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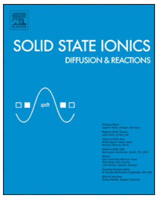

The effects of lithium salt and solvent on lithium metal anode performance

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ABSTRACT

In this study, the effects of lithium salts (i.e. $LiPF_6$, $LiClO_4$ and $LiN(SO_2CF_3)_2$) and solvents (i.e. carbonate and ether type) on the Li metal anode electrochemical performance are systematically studied. It is found that $LiN(SO_2CF_3)_2$, denoted as LiTFSI, in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) as electrolyte offers the best performance with a cycle life of 1100 h under the capacity of 2 mAh/cm^2 and current density of 2 mA/cm^2. Lithium stripping/plating produces porous loose lithium powders rather than dendrites. Both lithium salts and solvents have influences on the lithium powder nucleation and growth. In the LiTFSI-DOL/DME system, lithium metal after stripping/plating has a relative flat and dense surface, which concomitantly brings in a low charge transfer resistance, low solid electrolyte interphase resistance, and elongated cycle life. A high Li^+ transference number and a high Li^+-solvent interaction force are beneficial to an even Li^+ flux and a stable Li-electrolyte interface. This study sheds light on the importance of electrolytes for high performance lithium metal anodes.

1. Introduction

Lithium metal-based batteries, e.g. Li-sulfur, Li-oxygen, Li-layer cathodes $Li[Li_xMn_yNi_zCo_{1-x-y-z}]O_2$, offering energy densities of > 500 Wh/kg are good candidates for applications in the electrical vehicles [1–3]. There are three main challenges for the lithium metal anodes. One is that Li metal is highly chemical active, which can easily have spontaneous reactions with the ambient air and conventional non-aqueous liquid electrolytes to form a solid electrolyte interphase (SEI). Since the formed SEI layer is normally heterogeneous and anisotropic, it can lead an inhomogeneous lithium nucleation and growth. Meanwhile, the exposed newly formed lithium can consume electrolytes resulting in a low Coulombic efficiency and a short cycling life. Formation of a stable SEI layer via physical coating and in-situ chemical reaction as well as choosing stable electrolytes such as solid-state electrolytes are common ways to diminish the parasitic reactions [4–7]. One is that it has a huge volume expansion as lithium is a host-free metal (1 mAh/cm^2 metal corresponding to a thickness of 4.8 μm). Such an expansion can bring in a high contact resistance especially in the solid-state battery system. Meanwhile, the aforementioned artificial surface coating layer can normally be exfoliated after several cycles. Introducing 3D current collectors such as carbon sponges, Cu nano-rods, Ni foams have been demonstrated effective routes [8–10]. Another is that the Li^+ flux, highly affected by the lithium metal surface state and the lithium ion diffusion rate [11], is usually uneven, which leads to a preference of island-by-island growth instead of film-by-film growth. Increasing the lithium ion concentration, selecting proper electrolyte additives, and decreasing the applied current density have been proved effective strategies in enhancing lithium metal anode life [6].

Electrolytes consisting of various lithium salts and solvents have important influences on the lithium metal nucleation and growth in the lithium plating process. According to the sand's equation $t_{\mathrm{sand}} = \pi D_{app}\frac{(Z_c C_0 \mathrm{F})^2}{4(Jt_a)^2}$, mossy morphology rather than dendrites tend to form a high apparent lithium ion diffusion rate (D_{app}), high Li^+ concentration (C_0), low operation current density (J), and high anion transference number (t_a) [12, 13]. Suo and coauthors demonstrated a superior Li metal anode cyclic performance in 7 M LiTFSI-DOL/DME electrolyte [14]. Lu et al. fabricated a Li-containing polymer electrolyte membrane with high $t_{Li+} \approx 0.84$ that exhibited a uniform lithium electro-deposition [15]. Qian et al. reported a Li-Li cell can cycle > 6000 cycles under a current density 10 mA/cm^2 in 4 M LiTFSI and 1,2-dimethoxyethane as electrolyte, ascribed to a high Li^+ concentration and a high solvent-Li^+ solvation ability [16].

In this work, we are trying to make a fundamental study on the effect of electrolytes in terms of lithium salts and solvents on the performance of lithium metal anodes. The $LiPF_6$, $LiClO_4$, and LiTFSI are the most commonly used lithium salts. The carbonate EC/DMC and ether

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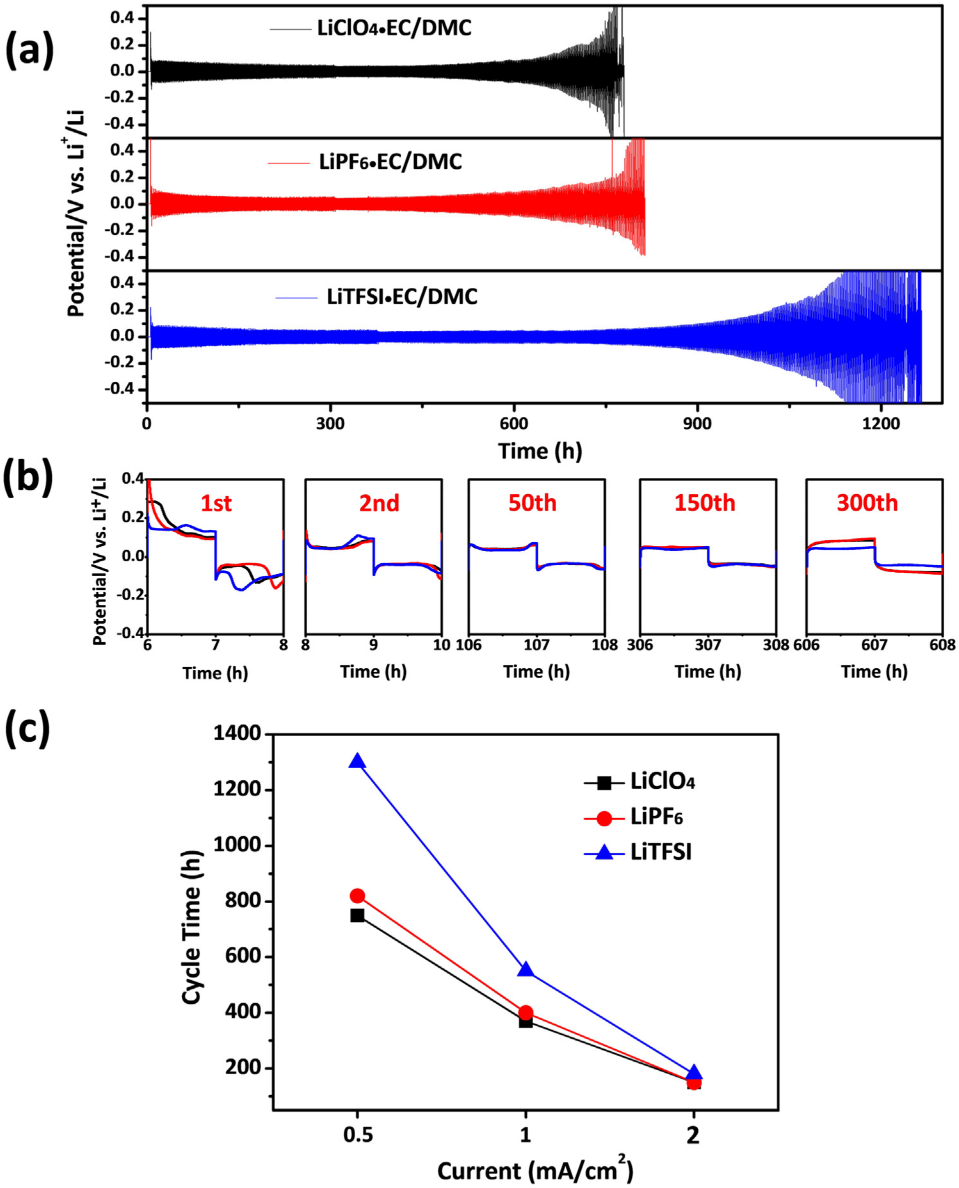

Fig. 1. (a) Cycling performance of Li-Li symmetric cell in different lithium salts with carbonate-based solvents with a capacity of 0.5 mAh/cm^2 at a current density of 0.5 mA/cm^2. (b) Enlarged galvanostatic charge-discharge curves at different cycles based on a. The cells are rested for 6 h at the very beginning for a better permeation between the electrolytes and the metal. (c) Rate performance of the Li-Li cell with different current rates with the 1 hour-charging and 1 hour-discharging per cycle.

DOL/DME are also the most popular solvents. Their concentrations are set to be 1 M. The cycling performance under different current densities, resistance evolution including charge transfer resistance (R_{ct}) and surface film resistance (R_f), as well as the lithium metal morphology variation during plating and stripping are systematically studied. It is found that the LiTFSI has the best compatibility with DOL/DME electrolyte, in which the Li-Li cell presents the best cycling life and rate performance, smallest R_{ct} and stable R_f, and a smallest lithium metal morphology change after cycling. Interestingly, the dense lithium metal foil with thickness of 160 μm becomes a porous lithium powders on surface with a thickness about 300 μm after only 50 stripping/electroplating cycles. A higher Li^+ transference number and a higher Li^+-solvent interaction are suspected to guarantee a more even Li^+ flux and a stable Li-electrolyte interface.

2. Experimental and characterizations

Three different lithium salts, $LiPF_6$ (> 97%, Shanghai Aladdin), $LiClO_4$ (> 98%, Shanghai Aladdin), and LiTFSI (> 99%, Shanghai Aladdin), were separately dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC, volume ratio of 1:1, purchased from Guotai Huarong Co. Ltd.) to produce 1 mol/L carbonate electrolyte. The ether-based electrolyte 1 M LiTFSI-DOL/DME (Guotai Huarong Co. Ltd.) was used as received. The lithium metal foil has a thickness of 160 μm. Symmetric Li-Li 2032-type coin cells were assembled in an argon-filled glove box. The electrolytes were fixed to be 40 μL per cell.

Galvanostatic charge-discharge measurements were performed on instrument CT2001A (LANHE Co., China). An electrochemical workstation model CHI660B (Chen-Hua Instruments Inc.) was used to carry out electrochemical impedance spectroscopy (EIS) measurements. A 5 mV bias was applied on the cells with the frequency ranging from 10^{-2} to 10^5 Hz. Scanning electron microscopy (SEM, FEI NanoSEM