changes with etching time indicate the component distribution along the normal direction of the membrane. The LiF peak in the Li 1s spectra is predominant in the shallow region close to the surface, while the Li2O peak is more intensified in the interior of the membrane. The states of other elements in the O 1s, F 1s and S 2p spectra also change in a consistent manner with this tendency. The SEI structure is simply depicted as a LiF-rich layer covered over a Li2O-rich interior. A suitable mixture of LiF and Li2O is thus considered beneficial to exhibit stable plating/stripping performance without dendrite growth.

The relative elemental ratios of Li, O, F and S were calculated from the peak areas in the XPS spectra using the following equation:

\[
\text{Atomic concentration (\%)} = \frac{A_i / RSF_i}{\sum_i A_i / RSF_i}
\]  

where A and RSF indicate the peak area and the relative sensitivity factor, respectively. RSF values for each element are Li 1s (0.059), F 1s (4.260), O 1s (2.850) and S 2p (1.740). The estimated ratios in 100% LiNO3, LiNO3-LiFSI (40:60 mol%) and 100% LiFSI electrolytes are compared in Fig. 9. There are almost no F or S present in the SEI with the 100% LiNO3 electrolyte; however, the intensities of these elements increase with the ratio of LiFSI and become comparable to Li and O present in the 100% LiFSI electrolyte. Conversely, Li and O elements are least with the 100% LiFSI electrolyte and most with the 100% LiNO3 electrolyte. These results support that Li2O and LiF in the SEI are derived from the decomposition of LiNO3 and LiFSI, respectively, and their contents can be changed by adjustment of the compositions of LiNO3 and LiFSI in the electrolyte solution. Combined with the data in Fig. 5, the electrochemical performance can also be optimized.

**Electrochemical analysis of lithium metal electrode.**—The SEIs derived from each electrolyte salt were characterized with respect to electrical resistance. The inset in Fig. 10 shows a typical impedance spectrum of the lithium metal anode in the three-electrode system. The large semicircle marked as (a) is assigned to the resistance of the SEI membrane. The small component (b) is the charge transfer resistance of the lithium metal electrode during charge/discharge in the 100% LiNO3, LiNO3-LiFSI (40:60 mol%) and 100% LiFSI electrolytes. The SEI resistances (a) are plotted as a function of cycle number. In the LiNO3 electrolyte, the SEI resistance increases almost linearly with the number of cycles, which indicates that the Li2O-rich SEI does not have good passivation ability and the membrane thickness becomes continuously larger. This is in good agreement with the increase in the polarization with the charge/discharge cycle, as shown in Fig. 2. On the other hand, the other two LiFSI-containing electrolytes show small and constant SEI resistances. This indicates that LiF in the membrane has good passivation ability, which prevents further decomposition of the electrolyte after the first cycle.

The polarization magnitude during one charge process was investigated. As illustrated in Fig. 11, the initial and end polarizations are denoted as (1) and (2), respectively, and their changes with the cycle number are monitored. In the 100% LiNO3 electrolyte, polarizations (1) and (2) are of a similar magnitude, which indicates that charging proceeded at a constant voltage. The increase of (1) and (2) with the cycle number is due to the increase of the SEI resistance, as evidenced in Fig. 10. In the LiNO3-LiFSI (40:60 mol%) electrolyte, polarizations (1) and (2) are constant with the cycle number, and the difference between them remains small. The 100% LiFSI electrolyte shows constant polarization; however, a large difference is evident between the initial and end polarizations. This is considered to be due to concentration polarization in the SEI membrane because the increased polarization returns to its original value at the beginning of the next process. A LiF-rich SEI is accompanied by a slow diffusion rate of lithium ions, so that the concentration gradient in the membrane gradually increases with time. The LiNO3-LiFSI (40:60 mol%) electrolyte is thus suitable for a lithium metal electrode because the resultant SEI membrane has both ionic conductivity and electrochemical stability.

Figure 12 shows polarization curves and SEM micrographs of lithium metal deposited at the early stage of charging in the 100% LiNO3, LiNO3-LiFSI (40:60 mol%) and 100% LiFSI electrolytes. Both the 1st and 5th polarization curves are shown in Figs. 12a–12c. The sharp peak-shaped drop in voltage indicates lithium metal nucleation on the copper electrode. There is a lead time until this sharp peak appears in the LiNO3 and LiNO3-LiFSI (40:60 mol%) electrolytes, while in the LiFSI electrolyte the peak appears immediately after the process begins. The lead time is considered to be the time necessary to prepare the SEI membrane. Once this passivation layer is accomplished, a lead time is not necessary in subsequent cycles. This is confirmed by the positions of the voltage drops in the 5th cycle, which appear at the same time that charging starts. The very short lead time for the LiFSI electrolyte could be explained by quick passivation with the LiF-rich SEI membrane. It is noteworthy that this phenomenon is no longer evident in the 5th cycle, because LiF tends to form a dense layer with less pores or cracks. After the copper surface is well-passivated in the 5th cycle, it becomes difficult for lithium ions to reach the copper electrode surface, which is consistent with the large concentration polarization that occurs with this membrane.
Figure 10. SEI resistance on the copper working electrode of a three-electrode cell after each lithium plating process in 4 M LiNO$_3$/DMSO, 4 M LiNO$_3$:LiFSI (40:60 mol%)/DMSO, and 4 M LiFSI/DMSO. The inset shows the impedance spectrum where (a) is assigned to SEI resistance.

Figure 11. Comparison between initial cell polarization at 15 $\mu$Ah and end cell polarization at 350 $\mu$Ah for one lithium plating curve in (a) 4 M LiNO$_3$/DMSO, (b) 4 M LiNO$_3$:LiFSI (40:60 mol%)/DMSO, and (c) 4 M LiFSI/DMSO at 0.2 mA cm$^{-2}$.

Figure 12. 1st and 5th charge curves between 0 and 150 $\mu$Ah in (a) 4 M LiNO$_3$/DMSO, (b) 4 M LiNO$_3$:LiFSI (40:60 mol%)/DMSO, and (c) 4 M LiFSI/DMSO at 0.2 mA cm$^{-2}$. SEM micrographs of the copper working electrodes after lithium plating at 0.2 mAh cm$^{-2}$ (353 $\mu$Ah).
The SEM micrographs show that spherical-shaped deposits are formed at the end of the 1st lithium metal plating in the 100% LiNO₃ and LiNO₃-LiFSI (40:60 mol%) electrolytes. In the case of LiFSI electrolyte, lithium dendrite formation was observed, as shown in Fig. 12f. This is in good agreement with the discussion that the LiF-rich passivation membrane from the 100% LiFSI electrolyte is sufficiently dense to cause the dendritic growth of lithium and a short cycle life of 21 cycles with this electrolyte.

Conclusions

The mechanism of lithium deposition in mixed-salt electrolytes was considered from the results obtained in this study. The inorganic SEI membranes formed generally have some open-spaces such as pores. Lithium ion transport and metal deposition occurs through the pores filled with liquid electrolyte or its decomposed moieties. The aggregation state of inorganic components determines the size, number, and distribution of pores; dense passivating LiF particles give only narrow gaps, while Li₂O particles are considered to result in large pores. These parameters can be adjusted by mixing LiF and Li₂O in the same SEI membrane. This work revealed that the SEI membrane is optimized when two different lithium salts are mixed around equimolar ratios. These results will contribute to the future development of artificial SEI membranes. The distribution of components in the thickness direction of the membrane, the stability during the stripping process, and the role of organic components were not discussed in this research. Further research on these subjects in the future is expected to bring the metallic lithium negative electrode one step closer to practical application.

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