



# Enhanced cycling performance of a Li metal anode in a dimethylsulfoxide-based electrolyte using highly concentrated lithium salt for a lithium–oxygen battery



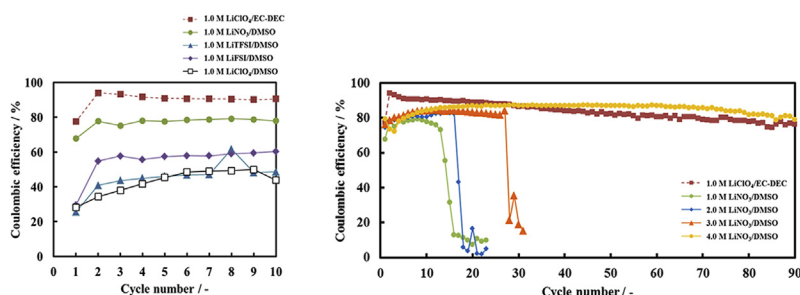
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## HIGHLIGHTS

- Lithium salts affect SEI compounds and the cycling of a Li anode in DMSO solvents.
- Li salts that produce soluble by-products on SEIs should not be selected.
- Free DMSO molecules should be limited to achieve stable cycling for the Li anode.
- One DMSO-based solvent yielded long cycling comparable to carbonate-based solvents.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Stable charge–discharge cycling behavior for a lithium metal anode in a dimethylsulfoxide (DMSO)–based electrolyte is strongly desired of lithium–oxygen batteries, because the Li anode is rapidly exhausted as a result of side reactions during cycling in the DMSO solution. Herein, we report a novel electrolyte design for enhancing the cycling performance of Li anodes by using a highly concentrated DMSO-based electrolyte with a specific Li salt. Lithium nitrate ( $\text{LiNO}_3$ ), which forms an inorganic compound ( $\text{Li}_2\text{O}$ ) instead of a soluble product ( $\text{Li}_2\text{S}$ ) on a lithium surface, exhibits a >20% higher coulombic efficiency than lithium bis(trifluoromethanesulfonyl)imide, lithium bis(fluorosulfonyl)imide, and lithium perchlorate, regardless of the loading current density. Moreover, the stable cycling of Li anodes in DMSO-based electrolytes depends critically on the salt concentration. The highly concentrated electrolyte 4.0 M  $\text{LiNO}_3/\text{DMSO}$  displays enhanced and stable cycling performance comparable to that of carbonate-based electrolytes, which had not previously been achieved. We suppose this enhancement is due to the absence of free DMSO solvent in the electrolyte and the promotion of the desolvation of Li ions on the solid electrolyte interphase surface, both being consequences of the unique structure of the electrolyte.

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## 1. Introduction

Dimethylsulfoxide (DMSO) is an attractive solvent for use in

lithium–oxygen ( $\text{Li}-\text{O}_2$ ) batteries because carbon cathodes stay stable in it and because of its superior Li ion conductivity,  $\text{O}_2$  diffusion coefficient, discharge voltage, and specific capacity [1–3]. In recent literature, much attention has been paid to cathode materials for stable charge–discharge cycling, and some studies of  $\text{Li}-\text{O}_2$  batteries have reported more than one hundred cycles using DMSO-based electrolytes [4–6]. For anode materials, thick lithium

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foils are commonly used in the cell, of which a part is charged and discharged sequentially during cycling. This permits calculations of the cycling performance of a Li–O<sub>2</sub> cell to ignore the effects of anode behavior: the coulombic amount used during cycling is quite small compared to the electrochemical equivalent of a lithium anode.

However, the coulombic efficiency of lithium metal anodes in DMSO-based electrolytes is known to be much lower than that in typical carbonate-based electrolytes: <35% in the former compared with >80% in the latter [7–9]. This means that the lithium metal is exhausted during cycling in DMSO-based electrolytes, even in Li–O<sub>2</sub> cells, which exhibit superior cycling performance as a result of their cathode materials. Thus, the low coulombic efficiency of lithium anodes will definitely become a serious problem facing the use of Li–O<sub>2</sub> batteries in large-scale energy storage applications, where the amount of charge during cycling is close to the electrochemical equivalent of the lithium anode in the cell.

One reason for this poor coulombic efficiency of lithium anodes in DMSO-based electrolytes is thought to be the unstable solid electrolyte interphase (SEI) that forms on the lithium surface as a result of side reactions with the electrolyte. Indeed, as one study found, when stable SEI compounds such as Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O, and LiF are formed on the lithium surface prior to cycling, a lithium metal anode in 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/DMSO exhibited an enhanced coulombic efficiency (≈85%) [10].

Another reason for the poor coulombic efficiency is thought to be the direct reduction of the Li ion–DMSO complex that penetrates the SEI layer on the lithium surface. Ideally, desolvation of Li ions should occur at the interface between the electrolyte and SEI layer to prevent side reactions related to solvents. However, Li ions coordinated with DMSO molecules are thermodynamically stable, since DMSO strongly interacts with Li ions because of the molecule's high Gutmann donor number [11]. Yamada et al. reported that a lithium ion coordinated by four DMSO molecules is stable enough to penetrate SEI layers on the surface of a graphite anode without desolvation, and to intercalate into the graphite layer [12]. Therefore, it is possible that a similar phenomenon may occur for lithium metal anodes.

Highly concentrated electrolytes have been proposed for the design of electrolytes that promote stable anode cycling [13,14]. Cells that incorporate this kind of electrolyte show unique features, such as enhanced electrolyte stability when in contact with lithium metal and decreased dendritic morphology of the deposited lithium. These features are related to the amount of free DMSO solvent and to the coordinated structure of Li ions in the electrolyte. We believe that these properties are crucially important for the design of a DMSO-based electrolyte in which side reactions related to the reduction of the DMSO solvent readily occur.

With this viewpoint in mind, we examine the effects of lithium salt concentration in DMSO-based electrolytes on the charge–discharge cycling performance of a lithium metal anode. The types of lithium salts that have been reported to affect the composition of SEIs [15–17] are also evaluated in this study. We discuss the results with respect to the surface morphology of the deposited lithium, the chemical structure of the SEI, and the structure of the solvent in the electrolyte.

## 2. Experimental procedure

A CR2032 coin-type cell was used to evaluate the cycling performance of lithium metal anodes. We prepared a nickel foil (12 mm in diameter, 99% purity) for use as a working electrode, and an as-received lithium foil for use as a counter electrode. The coin cells were assembled in an Ar-filled glove box with a dew point below –110 °C (<1.6 ppb of H<sub>2</sub>O).

Dehydrated DMSO (<10 ppm H<sub>2</sub>O content, >99.0% purity) (Wako Pure Chemical Industries) was used as the solvent for the electrolytes without further purification. For the preparation of electrolytes, the lithium salts of LiTFSI (>99.0% purity, Kishida Chemical), lithium bis(fluorosulfonyl)imide (LiFSI) (>99.5% purity, Kanto Chemical), and lithium nitrate (LiNO<sub>3</sub>) (>99.9% purity, Wako Pure Chemical Industries) were dried in vacuum overnight at 120 °C. The lithium salts of LiTFSI, LiFSI, and LiNO<sub>3</sub> were then each dissolved into DMSO solvents. The lithium salt of lithium perchlorate (LiClO<sub>4</sub>) (>99.0% purity, Tomiyama Pure Chemical Industries) was used as-received, and dissolved into DMSO solvent. An electrolyte of 1.0 M LiClO<sub>4</sub>/ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 EC/DEC volume ratio, lithium battery grade; Tomiyama Pure Chemical Industries) was also used for comparison. All of the electrolytes used in this study, except 1.0 M LiClO<sub>4</sub>/DMSO (<60 ppm H<sub>2</sub>O content), were confirmed to be less than 30 ppm of the H<sub>2</sub>O content via Karl Fischer titration (AQ-7, Kyoto Electronics Manufacturing).

For the cycling test, 0.5 mAh cm<sup>–2</sup> of lithium was initially electrodeposited (charged) on the working electrode at 0.2 mA cm<sup>–2</sup> or at 1.0 mA cm<sup>–2</sup>, and the same charge amount of lithium was stripped (discharged) from the working electrode until the voltage reached 1.0 V against the counter electrode's potential. This charge–discharge cycling was performed sequentially in each subsequent cycle. We estimated the coulombic efficiency as:

$$\text{Coulombic efficiency (\%)} = \frac{Q_{\text{stripped}}}{Q_{\text{deposited}}} \times 100, \quad (1)$$

where  $Q_{\text{deposited}}$  and  $Q_{\text{stripped}}$  are the amounts of charge during charging and discharging, respectively.

The elementary chemical state on the Li surface was revealed using X-ray photoelectron spectroscopy (XPS) (VersaProbe II, ULVAC-PHI). Monochromatic Al–K radiation (1486.6 eV), operated at a power of 25 W (15 kV), was utilized as the X-ray source. The samples were washed with pure dimethyl carbonate, dried under a vacuum, and then transferred to chambers using a transfer vessel under an Ar atmosphere. We observed the surface morphology of the electrodeposited lithium using a field-emission scanning electron microscope (FE-SEM) (S-4500 S, Hitachi).

The coordination structure of the Li ion–DMSO complex in each solution was measured using confocal Raman microscopy (inVia Reflex, Renishaw) with a 532 nm line (50 mW) from a helium-cadmium laser for excitation. We recorded the Raman spectra with a resolution of 2 cm<sup>–1</sup>. Test solutions were prepared by putting each electrolyte into individual quartz cells, and then sealing each cell with silicone rubber in a dry room with a dew point below –60 °C (<10 ppm H<sub>2</sub>O) so it would not be exposed to ambient air.

We measured the ionic conductivity using a four-point-probe conductivity meter with a frequency of 1 kHz (1116E, Fuso Electro Chemical System).

## 3. Results and discussion

Fig. 1 shows the coulombic efficiencies of the lithium metal anodes in the DMSO-based electrolytes using lithium salts of 1.0 M LiClO<sub>4</sub>, 1.0 M LiTFSI, 1.0 M LiFSI, and 1.0 M LiNO<sub>3</sub>. The current density was set to be 0.2 mA cm<sup>–2</sup> (Fig. 1(a)) and 1.0 mA cm<sup>–2</sup> (Fig. 1(b)). The results for the carbonate-based electrolyte of 1.0 M LiClO<sub>4</sub>/EC–DEC are also presented for comparison. Carbonate-based electrolytes have been widely researched in Li–metal batteries, and the coulombic efficiency of lithium metal anodes in these electrolytes is known to be much higher than that in DMSO-based electrolytes due to formation of more stable SEI on the

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