



Short communication

Role of the solid electrolyte interphase on a Li metal anode in a dimethylsulfoxide-based electrolyte for a lithium–oxygen battery



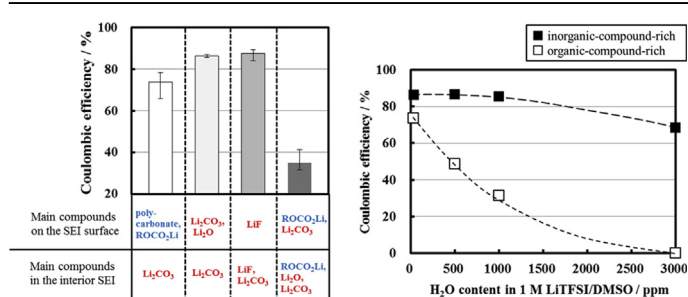
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HIGHLIGHTS

- Inorganic compounds of a SEI enhance the cycling of a Li metal anode in the DMSO.
- Inorganic compounds should form on the SEI surface and interior.
- Organic compounds should not be a dominant component of the SEI.
- The inorganic layer protects the Li anode against H₂O.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of the solid electrolyte interphase (SEI) on a Li anode on the charge–discharge cycling performance in 1 M LiTFSI/dimethylsulfoxide electrolyte solution is examined by using charge–discharge cycling. The chemical structure of the surface and interior of the SEI strongly affects the cycling performance of the anode. The observed coulombic efficiency is low (<45%) when organic compounds such as lithium alkyl carbonates and polycarbonate form predominantly on the surface and interior. However, when inorganic compounds such as Li₂CO₃, Li₂O, and LiF form instead, the coulombic efficiency increases to >85%. This enhanced efficiency remains constant regardless of the O₂ content and despite <1000 ppm concentration of the contaminant H₂O in the electrolyte. Thus, the lithium surface should be protected by inorganic compounds prior to cycling to prevent it from undergoing side reactions with the electrolyte during cycling in the electrolyte.

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1. Introduction

Lithium–oxygen (Li–O₂) batteries are anticipated to be useful in large-scale energy storage because of their theoretically high energy density. The use of dimethylsulfoxide (DMSO) and tetraethylene glycol dimethyl ether (TEGDME) as solvents has been

widely studied in recent years; experiments using these electrolytes for >100 cycles have been carried out [1–3]. Compared with those in TEGDME, the Li ion conductivity, O₂ diffusion coefficient, discharge voltage, specific capacity, and stability of carbon cathodes in DMSO are higher [4–6]. However, the Li metal anode is unstable in DMSO [1,7]. This problem may be due to formation of an unstable solid electrolyte interphase (SEI) on the lithium surface caused by side reactions during cycling [8]. To prevent these side reactions, a stable SEI should be formed on the lithium surface before or during cycling. To stabilize the lithium anode for a Li–O₂ battery using DMSO solvent, investigations have attempted to use a lithium

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anode dipped in LiClO₄/propylene carbonate (PC) electrolyte and another in an electrolyte containing LiNO₃ [1,9]. Both approaches may be suitable for modifying the lithium surface to prevent side reactions during cycling. However, a chemical structure of the SEI that is suitable for DMSO solvents has not yet been explored. In our previous study, we found that inorganic compounds on the SEI surface, such as Li₂CO₃ and LiF, play an important role in preventing side reactions, thereby enhancing the cycling performance of the lithium metal anode [10–12].

Inspired by this finding, we examined the effects of SEI compounds on a lithium surface on the coulombic efficiency of a lithium anode in 1 M LiTFSI/DMSO electrolyte by following the procedure proposed by Koch et al. [13]. The dependence of the coulombic efficiency on the amount of H₂O in the electrolyte, a potential impurity in the Li–O₂ cell, was also examined by using lithium anodes having SEIs of different chemical structures.

2. Experimental procedure

A three-electrode beaker cell was used to perform electrochemical characterization. We prepared a nickel disc (5 mm diameter, 99.99% purity) for use as the working electrode, and we used lithium foil for the reference and counter electrodes. The coulombic efficiency of the lithium metal anode was estimated by using charge–discharge cycling according to Koch's method [13]. To prepare the lithium metal anodes, 5.1C cm^{−2} of lithium was initially electrodeposited onto a nickel substrate at 2.0 mA cm^{−2} in the electrolyte solutions 1 M LiClO₄/ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 EC/DEC volume ratio, lithium battery grade; Tomiyama Pure Chemical Industries), 1 M LiPF₆/EC-DEC (50:50 EC/DEC volume ratio, lithium battery grade; Kishida Chemical), and 1 M LiNO₃/DMSO (<50 ppm H₂O content) that was prepared by mixing as-received LiNO₃ salt (Sigma–Aldrich) and dehydrated DMSO solvent (Kanto Chemical). An electrolyte solution of 1 M LiClO₄/EC-DEC purged with carbon dioxide gas (<50 ppm H₂O content, 99.99% purity) for 3 h was also used to prepare the Li anode. The obtained Li anodes were then transferred to an electrolyte solution of 1 M LiTFSI/DMSO (Tomiyama Chemical), which had a H₂O content of <30 ppm. 1.0C cm^{−2} of lithium was discharged (dissolved) and charged (deposited) at 2.0 mA cm^{−2} in each subsequent cycle. Before it was transferred to the 1 M LiTFSI/DMSO solution, the working electrode was rinsed with 1 M LiTFSI/DMSO to remove residual solvent. A cycling test in 1 M LiClO₄/EC-DEC solution was also conducted for comparison. The endpoint of the cycling life was detected at a potential of 1 V vs. Li/Li⁺. All charge–discharge tests were conducted in an Ar-filled glove box with dew point below −90 °C (<0.1 ppm H₂O).

The chemical state of elements on the Li surface was analyzed by Fourier transform infrared (FTIR) spectroscopy (Shimadzu, IR Prestige-21) and by X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, VersaProbe-II). FTIR spectra were carried out in the attenuated total reflection mode using a Ge prism at a resolution of 8 cm^{−1} and an accumulation of 200 scans. Settings for XPS analysis were the same as those described in our previous paper [10]. Prior to these measurements, all samples were washed with pure dimethyl carbonate, dried under vacuum, and then transferred to the machines without exposing them to the ambient atmosphere.

3. Results and discussion

Fig. 1 shows the XPS spectra of the lithium initially deposited at 5.1C cm^{−2} in the 1 M LiClO₄/EC-DEC electrolyte with and without CO₂ bubbling. To understand the details of the chemical structure of the SEI surface and interior, XPS analysis with and without Ar⁺ etching were conducted. SEI compounds formed on the surface

layer without CO₂ bubbling were markedly different from those formed with bubbling. That is, the main products of the side reactions with the electrode in the former case were lithium alkyl carbonates (ROCO₂Li) and polycarbonate, the peaks of which appeared at 533.0 and 534.5 eV, respectively [14]; those of the side reactions with the electrode in the latter case were Li₂CO₃ and Li₂O, the peaks of which appeared at 531.5 and 529 eV, respectively [15]. Peak resolution of the O1s spectra with respect to ROCO₂Li and polycarbonate (533.8 eV), Li₂CO₃ (531.5 eV), and Li₂O (529.0 eV), indicates that the former SEI was composed of ROCO₂Li and polycarbonate (80.2%), Li₂CO₃ (15.4%), and Li₂O (4.4%); whereas the latter SEI was composed of Li₂CO₃ (61.6%), Li₂O (27.1%), ROCO₂Li and polycarbonate (11.3%). The Li1s spectra also show a difference in chemical structures of the SEIs, similar to that shown by the O1s spectra. Li₂CO₃ may form *via* the reaction between ROCO₂Li and CO₂ or H₂O [10,12], and Li₂O may form *via* the reaction between H₂O and Li⁺ [16]. Chemical structures of the interior of SEIs deposited in electrolytes with and without CO₂ showed similar properties; both contained Li₂CO₃ as main constituent, as well as small amounts of ROCO₂Li and polycarbonate.

To support XPS data mentioned above, FTIR analysis of the lithium initially deposited at 5.1C cm^{−2} in the 1 M LiClO₄/EC-DEC electrolyte with and without CO₂ bubbling was conducted. As shown in Fig. S1, absorption peaks for both electrodeposited Li surfaces at 1647, 1317, 1100, and 820 cm^{−1}, which are attributed to ROCO₂Li [14,17], and those at 1520–1430 and 875 cm^{−1}, which are attributed to Li₂CO₃ [17,18], are observed. These spectra have similar features except for the intensities of the Li₂CO₃ peaks; those for lithium electrodeposited in electrolyte with CO₂ bubbling are slightly higher than those for lithium electrodeposited without bubbling. FTIR spectroscopy also confirmed that these SEI films were composed of ROCO₂Li and Li₂CO₃, and the SEI formed with CO₂ has higher amount of Li₂CO₃ than that without CO₂.

The charge–discharge test was performed in 1 M LiTFSI/DMSO electrolyte by using lithium anodes whose SEI surface structure was varied to estimate the coulombic efficiency of the lithium metal anode. A cycling test was also conducted in 1 M LiClO₄/EC-DEC electrolyte for comparison. Fig. 2 shows the coulombic efficiencies of lithium anodes with two different SEI surfaces, *i.e.*, an organic-compound-rich surface and inorganic-compound-rich surface, in electrolyte solutions of 1 M LiClO₄/EC-DEC or 1 M LiTFSI/DMSO. The typical potential profile during cycling in 1 M LiClO₄/EC-DEC and 1 M LiTFSI/DMSO are shown in Fig. S2. Both lithium anodes had a coulombic efficiency of >90% in 1 M LiClO₄/EC-DEC solution, and the efficiency increased slightly when lithium anode with an inorganic-compound-rich surface was used. This phenomenon is in agreement with our previous study [10]. The coulombic efficiency of both anodes in 1 M LiTFSI/DMSO solution was found to be lower than that in 1 M LiClO₄/EC-DEC electrolyte. This means that side reactions on the lithium surface in 1 M LiTFSI/DMSO occur more readily than they do in 1 M LiClO₄/EC-DEC. In general, when the SEI layer breaks down after charge–discharge cycling, a fresh lithium surface becomes exposed and reacts with the electrolyte. This reaction induces repair of the SEI layer on the lithium surface, and the repaired layer contributes to the prevention of side reactions in subsequent cycles. However, formation of a stable SEI on a lithium surface in a DMSO-based electrolyte is difficult [8]. Therefore, side reactions during cycling in 1 M LiTFSI/DMSO electrolyte tend to occur where the SEI layer has broken down, leading to lower coulombic efficiency of the lithium metal anode.

A significant improvement in the cycling performance in 1 M LiTFSI/DMSO was observed when lithium anode with inorganic-compound-rich surface was used in place of that with an organic-compound-rich surface. The coulombic efficiency obtained with the former anode was 86.3%, which is 12.5% higher than that of the

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