



Polyethylene separators modified by ultrathin hybrid films enhancing lithium ion transport performance and Li-metal anode stability



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ARTICLE INFO

Article history:

Received 20 April 2017

Received in revised form

4 October 2017

Accepted 17 October 2017

Available online 1 November 2017

Keywords:

Li-metal anode

Li⁺ ion transference number

Ionic conductivity

Cycling performance

ABSTRACT

Poor stability of lithium metal anodes in liquid electrolytes hinders its practical application in rechargeable batteries with very high energy density. Herein, we present an approach to tackle the intrinsic problems of Li metal anodes from the standpoint of separators. By a facile and versatile method based on mussel-inspired surface chemistry, a hybrid polydopamine/octaammonium POSS (PDA/POSS) coating was spontaneously formed on the surface of PE separators through the self-polymerization and strong adhesion feature of dopamine. This ultrathin PDA/POSS coating endows PE separators with different surface characteristics while keeping its microporous structure almost unchanged. The altered surface characteristics influence the separator/electrolyte interaction, and lead to remarkable enhanced ionic conductivity (from 0.36 mS cm⁻¹ to 0.45 mS cm⁻¹) and Li⁺ ion transference number (from 0.37 to 0.47) of PE separators as well as the improved stability of lithium/electrolyte interface, which effectively decreases the electrode polarization and suppresses the lithium dendrites formation, contributing to superior C-rates capability and cycling performance of cells.

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1. Introduction

On the urgent needs of high-capacity and safety batteries [1] for practical use, large theoretical capacity materials and systems which mainly based on the lithium metal anodes, such as the Li-O₂ [2,3] and Li-S batteries [4–6], are being widely researched. However, both suffer from a deep-rooted challenging problem: the electrochemical instability of the lithium/electrolyte interface which leads to unstable solid-electrolyte interphase (SEI) layers and uncontrolled lithium dendrite growth on the Li metal surface during the repeated charge-discharge cycles [7]. It not only causes repeated damage to the SEI film which leads to continuous consumption of lithium and poor Coulombic efficiencies (CEs) [8,9], but even pierces the separator which may lead to short-circuit and safety issues [10].

To stabilize lithium anodes is perceived to be a prerequisite for

the breakthrough of Li-metal batteries. The Li dendrite formation and growth originates from the Li⁺ concentration gradient during the charge/discharge process and the surface non-uniformity of the deposition [11]. Many recent works tackle it from different methods to avoid the negative effects caused by Li dendrite. For example, the 3D current collector with high surface area and uniform electric field can decrease the current density and tune charges more homogeneous on the Li surface [12]. Cation additives, such as Cs⁺ and B³⁺ ions [13], Cu(CH₃COO)₂ [14,15], etc., some of them help to construct stable SEI film to suppress dendrite growth. The artificial SEI, such as LiF etc. [16–18], has been used to construct robust layer to avoid an uncontrolled SEI forming process. The functional groups/layer on the separator can weaken the solvation effect of Li⁺ ions and promote the Li⁺ transportation between the cathode and anode, which is helpful to reducing the Li⁺ ion depletion on the anode surface and suppressing Li dendrite growth [19].

Many modelling and simulations [20,21] have been carried out trying to figure out the origin of the inherent problems of lithium anodes from fundamental perspective, which reveals that the pivotal variables of ion transport, i.e. the ionic conductivity σ and Li⁺ ion transference number t_{Li^+} , are critical for the stability of

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lithium anodes. High ionic conductivity and Li^+ transference number can alleviate the concentration gradient, which would extend the so-called “Sand's time” to effectively suppress the formation of lithium dendrites [22,23].

The transport of ions in the electrolyte depends on the size of solvated ions and interactive environment [24–26]. The former depends on the electrolyte variables such as the salt concentration and the solvent nature [27,28], etc. The latter is related to van der Waals interactions and Coulombic interactions that occur with the surrounding neutral and charged species [29,30]. Because the lithium ions and counter ions transport through the electrolyte-filled separator, it is reasonable to assume that the ion migration in the electrolyte would be affected by the interactive environment provided by the separator, which would depend on the morphological characteristics of the separator such as pore structure, as well as the surface characteristics of the separator [31,32]. Currently, numerous efforts have been made to modify the ion transport in electrolytes by designing and optimizing the electrolyte components [33–35]. Relatively, the effects of separators on the ion transport in electrolytes did not get enough attention.

In this work, a simple dipping coating process of PE separators in the dopamine/octaammonium POSS mixed solution was carried out to modify the surface characteristics of PE separator while keeping its microstructure unchanged. The altered surface characteristics can influence the separator-electrolyte interactions, leading to significantly enhanced ionic conductivity and Li^+ ion transference number, which contributes to improved stability of lithium metal anodes and superior cell performances. This work provides a new perspective to tackle the intrinsic problems of Li metal anodes.

2. Experimental section

2.1. Materials

Octaammonium POSS was purchased from Hybrid Company (USA). Anhydrous methanol (CH_3OH), N-methylpyrrolidone (NMP), graphite, concentrated hydrochloric acid, were purchased from Sinopharm chemical reagent Co. Ltd (SCRC). Dopamine hydrochloride and tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl) were purchased from Aldrich. PE separators were provided by SK Innovation (thickness: 14 μm , porosity: ~50%). Li metal was obtained from China Energy Lithium Company (Tianjin, China). The liquid electrolyte consisting of 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1/1/1, by volume) was purchased from Guotai Huarong Company (Zhangjiagang, China). All the chemicals were used as received without further purification.

2.2. Preparation of PDA/POSS-modified PE separators

The fabrication of PDA/POSS-modified PE separators is schematically illustrated in Scheme 1. First, PE separators were ultrasonically cleaned with ethanol for 20 min and then dried in the vacuum oven at 45 °C for further use. The sequential self-deposition process of PDA and POSS is driven by the Michael addition and Schiff base reaction, which consists of the following steps: the pretreated PE separators were immersed into the mixed solution of Dopamine (1.5 mg mL^{-1}) and Octaammonium POSS for 15 h to undergo the polymerization through the imidization between o-quinone groups and amino groups which occurs at room temperature.

The mixed solution was Tris-HCl (10 mM)/methanol (1:1 v/v), and its pH value was adjusted to 8.5 by HCl (1 mol L^{-1}) aqueous solution. The modified PE separators with PDA/POSS mixture is

recorded as PDA/POSS (m:n) @ PE, where the (m:n) represents the weight ratio of Dopamine to POSS.

2.3. Characterization of separators

A quartz crystal microbalance (QCM) device (Agilent, 53131A) was used to test the deposited mass of PDA/POSS. The surface and cross-sectional morphologies of separators, as well as the elemental distribution were investigated using a field emission scanning electron microscope (FE-SEM) combined with energy dispersive X-ray spectroscopy (EDS) (S-4800). The contact angle of separators was measured by a commercial drop shape analysis system (KRUSS, DSA100). The Gurley value was determined by measuring the time for 100 cm^3 air to pass through a Gurley densometer (UEC, 1012A) under a given pressure. The electrolyte uptake of membranes was calculated as the following equation:

$$\text{uptake (\%)} = (W_t - W_0)/W_0 \times 100\% \quad (1)$$

where W_0 and W_t represent the weight of separators before and after being immersed in the liquid electrolyte for 1 h in a glovebox, respectively. TGA and DSC were tested on TA Q500 HiRes under N_2 atmosphere. The thermal shrinkage of separators was determined by measuring the dimensional change of them after exposure to various temperatures for 0.5 h. The tensile strength and rupture force of separators were measured by AUTO tensile tester (Labthink, XLW (PC)). The chemical composition and the functional groups on the surface of different separators was analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C ESCA) with Mg $K\alpha$ radiation and the Fourier transformed infrared spectroscopy (FT-IR, Nicolet6700), respectively.

2.4. Electrochemical analysis

The ion conductivity of separator was measured by the AC impedance analysis using an electrochemical workstation (Chenhua, CHI660E) over a frequency range of 0.1 Hz–1 MHz, the electrolyte-soaked separators were sandwiched between two stainless steel (SS) electrodes to assemble blocking-type cells for measurements. The ion conductivity was calculated by:

$$\sigma = d/(R \times S) \quad (2)$$

where σ , d , S and R are the ionic conductivity, the thickness of separators and the area of stainless steel electrodes, and the bulk resistance, respectively.

The Li^+ ion transference number was analyzed by the combination of chronoamperometry and electrochemical impedance spectra (EIS) of Li/separator/Li cells according to the following equation:

$$t_{\text{Li}^+} = I_s(\Delta V - I_0 R_0)/I_0(\Delta V - I_s R_s) \quad (3)$$

where I_0 and I_s are the initial and steady-state current obtained by the chronoamperometry, respectively. R_0 and R_s are the interfacial resistance before and after polarization measured by AC impedance analysis, respectively. ΔV is the potential difference (10 mV). The interfacial characteristic of lithium/electrolyte was investigated by the impedance analysis of Li/separator/Li cells over storage. The frequency range for measurement was 10 mHz–1 MHz at ambient conditions.

The coin-type cells were assembled by sandwiching the electrolyte-soaked separators between Li/Li in the argon-filled glovebox (MBRAUM, W13006-2) to investigate lithium plating/stripping cycling behavior of symmetric Li/separator/Li cells under

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