



## Fast assemble of polyphenol derived coatings on polypropylene separator for high performance lithium-ion batteries



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### ABSTRACT

Improving the wettability of liquid electrolyte to polyolefin separators plays a significant role in the fabrication of high performance lithium-ion batteries. Herein, we report a facile surface coating method to enhance the wetting capacity of commercially available polypropylene (PP) separator. Natural polyphenol tannic acid (TA) and sodium periodate are selected as the coating precursor and inorganic trigger, respectively. Coating formation is initiated by the absorption of tannin molecules on the separator surface and then triggered by a single contact (5 min) with sodium periodate solution. After being modified, wettability of the separator can be significantly enhanced without damaging its original advantage properties, which accordingly resulted in higher electrolyte uptake and better interfacial compatibility. Furthermore, the LiCoO<sub>2</sub>/graphite full cells assembled with the modified separator displays an excellent cycle stability with coulombic efficiency exceeding 99.9% and superior rate performance. The ease, low cost and scalability of this coating process, combine with the general surface binding affinity of polyphenol, making this surface modification technique suitable to upgrade other inert substrates for various applications.

### 1. Introduction

With the rapid development of modern society and technology, advanced energy storage technologies will be more and more needed in the coming decades [1]. Lithium-ion batteries (LIBs), as one of the most popular types of rechargeable batteries, have been widely used in portable electronic devices since 1990s, owing to their outstanding advantages including high energy density, no memory effect, long cycle life, and low self-discharging [2]. Nowadays, LIBs are increasingly being applied in the fields of smart grids, hybrid vehicles, and especially pure electric vehicles [3]. LIBs generally consist of the cathodes, anodes, electrolytes and separators. The role of a separator is to ensure physical isolation between the cathode and anode while serving as an electrolyte reservoir to enable ionic transport [4,5]. Despite it does not directly involve in any electrochemical reaction, the separator is important as a foundation to affect the battery performance such as battery safety, cycle stability, and service life [6]. Polyolefin-based microporous separators (typically polypropylene (PP) and polyethylene (PE)) are the dominant products in current LIBs market, thanks to their low cost, excellent mechanical strength, high electrochemical stability, appropriate microporous structure, and smart thermal shutdown

properties. However, the lack of polar groups leads to low surface energy and endows the separators with highly hydrophobic surface [7–9]. Consequently, these inert substrates exhibit poor compatibility with the commonly used electrolyte solvents such as ethylene carbonate and ethylmethyl carbonate, thus hampers the absorption and diffusion of the liquid electrolyte within the porous polymeric membrane and ultimately results in a reduced cell performance [10,11].

To address this problem, a number of surface modification approaches have been reported to improve the wettability of commercial polyolefin membrane separators, included (i) introducing hydrophilic monomers onto the separators surfaces by chemical grafting [7,12]; (ii) binding polymers and/or inorganic materials through physical coating [13–15]. Besides, mussel-inspired surface coating has gained much attention for its versatile adhesion capacity [16,17]. In 2011, Park et al. coated PE separator through a simple dipping process in buffered dopamine solution with pH 8.5. Dopamine was self-polymerized into polydopamine (PDA) in this weak alkaline aqueous solution. The PDA-treated PE separator showed improved wettability, electrolyte uptake, and ionic conductivity without sacrificing its original superiority [18]. Furthermore, poly(ethylene glycol), poly(ethylene oxide) and poly(methyl methacrylate) were immobilized onto polyolefin substrates to

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further improved their performance with PDA as a reliable intermediate layer in our previous work [19–21]. Similarly, Wang et al. replaced dopamine with catechol and polyamine to transform PP separator from hydrophobic to hydrophilic based on the interaction between the amine groups and catechol [22]. However, these mussel-inspired coating methods may be out of practical significance because of the high price of dopamine and the slow self-polymerization rate [23].

Tannic acid (TA) is a kind of hydrolysable polyphenol which can be extracted from natural plant with much lower cost than dopamine [24,25]. The high content of hydroxyphenyl in TA makes it a suitable coating precursor for various surface modifications through covalent or noncovalent interactions [26,27]. Although TA coatings can also be formed spontaneously on many substrates similar to PDA coatings, the time-consuming feature of this coating method is still an inevitable impediment for industrial applications [28,29]. It will be of great significance to achieve any acceleration in the formation rate of TA derived coatings. Sodium periodate is an inorganic salt often used in organic chemistry to selectively oxidise particular groups [30,31]. It can also be used as the sole additive to realize the formation of catechol-based coatings by converting hydroxyphenyl to the corresponding quinones, and then the quinones self-polymerized although the actual mechanism remained unclear [32–35]. Recently, Ponzio reported the oxidative conversion of dopamine to PDA coatings with sodium periodate, and surface character of the substrate coated with the PAD coatings exhibited remarkably improvement after 24 h [36]. However, the rapid oxidization of nature polyphenol with sodium periodate to generate the corresponding coatings has not been reported.

In this work, TA was facilely assembled on the PP separator triggered by sodium periodate for the first time. To obtain optimized surface property, the coating steps were cycled with desired number (see Fig. 1). The TA derived coatings can effectively endow the substrates with enhanced wettability and accordingly improved electrochemical properties without damaging their pore structures. Importantly, the modified separator can definitely promote the cycle stability and rate performance for the LiCoO<sub>2</sub>/graphite full cells assembled with it.

## 2. Experimental section

### 2.1. Materials

PP separator was purchased from Celgard Company (Celgard 2500, USA). TA (MW = 1701.23 Da, analytical reagent) and sodium periodate (NaIO<sub>4</sub>) were purchased from Aladdin Chemistry Co. Ltd. (China) and used without further purification. Ultrapure water used in the experiments was purified using a Millipore water purification system (18.2 MΩ, Millipore, USA). The sodium periodate solution was prepared and used away from light. All solutions were freshly prepared for immediate use in each experiment.

### 2.2. Surface modification

The coating process was illustrated in Fig. 1. Briefly, after pre-wetted by ethanol, the PP separator was first dipped into TA aqueous solution (2.0 mg/ml) for 10 min (step 1), and then NaIO<sub>4</sub> aqueous

solution (0.1 mmol/ml) for another 5 min (step 2). To obtain suitable surface property, the above steps were repeated with desired cycle number. After each dipping step, the substrate was gently rinsed by ultrapure water for several times to remove unstable residues. Finally, the modified separator was thoroughly washed with ultrapure water before dried in a vacuum oven at 60 °C for 24 h. The as-prepared separator will be referred to as TAPP-n separator, where n represents the number of coating cycle. For an example, the TAPP-3 separator can be obtained by repeating the above process two more times.

### 2.3. Characterization

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet 6700, USA) was employed to analyze the changes in the functional groups on the surface of the PP separator before and after the surface modification. An X-ray photoelectron spectroscopy (XPS, PHI5000, USA) with Mg Kα excitation radiation ( $h\nu = 1253.6$  eV) was utilized to detect the chemical compositions in the near surface of the porous substrates. Pure water and liquid electrolyte contact angle measurements were determined using a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with video capture (the drop size was 3 μl). Surface morphologies of the bare and modified PP separators were observed by field emission scanning electron microscopy (SEM, Hitachi S4800, Japan). The element mappings were also detached using energy-dispersive X-ray spectroscopy (EDX, equipped with the SEM) to detect the carbon (C) and oxygen (O) distribution profiles of the modified separators. A Gurley densometer (4110N, Gurley, USA) was applied to measure the Gurley value of the separators with various number of coating cycles by recording the time of 100 cm<sup>3</sup> air to pass through the substrates. Weight gain percentage of the separator after the modification was calculated by the equation: weight gain percentage (wt%) =  $(m_1 - m_0)/m_0 \times 100\%$ , where  $m_1$  and  $m_0$  are the weight of the modified and bare substrates, respectively. Liquid electrolyte uptake was calculated according to the equation: electrolyte uptake (wt%) =  $(w_1 - w_0)/w_0 \times 100\%$ , where  $w_0$  and  $w_1$  are the weight of dry separator and liquid electrolyte swelled separator, respectively.

### 2.4. Electrochemical characterization

Ionic conductivity ( $\sigma$ ) was calculated according to the equation  $\sigma = L/(R_b \cdot A)$ , where  $R_b$ ,  $L$  and  $A$  are the bulk impedance (ohm), thickness of the separator (25 μm) and the effective area (1.96 cm<sup>2</sup>), respectively.  $R_b$  was determined by an electrochemical work station system (CHI 660 C, China) with the assembly of stainless steel (SS)/separator/SS in a blocking-type cell at a frequency range of 1 to 10<sup>5</sup> Hz in an AC mode. The intercept in the high frequency area on the real axis reflects the  $R_b$ . The interfacial resistance ( $R_{int}$ ) was determined similar to the bulk impedance on a nonblocking-type cell with the assembly of lithium foil (Li)/separator/Li. The distance between the semicircle intercepts on the real axis represents the  $R_{int}$ , and the cells were tested again after stored for 7 days to investigate the interfacial stability. The electrochemical stability window was investigated by the linear sweep voltammetry test from 0 to 6 V (vs. Li<sup>+</sup>/Li) at a scan rate of 10 mV/s with the assemble of SS/separator/Li. SS was used as working electrode, and Li as both the counter and reference electrodes.

The liquid electrolyte was prepared by dissolving LiPF<sub>6</sub> in the mixed solvent of ethylene carbonate, dimethyl carbonate, and ethylmethyl carbonate (1 M, 1:1:1, mass ratio). In addition, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (1 M, dioxolane/dimethoxy ethane = 1/1, volume ratio, LiNO<sub>3</sub> (1 wt%)) was used as another electrolyte to further illustrate the validity of the presented method. If there is no special explanation, the liquid electrolyte used in this work refers LiPF<sub>6</sub>. Both the electrolyte and electrodes (LiCoO<sub>2</sub> (LCO), LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (NCM-523), natural graphite(C)) were got from Shenzhen Kejing Star Technology Co., LTD. Load amount are 11–13 mg

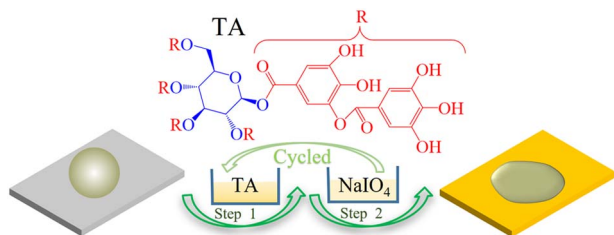


Fig. 1. Schematic illustration of the coating process and the chemical structure of TA.

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