



Chemical aspect of oxygen dissolved in a dimethyl sulfoxide-based electrolyte on lithium metal



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ARTICLE INFO

Article history:

Received 3 October 2013

Received in revised form 6 January 2014

Accepted 6 January 2014

Available online 21 January 2014

Keywords:

Dimethyl sulfoxide

Lithium metal

Oxygen

Solid-electrolyte interphase

X-ray photoelectron spectroscopy

ABSTRACT

The chemical stability of Li metal in a rechargeable Li–O₂ cell was examined by investigating the physicochemical changes that occurred during storage of Li in an electrolyte comprising dimethyl sulfoxide (DMSO) with dissolved O₂. During prolonged storage of Li in the oxygenated electrolyte, the Li surface became moss-like and its interfacial resistance increased. Analyses of reaction products using XPS and FT-IR revealed that the bis(trifluoromethyl sulfonyl) imide (TFSI) anions and DMSO solvent could have decomposed significantly through a further reaction path induced by O₂. Furthermore, the formation of an unstable solid-electrolyte interphase by O₂ causes degradation of the Li metal and deterioration of the electrolyte. This investigation shows that the Li anode should be protected from O₂ by modification of Li and the separator to ensure long-term stability of the Li–O₂ cell.

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1. Introduction

Rechargeable non-aqueous lithium–oxygen (Li–O₂) batteries that use Li metal as an anode have received increasing attention in recent years owing to their extremely high energy density. A non-aqueous Li–O₂ battery, which is based on the net reaction of $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ ($E^0 = 2.96\text{ V}$), has a theoretical specific energy as high as 3505 Wh kg^{-1} , which far exceeds that of conventional Li-ion batteries (LIBs) [1–4]. The use of Li metal, one of the major components in a Li–O₂ cell, is a prerequisite for achieving this energy density because Li has a high specific capacity (3860 mAh g^{-1}) and the lowest known redox potential (-3.05 V versus standard hydrogen electrode) [5,6]. When highly reactive Li comes into contact with a non-aqueous electrolyte, however, reduction of the electrolyte occurs, resulting in the immediate formation of a solid-electrolyte interphase (SEI) on its surface. Furthermore, dendritic Li growth during cycling can cause an internal short circuit in the

battery [6]. For these reasons, the use of Li metal as an anode has been questioned because of the limited cycle life and safety of rechargeable Li-metal battery systems [7].

These problems are likely to be exacerbated in Li–O₂ battery systems. Unlike LIBs, which are perfectly sealed from surrounding air, these systems are open to an O₂ atmosphere as oxygen is required to participate in the electrochemical reactions at the air cathode. Inevitably, O₂ contamination through the electrolyte can initiate deterioration of Li metal at the anode during prolonged storage as well as electrochemical cycling; this is considered the primary problem for long-term cell performance [1,8]. A better understanding of the chemical stability of Li metal in the presence of O₂ is thus essential for the practical development of improved Li–O₂ batteries.

Recently, Younesi et al. used X-ray photoelectron spectroscopy (XPS) to reveal that an inferior SEI can be formed on the Li metal in a Li–O₂ cell that employs propylene carbonate (PC) as the electrolyte solvent [8]. However, PC has not been widely used as an electrolyte solvent of Li–O₂ batteries because of its susceptibility to nucleophilic attack by the superoxide anion radicals at the air cathode [9,10]. Along with these problems, non-carbonate solvents such as ethers [11,12], sulfoxides [13–15], and amides [16,17], have been intensively investigated; however, their compatibility with Li anodes in an O₂-rich environment has not been established.

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Herein, we focus on the chemical effect of O_2 dissolved in a dimethyl sulfoxide (DMSO)-based electrolyte on Li metal. Since DMSO is known to deliver good electrochemical performance and produce the ideal discharge product, Li_2O_2 [13–15], it was chosen as the electrolyte solvent in this work. The morphological and compositional changes of Li metal immersed in an O_2 -saturated electrolyte were systematically studied by field-emission scanning electron microscopy (FE-SEM) as well as XPS and Fourier-transform infrared spectroscopy (FT-IR). Additionally, the effect of oxygen in the electrolyte on Li's electrochemical properties was also evaluated.

2. Experimental

2.1. Sample preparation

Li metal foil (Honzo Metal, Japan) was cut into a circular shape with a diameter of 16.5 mm. Pure O_2 (99.999%) was added by a syringe tube to 20 mL of 1.15 M lithium bis(trifluoromethyl sulfonyl) (LiTFSI) in DMSO (Panax Etec, Korea) and left to dissolve for 3 h with stirring. The solution was purged continuously with O_2 during the test period at an O_2 flow rate of 200 mL min^{-1} . 3 mL of an electrolyte and a piece of Li metal were placed into an air-tight glass vial and stored in a glove box for 30 days. One vial was used for each of the electrolytes. To minimize the effect of residual water, all equipment such as vials and syringe tubes were dried at 150°C for 24 h in a vacuum chamber before use. The trace water content was confirmed by the Karl–Fisher titration method to be 46 ppm for O_2 -saturated DMSO, which is quite low compared to commonly used organic solvents.

2.2. Characterization

Following established procedures [18,19], the samples were rinsed with dimethyl carbonate (DMC) and dried in a vacuum chamber overnight. All samples were prepared in an Ar-filled glove box and sealed in polyethylene pouches to prevent exposure to ambient air. For the XPS measurements, we used a portable glove box with continuous purging of Ar (about 10 min) connected to the XPS sample chamber. A pouch was removed in the portable glove box and transferred into the XPS sample chamber. To assess the morphologies of the prepared samples, FE-SEM (Sirion, FEI) images were obtained. The chemical composition of the surface film on Li metal was analyzed by FT-IR spectroscopy (IFS66 v/S & Hyperion 3000, Bruker) and XPS (Thermo VG scientific) with $Mg K_{\alpha}$ as an X-ray source. For the XPS analysis, all spectra were calibrated against the hydrocarbon peak at a binding energy of 285.0 eV [8,20]. All high-resolution spectra were deconvoluted by a standard Shirley background function and Lorentzian–Gaussian curves using XPS-PEAK and Avantage programs.

2.3. Electrochemical test

For the electrochemical impedance spectroscopy (EIS) measurements, coin-type Li–Li symmetric cells were fabricated and Nyquist plots of the cells were obtained using a Solartron 1255 frequency response analyzer (FRA) together with a Solartron 1287 electrochemical interface over a frequency range of 1 MHz to 0.1 Hz. For the Li– O_2 battery test, the air cathodes were prepared by casting a slurry consisting of 24 wt.% Ketjen black (EC-600JD, Mitsubishi Chemical), 42 wt.% α -manganese oxide (α - MnO_2) nanowires, 34 wt.% polytetrafluoroethylene (PTFE, Aldrich, USA) binder, and ethanol as a solvent onto a piece of carbon paper (TGPH-030, NARA Cell-Tech, Korea). After the slurry was dispersed, the air cathodes were dried at 130°C for 24 h. For the electrochemical characterization, the coin cells were assembled in a glove box. Each coin-type cell was composed of a Li metal anode, a glass-fiber membrane (Chmlab, Germany) impregnated with an electrolyte such as 1.15 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) or 1.15 M LiTFSI in DMSO (Panax Etec, South Korea), and the air cathode. Galvanostatic charge and discharge tests were conducted in a time-controlled mode at a current density of $100 \text{ mA g}_{\text{carbon}}^{-1}$ for 10 h ($1000 \text{ mAh g}_{\text{carbon}}^{-1}$) using a WBCS 3000 battery cyler (WonAtech, Korea). For these tests, the cell was placed in an O_2 -filled chamber (the pressure was slightly higher than 1 atm of pure O_2 (99.999%)) at room temperature.

3. Results and discussion

Before we discuss our results in detail, it should be noted that we clearly observed a black passivation layer on the Li electrode after disassembling the cycled Li– O_2 cell with the DMSO electrolyte (Fig. S1 in Supplementary data), which is identical to recently reported results [8,21,22]. In particular, while the side of the Li metal looked glossy, the center of the Li metal that was directly facing the air cathode was covered with an identical black layer. Thus, we truly believe that gaseous oxygen had diffused into the Li anode through the DMSO electrolyte and potentially contributed to the formation of a passivation layer on the Li metal. This type of deteriorated Li metal with an inferior SEI layer can steadily deplete the electrolyte and hinder the long-term operation of the Li– O_2 cell. To evaluate the long-term reliability of Li– O_2 cells, we examined the chemical contribution of oxygen to Li metal degradation.

First, we assume that the surface of the Li metal in a Li– O_2 cell is similar to that of Li metal immersed in an electrolyte– O_2 solution. A simple storage test in various solutions can provide some insight into the chemical stability of Li metal. After prolonged storage, chemical deterioration of Li metal in the oxygenated electrolyte could be seen even by the naked eye, as shown in Fig. 1. While the Li metal maintained its original metallic color in the pure electrolyte with residual water content of 46 ppm even after 30 days of

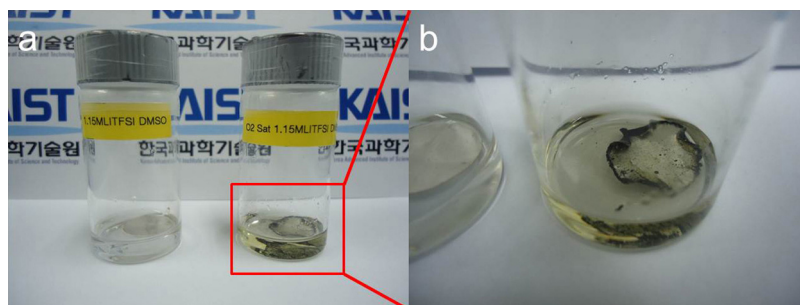


Fig. 1. Digital image of lithium metals immersed in (left of (a)) 1.15 M LiTFSI–DMSO and (right of (a) and (b)) 1.15 M LiTFSI–DMSO– O_2 solutions for 30 days.

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