



A bifunctional electrolyte additive for separator wetting and dendrite suppression in lithium metal batteries

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ARTICLE INFO

Article history:

Received 5 December 2017

Received in revised form

7 March 2018

Accepted 14 March 2018

Available online 15 March 2018

Keywords:

Lithium dendrite suppression

Separator wettability

Bifunctional additive

Pluronic P123

Electrolyte

ABSTRACT

Reformulation of electrolyte systems and improvement of separator wettability are vital to electrochemical performances of rechargeable lithium (Li) metal batteries, especially for suppressing Li dendrites. In this work we report a bifunctional electrolyte additive that improves separator wettability and suppresses Li dendrite growth in Li metal batteries. A triblock polyether (Pluronic P123) is added as an additive into a commonly used carbonate-based electrolyte. It is found that addition of 0.2–1% (by weight) P123 into the electrolyte can effectively enhance the wettability of polyethylene separator. More importantly, the adsorption of P123 on Li metal surface can act as an artificial solid electrolyte interphase layer and suppress the growth of Li dendrites. A smooth and dendrite-free Li morphology can be achieved in the electrolyte with 0.2% P123. The Li||Li symmetric cells with the 0.2% P123-containing electrolyte exhibit a relatively long cycling stability at high current densities of 1.0 and 3.0 mA cm⁻².

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1. Introduction

In a practical battery, ionic conduction between the cathode and the anode is carried out by the diffusion of ions in the electrolyte through the separator. Good wettability of the separator by the electrolyte is vital to the electrochemical performance of the battery, and also facilitates the electrolyte filling during the battery assembly process. However, commonly used polyolefin separators including polyethylene (PE) and polypropylene (PP) have drawbacks of relatively poor wettability toward nonaqueous electrolytes [1,2]. Lots of efforts have been made to enhance the separator wettability by surface modification of the separators with various ceramic-coatings or fabrication of novel separators [3–8]. Besides the surface properties of the separator, the wettability of a separator toward electrolyte is also strongly influenced by the electrolyte used. As indicated in our recent publications, electrolyte components including solvents, lithium salts and their concentrations, and additives can greatly affect the wettability of separators by the electrolytes [9,10]. Nevertheless, seldom studies on enhancing separator wettability in terms of the electrolyte,

especially functional electrolyte additives for separator wetting, were reported.

Recently, lithium (Li) metal has also been considered to be one of the most attractive anode materials for the next-generation high-energy-density batteries, because both its high theoretical specific capacity and lowest redox potential are the significant requirements of the anode materials for high-energy-density batteries [11,12]. Especially, Li metal batteries (LMBs) have attracted extensive attention because of its high energy density and similarity as the state-of-the-art Li-ion batteries that have achieved huge commercial successes. However, the LMBs face the severe challenge on the safety issues related to Li dendrite growth during repeated stripping and deposition processes. As Ryou and co-workers reported [6], the polydopamine modification increased the wettability of the PE separator toward nonaqueous electrolytes and resulted in the uniform distribution of Li⁺ ion flux. As a result, the growth of Li dendrites on Li metal anode was suppressed effectively. That work proved that good separator wettability can definitely contribute to Li dendrite suppression. In addition, the growth of Li dendrites is tightly related to the solid electrolyte interphase (SEI) on Li metal [11,13,14]. Both a robust in-situ formed SEI [15–17] and an ex-situ coating layer (artificial SEI) [18,19] can function as a barrier layer to suppress the growth of Li dendrites. In this work, we develop a triblock polyether, Pluronic P123 as a bifunctional electrolyte additive for separator wetting and Li dendrite suppression

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in LMBs. On one hand, addition of 0.2–1% (by weight) P123 into the electrolyte could effectively enhance the wettability of PE separator. On the other hand, the adsorption of P123 on the Li metal surface can act as an artificial SEI layer and contribute to the suppression of Li dendrite growth.

2. Experimental

Propylene carbonate (PC), dimethyl carbonate (DMC) and lithium hexafluorophosphate (LiPF₆) of battery grade were ordered from Shenzhen Capchem Technology Co. Ltd and used as received. Pluronic P-123, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), HOCH₂CH₂(OCH₂CH₂)₇₀[OCH₂CH(CH₃)₂]₂₀-(OCH₂CH₂)₇₀CH₂CH₂OH with an average molecular weight of 5800 was purchased from Sigma-Aldrich. It was stored in a glovebox and dried under vacuum at 80 °C for 24 before use. An electrolyte of 1 M LiPF₆/PC was prepared in an argon-filled glovebox (MBraun) and used as the control electrolyte. Similarly, a small content (0.2, 0.5, 1% by wt.) of P123 was added into the control electrolyte to give the P123-containing electrolytes. Clear and uniform P123-containing solutions without any precipitate or flocculence were obtained after 2 h stirring.

Contact angles and electrolyte uptake were measured to evaluate the separator wettability toward electrolytes with and without P123. The separator used in this work was Celgard 2730 PE membrane. The electrolyte uptake experiment was conducted according to the procedures reported in our previous paper [9]. Each electrolyte uptake value was presented as the average over five parallel tests. A contact angle tester (Kruss DSA10-Mk2) was used to analyze the contact angles between the PE separator and electrolytes with and without P123. The ionic conductivities of the wetted PE separators after being immersed in certain amount of electrolyte for 2 h were measured by an electrochemical impedance spectroscopy (EIS) method on a CHI660e electrochemical workstation (Shanghai Chenhua). The impedance measurements were performed on the electrolyte-immersed separators sandwiched between two stainless steel (SS) electrodes over a frequency range of 100 kHz to 1 Hz with an AC amplitude of 10 mV. The ionic conductivity (σ) was calculated using the following equation:

$$\sigma = \frac{d}{S \times R_{\text{separator}}} \quad (1)$$

where d and S are the thickness and the dimensional area of the separator, respectively, and $R_{\text{separator}}$ is the bulk impedance of the wetted separator obtained at the high frequency intercept of the Nyquist plot on the real axis.

In order to evaluate the effect of P123 on Li dendrite suppression in LMBs, coin cells of Li||Cu were assembled in the glovebox with Li foil as anode, Cu foil as cathode, and Celgard 2730 PE membrane as separator. To standardize the testing, 80 μ L of electrolyte was used in each coin cell. Li metal was deposited on the Cu foil substrates (Φ 16 mm) in the electrolyte with or without P123 at 0.1 mA cm⁻² for 15 h on an Arbin BT2000 battery cycler. The Cu electrodes with deposited Li from Li||Cu cells were washed with anhydrous DMC to remove the residual electrolytes. After drying under vacuum in the antechamber of the glovebox, optical pictures of the deposited Li electrodes were taken with a digital camera. Scanning electron microscopy (SEM) images of the deposited Li electrodes were obtained with a field-emission scanning electron microscopy (FE-SEM, Hitachi SU8020) at an accelerating voltage of 5 kV. Meanwhile, Li||Cu cells also were used to study the Coulombic efficiency (CE) of the electrolytes with and without P123 additive. The CE tests were carried out by first depositing 1 mAh of Li onto the Cu electrode, followed by Li stripping up to 1 V. In order to exclude the

influence from the separator, Li deposition on a Cu substrate (10 mm \times 10 mm) was carried out in a three-electrode electrochemical cell placed in the glovebox. X-ray photoelectron spectroscopy (XPS) analysis on the elements in the SEI layers on Li deposits was carried out on an ESCALAB250 spectrometer. Fourier transform infrared spectrometer (FTIR, Nicolet-670) data were collected from 4000 to 500 cm⁻¹. Cyclic voltammetry (CV) of a three-electrode electrochemical cell using a Cu electrode (1 cm \times 1 cm) as a working electrode and Li metal as both the reference and the counter electrodes was performed on the CHI660e electrochemical workstation at a scan rate of 50 mV s⁻¹ with the scan range of -1.0–2.5 V. In order to investigate the stability of Li metal in the electrolytes with and without P123, Li||Li symmetric cells (CR2032-type) were assembled with Li metal discs (Φ 15.6 mm) used as both the working and the counter electrodes. All the tests excluding those indicated specifically were carried out at room temperature (25 °C).

3. Results and discussion

Good separator wettability is not only vital to the cell performance of LMBs, but also facilitates an evenly distributed Li⁺ ionic flux which is essential for uniform Li deposition and Li dendrite suppression [6,10]. In general, triblock polyether compounds are widely used as surfactants to improve liquid/solid wettability by reducing the surface tension of liquid in surface science. Herein, a triblock polyether compound Pluronic P123 was introduced into the electrolyte as a wetting agent to improve the PE separator wettability toward nonaqueous electrolytes of LMBs. As shown in Fig. 1a, the effect of P123 on separator wettability is evaluated by the contact angles between the PE separator and the electrolytes with and without P123. The control electrolyte of 1 M LiPF₆/PC has a high contact angle of 80.5° on the PE separator, which means a poor wetting between the electrolyte and the separator. When 0.2% P123 was added into the control electrolyte, the lower contact angle of 64.3° indicates the improved separator wettability toward the electrolyte by P123. Furthermore, the electrolyte uptakes of the PE separator also prove the effect of P123 as show in Fig. 1b. The control electrolyte of 1 M LiPF₆/PC has a low uptake of ~30%. Due to the high dielectric constant of PC, the electrolyte of 1 M LiPF₆/PC with high polarity usually exhibits high surface tension on the nonpolar PE separator according to the like-dissolves-like rule, thus the control electrolyte cannot well spread on the PE separator to give a high electrolyte uptake. However, by adding 0.2% P123, the electrolyte uptake has been greatly enhanced to above 80%. With continually increasing the content of P123 to 0.5 and 1%, the electrolyte uptake still keeps stable at ~80%. Like a surfactant, the block of [-OCH₂-CH(CH₃)-]_n in P123 has good affinity with the nonpolar polyolefin separator and the block of [-OCH₂-CH₂-]_m in P123 has strong interaction with polar molecules in the electrolyte. Thus, P123 enables the electrolyte to well wet the PE separator and to increase the electrolyte uptake of the separator, which in turn will provide more pathways for Li⁺ transport and facilitate a well-distributed Li⁺ ionic flux over the surface of Li metal anode, thus could help suppress dendrites formation during Li deposition.

Fig. 1c shows the ionic conductivities of the PE separators infiltrated with various electrolytes, which were calculated from the EIS results (shown in Fig. S1). The ionic conductivity (σ) of the separator infiltrated with the control electrolyte is only 0.045 mS cm⁻¹, but it is increased ten times to 0.50 mS cm⁻¹ after 0.2% P123 was introduced into the electrolyte. Obviously, the ionic conductivity of the separator/electrolyte has been greatly improved because of the enhanced wettability by P123, even though a small amount of P123 here 0.2% could have negligible impact on the conductivity of the electrolyte bulk. Further increasing P123

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