Effect of polyphenol-polyamine treated polyethylene separator on the ionic conduction and interface properties for lithium-metal anode batteries

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ABSTRACT

Lithium metal is a promising anode candidate for the next-generation higher energy density batteries. In this work, a detailed study is carried out to clearly explore the influence of separator wettability on ionic conduction and interface properties for lithium-metal anode batteries. Firstly, polyphenol and polyamine are facilely assembled on the surface of polyethylene (PE) separator with the assistant of periodate. Wettability and electrolyte uptake of the polyphenol-polyamine treated PE separator improves significantly, which resulted in the increase of ionic conductivity and lithium-ion transference number (from 0.37 to 0.49). Subsequently, galvanostatic measurements and electrochemical impedance spectra (EIS) are performed on Li symmetric cells to investigate the effect of separator wettability on interface properties. It is found that the modified PE separator favors the electrochemical process by providing lower interfacial resistance, better interface compatibility, and more uniform deposition of Li^+, which correspondingly mitigate the formation of Li dendrites. Finally, lithium-metal anode cells ($LiCoO_2$ (LCO)/Li) assembled with different separators are tested, and superior battery performance is displayed in case of the polyphenol-polyamine treated substrate. These results are expected to be instructive for the design of more durable Li electrodes.

1. Introduction

Lithium-ion batteries (LIBs) have become a significant part of modern life for their important role in powering various electronic products and vehicles [1,2]. Meanwhile, lithium-metal batteries (LMBs) are promising candidates for the next-generation energy storage devices because of the highest theoretical capacity (3860 mAh g^{-1}) and lowest electrochemical potential (-3.04 V versus the standard hydrogen electrode) of Li anode [3]. There many tough challenges need to be addressed before Li anode can be an available alternative to conventional graphite-based anodes, the worst of which is the formation of Li dendrites [4,5]. Similar to many other metals, Li anode tends to form dendrites during repeated stripping/plating processes, which is the main cause of capacity fading and internal short circuit [6].

Plenty of efforts have been made to regulate the growth of Li dendrites, most of which were focused on the design of Li anodes, electrolytes, and current collectors [7–11]. In contrast, less attention was paid to the role of a separator, which is of great importance to ensure the safety of batteries. Essentially, the formation/growth of Li dendrites is due to the uneven deposition of Li^+ [12]. In general, the essential function of a separator is to ensure physical isolation between electrodes while serve as electrolyte reservoir to enable ionic transport. Nevertheless, the behavior of ionic transport can be significantly affected by both the porous structure and surface chemical composition of the separator [13,14]. Polyolefin-based microporous separators, such as polypropylene (PP) and polyethylene (PE), are of highly popularity owing to their outstanding advantages including reliable stability, sufficient mechanical strength and low cost [15]. Due to the lack of polar groups, these substrates exhibited poor compatibility with the commonly used polarized alkyl carbonates electrolyte solutions [16–18], which may resulted in constrained ionic migration, inferior interfacial compatibility, and unevenly stripping/plating of Li^+.

Recently, some reports demonstrated that proper surface treatment of polyolefin separators could be an effective way to improve the performance of LMBs. For example, Ryou et al. reported a polydopamine-coated PE separator with improved ionic conductivity and electrolyte uptake for high performance $LiCoO_2$/Li cell [19]. Chi et al. deposited a multilayer of ZrO_2/POSS on PE separator to enhance the rate capability and cycle life of LMBs [20]. Shin et al. demonstrated that graphene-coated PE substrate could stabilize the Li electrode in

LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O/Li cell [21]. However, there are few comprehensive studies on the influence of wettability on ionic transport and interfacial properties for the separator assembled with Li electrodes.

Herein, commercially available PE separators were facilely coated with multilayer of nature polyphenol tannic acid (TA) and polyethylene polyamine (PEPA) through layer-by-layer method (LBL), and further stabilized by a single contact with periodate. Wettability and surface morphologies of the bare and modified PE separators were analyzed carefully. Ionic conductivity, lithium ion transference number, and interfacial stability of the modified separator were fully investigated. Meanwhile, Li symmetric cells were fabricated to study the effect of separator wettability on the formation of Li dendrites during the repeated stripping/plating processes. Additionally, LiCoO$_2$ (LCO)/Li cells assembled with different separators were cycled to validate the practical efficiency of this surface modification technique.

2. Experimental section

2.1. Materials

Polyethylene separators Celgard 2730 (PE, thickness 20 μm) were got from Celgard Company. Tannic acid (TA, M$_W$ = 1701.23 Da), polyethylene polyamine (PEPA) and sodium periodate (NaIO$_4$) were purchased from Aladdin Chemistry Co. Ltd. (China) and used as received. PEPA solution was prepared in the presence of 0.1 M sodium acetate buffer (PH 5.0). Liquid electrolyte (LiPF$_6$, 1 M) containing vinylene carbonate (VC, 1 wt%) was prepared by dissolving lithium salts in the mixed solvent of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (1:1:1, mass ratio) (Shenzhen Kejing Star Technology Co., LTD., China).

2.2. Surface modification

The modification process was schematically presented in Fig. 1. Briefly, a piece of PE sample (pre-wetted with ethanol) was alternatively dipped in TA aqueous solution (2.0 mg/ml, 10 min, step ①) and PEPA solution (2.0 mg/ml, 10 min, step ②) with a certain cycle number. After each step, the sample was gently washed with water to remove unstable residues. Finally, the as-prepared sample was immersed into NaIO$_4$ solution (1.0 mg/ml, 10 min, step ③) to accomplish the whole process. The modified separator was thoroughly rinsed before dried in a vacuum oven at 60 °C for 24 h. In the optimized experiment, step ① and step ② were repeated two more times to endow the sample with suitable surface properties. The as-prepared PE separator was referred to as MPE in the following text.

2.3. Characterization

Surface wettability of the bare and modified separators were determined by measuring their liquid electrolyte or water contact angles (OCA20, Dataphysics, Germany) with a drop size of 3 μl. Field emission scanning electron microscopy (SEM, Hitachi S4800, Japan) equipped with energy dispersive X-ray spectroscopy (EDX) were applied to observe the surface morphologies and element distribution profiles of the separators. Gurley value was measured on a homemade device by determining the time (s) needed to pass certain volume of air (100 cm^3) through the separator (1 in^2) under certain pressure differential (1 kPa). Electrolyte uptake was measured by immersing a separator in liquid electrolyte for 2 h, and the excess liquid electrolyte on the separator surface was removed by filter before weighing. Electrolyte uptake was calculated by the following equation:

$$\text{Electrolyte uptake}(\%) = \frac{W_1 - W_0}{W_0} \times 100\% \tag{1}$$

where W_0 and W_1 were the weight of dry and electrolyte-soaked separator, respectively.

2.4. Electrochemical characterization

Ionic conductivity (σ) was calculated according to the equation:

$$\sigma = \frac{L}{AR_b} \tag{2}$$

where L was thickness of the separator, A was the effective area, and R_b was bulk impedance of the separator, respectively. R_b was determined by applying electrochemical impedance spectroscopy (EIS) (Chenhua, CHI660E, China) on the corresponding stainless steel (SS)/separator/SS blocking cell within a frequency of 0.1 to 10^6 Hz. The intercept in the high frequency area on the real axis reflects R_b. Lithium ions transference number (t_{Li^+}) was determined by combining chronoamperometry
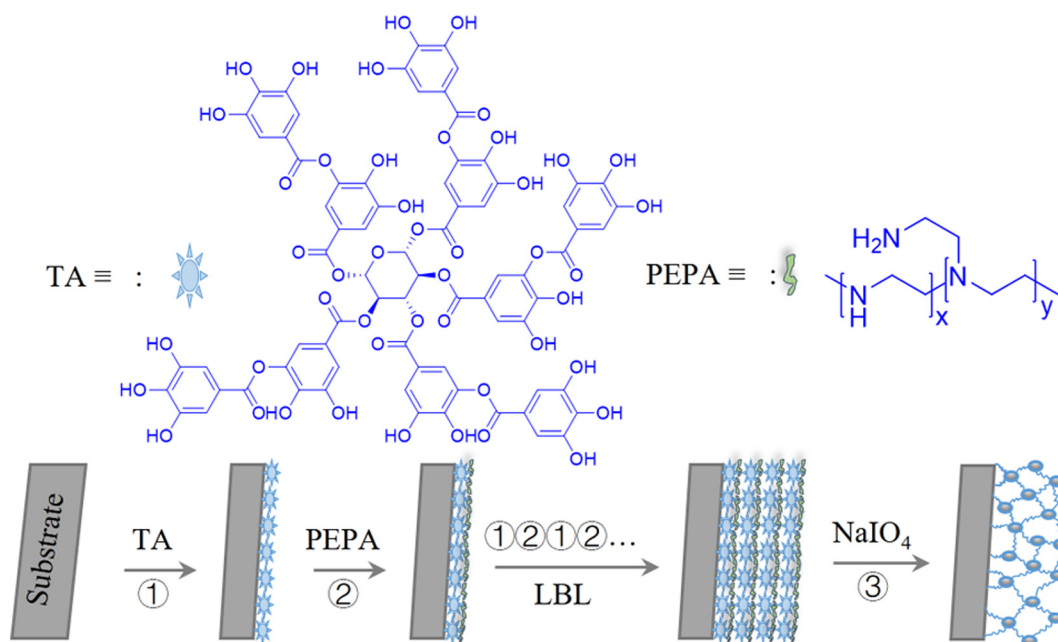

Fig. 1. Schematic representation of the surface modification process.