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Effects of compatibility of polymer binders with solvate ionic liquid electrolytes on discharge and charge reactions of lithium-sulfur batteries

Toshitada Nakazawa, Ai Ikoma, Ryosuke Kido, Kazuhide Ueno [1], Kaoru Dokko, Masayoshi Watanabe*

Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

HIGHLIGHTS

- A glyme-Li salt solvate ionic liquid is used as an electrolyte for Li-S batteries.
- Polyvinyl alcohol (PVA) is used as a binder in the sulfur composite cathode.
- Electrolyte uptake of PVA changes depending on the degree of PVA saponification.
- Discharge capacity of Li-S cell is increased by the partial swelling of the binder.

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ABSTRACT

Electrochemical reactions in Li-S cells with a solvate ionic liquid (SIL) electrolyte composed of tetraglyme (G4) and Li[TFSA] (TFSA: bis(trifluoromethanesulfonyl)amide) are studied. The sulfur cathode (S cathode) comprises sulfur, carbon powder, and a polymer binder. Poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA-*x*) with different degrees of saponification (*x*%) are used as binders to prepare the composite cathodes. For the Li-S cell containing PEO binder, lithium polysulfides (Li_2S_m, $2 \le m \le 8$), reaction intermediates of the S cathode, dissolve into the electrolyte, and Li_2S_m acts as a redox shuttle in the Li-S cell. In contrast, in the Li-S cell with PVA-*x* binder, the dissolution of Li_2S_m is suppressed, leading to high columbic efficiencies during charge-discharge cycles. The compatibility of the PVA-*x* binder with the SIL electrolyte changes depending on the degree of saponification. Decreasing the degree of saponification leads to increased electrolyte uptake by the PVA-*x* binder, increasing the charge and discharge capacities of Li-S cell. The rate capability of Li-S cell is also enhanced by the partial swelling of the PVA-*x* binder. The enhanced performance of Li-S cell containing PVA-*x* is attributed to the lowering of resistance of Li^+ ion transport in the composite cathode.

1. Introduction

Li-S batteries are attracting much attention as next generation energy storage devices [1,2]. The theoretical energy density of a Li-S battery is very high owing to the high theoretical capacities of a Li anode (3860 mAh g^{-1}) and an S cathode (1672 mAh g^{-1}). There have been numerous reports on Li anodes, nanostructured S cathodes, and electrolytes, and these have been summarized in recent review articles, for examples, see Ref. [3–12]. One issue that prevents the practical use of Li-S batteries is the dissolution of the S cathode into the liquid electrolytes during discharge and charge reactions [13,14]. The elemental sulfur (S_8) is electrochemically reduced to Li_2S at the cathode during discharge. Furthermore, lithium polysulfides (Li_2S_m, $2 \le m \le 8$) are formed as intermediates of the cathode reactions, and Li_2S_m, in particular, long Li_2S_m with $4 \le m \le 8$, dissolves into conventional liquid electrolytes [14]. The dissolution of the cathode active material causes significant problems such as rapid capacity fade and low coulombic efficiency for discharging and charging the Li-S battery. The dissolved Li_2S_m acts as a redox shuttle between the cathode and anode in the cell, and

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* Corresponding author.
E-mail address: mwatanab@ynu.ac.jp (M. Watanabe).

[1] Present address: Department of Applied Molecular Science, Graduate School of Medicine, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan.

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this shuttle effect causes the low coulombic efficiency during discharging and charging of the cell [14]. To solve this problem, additives for liquid electrolytes are used. These work by forming a passivation layer on the Li metal anode [15,16]. In addition, polymer electrolytes [17–20], inorganic solid electrolytes [21,22], and ionic liquid electrolytes [23–25] have also been proposed.

Recently, we reported that glyme-Li salt complexes can be used as thermally stable electrolytes for lithium batteries [26–32]. Glymes (G*n*, *n* in $CH_3–O–(CH_2–CH_2–O)_n–CH_3$) possess strong solvation power for Li^+ ions and form relatively long-lived (stable) solvates with Li^+ ions in certain molar ratios, $[Li(glyme)_x]^+$ [33–38]. Of particular interest, triglyme (G3) and tetraglyme (G4) form low melting complexes with Li[TFSA] (TFSA: bis(trifluoromethanesulfonyl)amide) in 1:1 M ratio. The molten complexes are representative solvate ionic liquids (SILs) composed of solvate $[Li(G3\ or\ G4)]^+$ cations and $[TFSA]^-$ anions [39–45]. As well as conventional ionic liquids, the SILs, [Li(G3)][TFSA] and [Li(G4)][TFSA], possess low volatility, non-flammability, ionic conductivity ($\sim 10^{-3}$ S cm^{-1}), and a wide electrochemical window. In addition, we reported that the solubility of Li_2S_m in [Li(G3 or G4)][TFSA] is very low, and the redox shuttle effect in a Li-S cell can be effectively suppressed using SIL electrolytes [30,31]. This led to the highly efficient discharge/charge and long charge-discharge cycle life (>400 cycle) of a Li-S cell [31].

In this study, we focus on the effects of the compatibility of polymer binders with SIL electrolytes on the electrochemical reactions of the S cathode. Typically, the S cathode is composed of S (active material), carbon powder (conductive agent), and a polymer binder, and the composite cathode has a porous structure [2–4]. Ion transport takes place in the pores during the electrochemical reaction of S. In the porous composite cathode, the binder interconnects the carbon particles to form the electron conduction network, and the surface of active material is partially covered with the binder. Therefore, the distribution of polymer binder in the cathode and the compatibility of the polymer with the electrolyte have a significant effect on the charge-discharge performance of Li-S cell. In this work, poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) with different degrees of saponification were used as binders to fabricate the composite cathode. The interactions between electrolyte and polymer binders and the electrochemical reactions of S cathode were analyzed. We found that the electrochemical reaction mechanism, discharge capacity, and rate capability of S cathode change depending on the compatibility of polymer binder with the electrolyte.

2. Experimental

2.1. Materials

Highly purified G4 was supplied by Nippon Nyukazai and used as received. A battery-grade Li[TFSA] was provided by Solvay Japan as courtesy sample. [Li(G4)][TFSA] electrolyte was prepared by mixing Li[TFSA] and G4 in 1:1 M ratio in an Ar-filled glove box. The ionic conductivity of [Li(G4)][TFSA] is 1.6 mS cm^{-1} at 30 °C [26].

PEO, PVA, and poly(vinyl acetate) (PVAc) were used in this study. Hereafter, PVA is denoted as PVA-*x* according to the degree of saponification (*x* mol %). The molecular weight (M_w) or degree of polymerization (d.p.) of polymers are as follows: PEO (Alfa Aesar, M_w = 1,000,000), PEO (Aldrich, M_w = 36,000), PVA-100 (Tokyo Chemical Industry, x = 97–100, d.p. = ca. 1750), PVA-90 (Wako Pure Chemical Industries, x = 86–90, d.p. = 3100–3900), PVA-80 (Tokyo Chemical Industry, x = 78–82, d.p. = ca. 2000), PVA-66 (JAPAN VAM & POVAL, x = 66, d.p. = 520), and PVAc (Alfa Aesar, M_w = 50,000).

Elemental sulfur (S_8) was purchased from Wako Pure Chemical Industries. Carbon powder (Ketjenblack, specific surface area of 1270 m^2 g^{-1}) was kindly supplied from Lion Corporation and used as received. Li metal was purchased from Honjo Metal Co. and used as received.

2.2. Measurements

The self-diffusion coefficients of G4, Li^+, and $[TFSA]^-$ in the electrolyte were determined by pulsed-field-gradient (PFG) NMR measurements. The measurements were performed on a JEOL-ECX400 NMR spectrometer with a 9.4 T narrow bore superconducting magnet equipped with a PFG probe and current amplifier. Detailed measurement conditions are reported elsewhere [46].

The S composite cathode was composed of S_8, carbon powder, and a polymer. S composite cathodes were prepared according to a previously reported method [24]. The mass ratio of S_8, carbon, and polymer in the S composite cathode was 60:30:10. The composite cathode was pasted on an Al foil current collector. The thickness of the composite cathode on Al foil was ca. 10 μm, and the mass loading of active material (S_8) was 0.5 mg cm^{-2}. The prepared composite sheet was cut into a circular shape (16 mm diameter). Coin cells (2032 type) were fabricated in an Ar-filled glovebox. The composite cathode sheet (16 mm diameter), porous glass separator (GA-55, Advantec), Li metal foil (16 mm diameter), and an electrolyte (160 μL) were encapsulated in a coin cell. Galvanostatic charge–discharge measurements for Li-S cells were conducted using an automatic charge/discharge instrument (HJ1001SD8, Hokuto Denko) at 30 °C. Li-S cell was prepared in a fully charged state, and the charge–discharge cycle is defined as follows: 1st discharge → 2nd charge → 2nd discharge → 3rd charge → 3rd discharge, and so on. The coulombic efficiency was defined as (*N*th discharge capacity)/(*N*th charge capacity). The specific capacity of the cell was calculated based on the mass of S_8, and the gravimetric current density of 1672 mA g^{-1} (1 C-rate) corresponds to a geometric current density of 0.8 mA cm^{-2}.

3. Results and discussion

Fig. 1 shows charge and discharge curves of the Li-S cells with PVA-100 and PEO (M_w = 1,000,000) binders. Both cells containing PVA-100 and PEO binders showed two plateaus at 2.3 and 2.0 V during discharge. In the voltage range of 2.4–2.0 V, S_8 is electrochemically converted into Li_2S_m (typically $m = 4$) through the formation of Li_2S_8 [4]. The flat voltage plateau at 2.0 V is ascribed to the reduction of Li_2S_4 into Li_2S. During charging, the cell containing PVA-100 binder had a single plateau at 2.3 V. This charging curves agrees well with our previous results using the [Li(G4)][TFSA] electrolyte [31]. In contrast, the cell containing PEO binder had two plateaus during charging, corresponding to the two plateaus in the discharge curves. The charge and discharge reaction mechanisms of the cells will be discussed later. The cell with PVA-100 binder exhibited an initial discharge capacity of 800 mAh g^{-1}, and the capacity slightly decreased to 700 mAh g^{-1} in the subsequent charge-discharge cycles, as shown in Fig. 1c. The initial discharge capacity of the cell with PEO binder was 1100 mA hg^{-1} and was much higher than that of the cell with PVA-100 binder, suggesting that the utilization of active material in the composite cathode was increased by using PEO binder. The capacity of cell with PEO decreased gradually as the number of charge-discharge cycles increased; in contrast, the cell with PVA-100 had stable charge and discharge capacities. Fig. 1d shows the coulombic efficiency of the cells. The coulombic efficiency of the cell containing PVA-100 was ca. 99% and was slightly higher than that of the cell containing PEO (ca. 97%). The discrepancy between the cells with PVA-100 and PEO