Mussel Inspired Modification of Polypropylene Separators by Catechol/Polyamine for Li-Ion Batteries

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Ⓢ *Supporting Information*

ABSTRACT: Inspired by the remarkable adhesion of mussel, dopamine, a mimicking adhesive molecule, has been widely used for surface modification of various materials ranging from organic to inorganic. However, dopamine and its derivatives are expensive which impede their application in large scale. Herein, we replaced dopamine with low-cost catechol and polyamine (only 8% of the cost of dopamine), which could be polymerized in an alkaline solution and deposited on the surfaces of various materials. By using this cheap and simple modification method, polypropylene (PP) separator could be transformed from hydrophobic to hydrophilic, while the pore structure and mechanical property of the separator remained intact. The uptake of electrolyte increased from 80% to 270% after the hydrophilic modification. Electrochemical studies demonstrated that battery with the modified PP separator had a better Coulombic efficiency (80.9% to 85.3%) during the first cycle at a current density of 0.1 C, while the discharging current density increased to 15 C and the discharge capacity increased by 1.4 times compared to the battery using the bare PP separator. Additionally, the modification allowed excellent stability during manifold cycles. This study provides new insights into utilizing low-cost chemicals to mimic the mussel adhesion and has potential practical application in many fields.

KEYWORDS: *bioinspired, catechol, Li-ion battery, mussel, polyamine, separator*
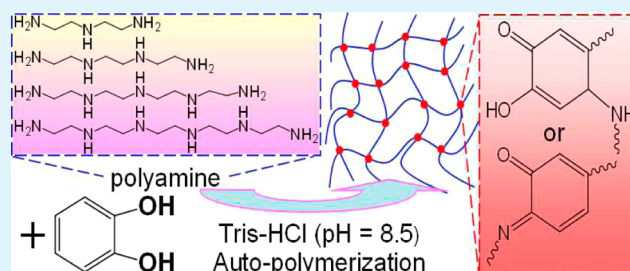
1. INTRODUCTION

Lithium-ion batteries (LIBs), which have features of high energy densities, long cycle lives, and only a slow loss of charge when idle, are one of the most popular types of rechargeable batteries for portable electronics.[1−3] Beyond consumer electronics, LIBs, especially high-power lithium-ion batteries, have expanded into the military, electric vehicles, and aerospace applications recently.[4−6] In order to meet the rapidly expanding customer demands, the performance of all battery components including anode, cathode, electrolyte, and separator needs further improvement.[7,8] Separators in LIBs play a key role in separating positive and negative electrodes to prevent electrical short circuit while permitting the transport of the ionic charge carriers.[9−11] Therefore, the separator is directly related to the safety and the power performance of the battery.[12,13] A good separator should be thin and electrochemically stable for the cyclic electrolyte and electrodes and have good wetting capability, enough mechanical strength, and thermal stability as well.[14] Polyethylene (PE) or polypropylene (PP) membranes with micropores and their laminates are the common precursors in preparing separators of LIBs.[15,16] However, due to the nonpolarity and low surface energy of PE and PP, the separators often exhibit poor compatibility with conventional liquid electrolytes such as ethylene carbonate (EC) and propylene carbonate (PC) and are difficult to wet, absorb, and reserve electrolyte, which directly affects the performance and cycle life of the batteries.[17,18] To overcome these defections, various methods including coating/grafting hydrophilic polymer and plasma modification have been developed to improve the hydrophilicity of the polymeric separators.[19−23] However, these methods may lead to some negative effects such as pore blocking.[24] Moreover, these methods often require sophisticated equipment and multistep operations with high cost, which are not preferable for the practical application in large scale.[25,26]

Inspired by the outstanding adhering ability of mussel on almost all types of surfaces, Ryou et al. developed a simple dipping process to generate polydopamine-coated PE separators, which could remarkably improve the power performance of battery.[27] However, dopamine is too expensive for extensive application.[28] Previously, Messersmith et al. recognized that catechol and amine groups were the two keys of oxidation

polymerization of dopamine to form strong adhesion.[29] Thus, it can be inferred that molecules with amine and catechol groups may possess a similar adhesive ability.

In this study, we first used a low-cost binary system, catechol and polyamine, to replace dopamine and obtained a hydrophilic PP separator successfully without sacrificing its mechanical and thermal properties. An enhanced electrochemical performance of Li-ion battery was realized by using the modified PP separator. This cheap surface modification method is universal and may be promising in practical application.

2. EXPERIMENTAL SECTION

2.1. Materials. Microporous PP separators prepared by biaxial stretching were supplied by Dalian Ecopower Technology Co. Ltd. HCl, catechol, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and trismetyl aminomethane (Tris) were purchased from Beijing Chemicals Co. (Beijing, China). $LiMn_2O_4$, carbon black, poly(tetrafluoroethylene), $LiPF_6$, EC, and dimethyl carbonate (DMC) were purchased from Aladdin Chemistry Co. Ltd. All of the chemicals were used as received.

2.2. Preparation of Catechol/Polyamine Modified PP. PP separators were first cleaned in an ultrasonic bath for 30 min, rinsed with isopropyl alcohol, and then blown dry by nitrogen. The clean separators were immersed into Tris-HCl solution (pH = 8.5, 10 mM) containing catechol (2 or 5 mM) and polyamine with the molar ratio of 1:1 for 24 h and then were taken out, rinsed with water, and blown dry by nitrogen.

2.3. Characterization. The surface morphologies and chemical composition of the separators were investigated by scanning electron microscopy (SEM) using a JEOL 6700F equipped with an energy dispersive X-ray analysis (EDX) microanalyzer. The acceleration voltage used for imaging was 5 kV. X-ray photoelectron spectrometry (XPS) was recorded on an ESCALab220I-XL spectrometer (VG Scientific) with an Al Kα X-ray source (1486.6 eV). Water contact angles were measured on a Contact Angle Meter (DSA100, Kruss Company, Germany) by a sessile drop method with 5 μL of water. The data was an average value of five measurements on different areas. Water flux was tested by fastening the separator in an ultrafiltration cup and then collecting and measuring the volume of fluid that leaked past the separator at a certain time and stress.

2.4. Electrochemical Measurements. The assembly process was conducted in an argon-atmosphere glovebox, and the charge−discharge tests were conducted by galvanostatic measurements with Land system. The cathode was composed of well mixed $LiMn_2O_4$, carbon black, and poly(tetrafluoroethylene) in a mass ratio of 85:10:5. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of EC and DMC with a volume ratio of 1:2. Lithium metal electrode was used as the anode. The discharge current densities were varied from 0.1 to 15 C under a voltage range between 3.0 and 4.5 V. For the electrochemical impedance spectroscopy (EIS) tests, the amplitude of the applied signal was 10 mV and the applied frequency ranged from 0.01 Hz to 100 kHz.

3. RESULTS AND DISCUSSION

3.1. Surface Modification with Catechol/Polyamine. The possible mechanism of the oxidation polymerization of catechol/polyamine was schematically presented in Figure 1. In an alkalescent Tris-HCl buffer solution, catechol will be oxidized and the generated quinoid structure can react with amine by Michael addition or Schiff base reaction.[30] With multiple reactive sites both in the oxidized catechol and polyamine, namely, benzene ring with four unsubstituted carbons and two quinones in catechol and several amines in polyamine, cross-linked network will be formed through the reaction. This reaction mechanism is similar to that of dopamine oxidation polymerization, except for not involving
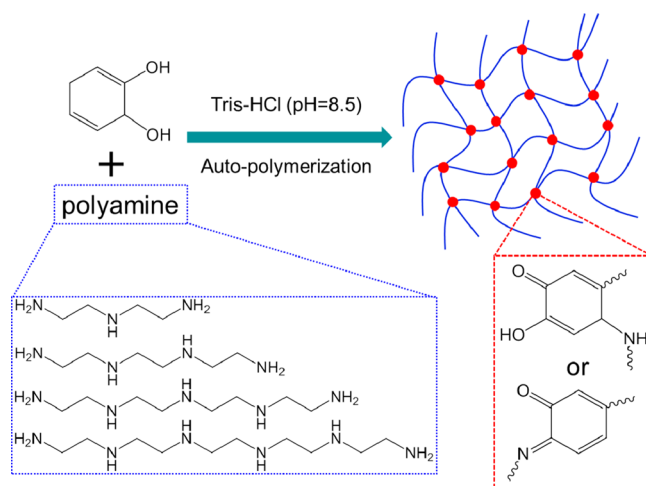

Figure 1. Schematic illustration of the possible oxidative polymerization mechanism of catechol and polyamine in a weakly alkaline Tris-HCl solution (pH = 8.5).

the intramolecular cyclization process of dopamine. Because primary amine is more active than secondary amine, the terminal amine of polyamine will preferentially react with catechol, and ethylene imine acts as spacer group. Thus, the cross-linking density of the resultant networks can be adjusted by changing the segment length from the number of the ethylene imines.

Herein, the appearance of polyamine is important to form a continuous and compact coating on the matrix. In a control experiment, glass was modified by catechol and catechol/diethylenetriamine, respectively. As shown in the inset of Figure 2, a homogeneous brown coating is formed on the catechol/
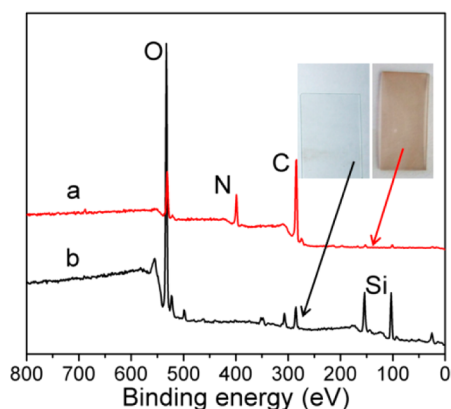

Figure 2. XPS spectrum of (a) catechol-diethylenetriamine and (b) catechol modified glass. Insets are the photographs of the modified samples.

diethylenetriamine modified glass. In contrast, catechol modified glass is colorless and transparent. XPS spectra of the catechol modified glass exhibits 12.9% C yet 26.7% Si among the C, Si, and O elements on the top surface, suggesting that a certain amount of catechol molecules can be adsorbed on the surface but a dense coating cannot be likely formed by catechol alone. For the catechol/polyamine modified glass, however, the XPS result shows obvious C and N peaks with a content of 67.2% and 14.2%, respectively, while the Si signal is only 0.6%. The results showed that a continuous compact
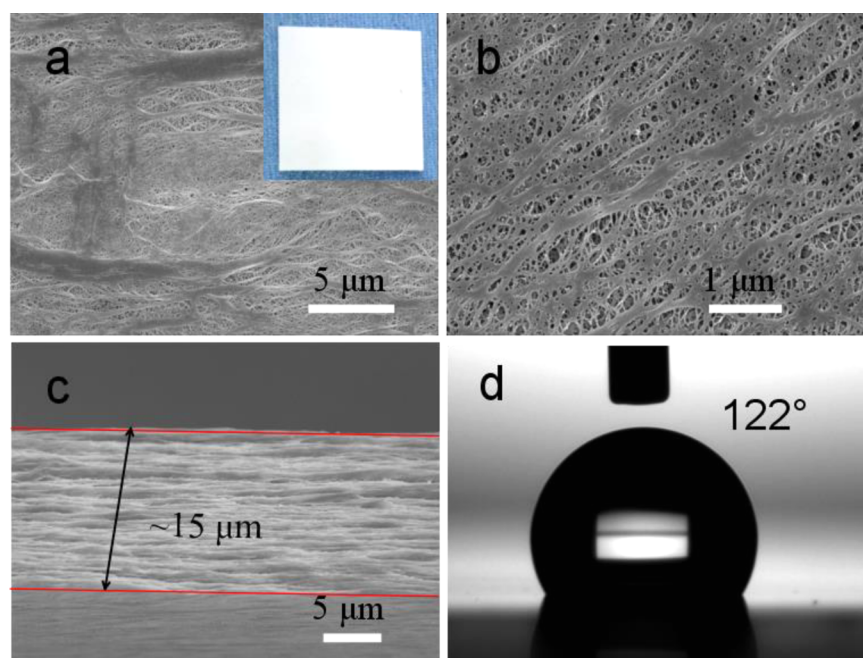
Figure 3. SEM images of (a, b) top and (c) cross-section view of the initial PP separator. The inset in (a) is a picture of the initial PP separator. (d) Photograph of a water droplet on the initial PP separator.
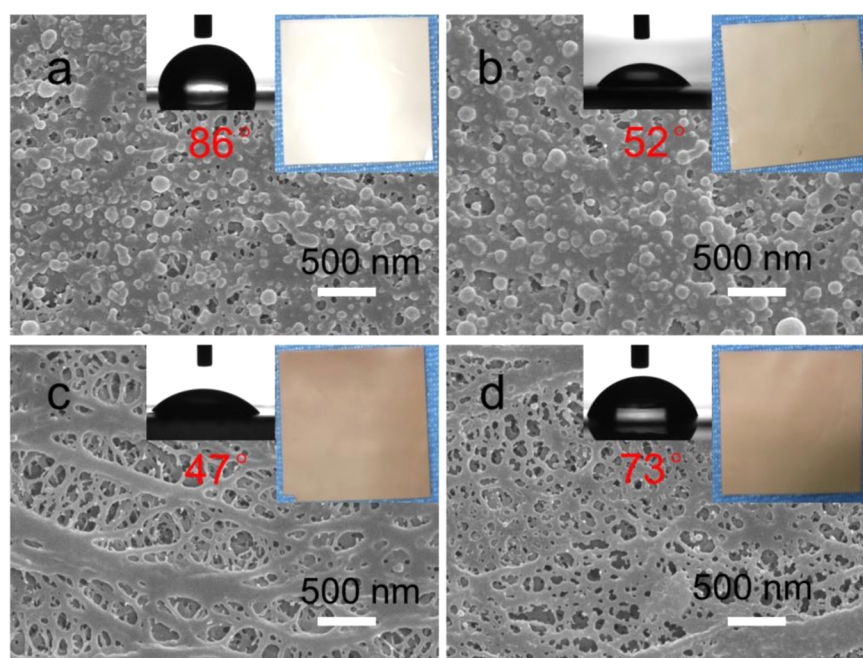

Figure 4. SEM images of the separator modified by immersing into Tris-HCl solutions containing 5 mM of catechol and 5 mM of (a) diethylenetriamine, (b) triethylenetetramine, (c) tetraethylenepentamine, and (d) pentaethylenehexamine, respectively, for 24 h. The insets are the corresponding photographs of the modified separator and water droplets on the separator.

coating was formed on the glass via the reaction of catechol and diethylenetriamine.[31]

Similar to the universality of the dopamine modification, a variety of organic or inorganic substrates could be modified by the autopolymerization of catechol/polyamine. The water contact angles of the modified surfaces, no matter if originally hydrophobic or hydrophilic, were comparable to each other after the catechol/polyamine modification, demonstrating the versatility of this surface modification method (Figure S1 in the Supporting Information).

3.2. Modification of PP Separator. The PP separator we used shows a porous morphology, with pore diameters of approximately dozens to hundreds nanometers (Figure 3a,b). The film thickness is about 15 μm and has obvious layered structure (Figure 3c). Because of the low surface tension of PP and the porous morphology, the separator shows a water contact angle as high as 122° (Figure 3d).

Such a high hydrophobicity is not desirable for the application as separator due to the poor compatibility with electrolytes. Herein, the surface morphology and wettability of

the PP separator modified by catechol and various polyamines are shown in Figure 4. The white PP separator turns brown after the modification and the color is uniform, indicating a homogeneous modification. The color of the modified film becomes denser from diethylenetriamine to pentaethylenehexamine, which may be ascribed to the increased amount of N in the polyamines. From the SEM images, we can see that the surface of the separator is covered by lots of microsized particles when using catechol/diethylenetriamine and catechol/triethylenetetramine, respectively (Figure 4a,b). Although the water contact angle of the separator decreases from 122° to 86° and 52°, respectively, after the modification, the particles block the pores in the separator, which is not tolerated for the battery application.[24] The morphology of the as formed microparticles is analogous to that of polydopamine polymerized from dopamine under a similar condition.[26] In contrast, catechol/tetraethylenepentamine and catechol/pentaethylenehexamine modified separators retain the original microporous structure and no microparticles can be observed on the surface. The contact angle decreases to 43° and 73°, respectively, after the modification (Figure 4c,d). It seems that the number of ethylene imines or the length of the spacer moieties in polyamine has a profound influence in the morphology of the polymerization product of catechol/polyamine. By using polyamine with a short chain, the distribution density of benzene in the resultant oligomer is high, which may facilitate the stacking and aggregation of oligomers through $\pi-\pi$ stacking, leading to the formation of nanoparticles. However, the benzene density, chain stiffness, and cross-linking density decrease with a greater number of ethylene imines in the polyamine, and a thin film is preferable to form instead of microparticles. Considering the desirable hydrophilicity and porous morphology, catechol/tetraethylenepentamine was used for further experiments.

The effects of reaction time and concentration on the wettability of the separator were investigated. As shown in Figure 5, water contact angles decrease slowly when the
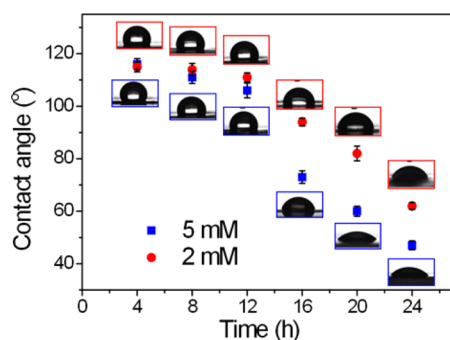

Figure 5. The water contact angles of the modified PP separators as a function of time. The concentrations of catechol/tetraethylenepentamine are 2 and 5 mM. Insets are the corresponding pictures of water droplets on the separator.

reaction time is less than 12 h and then diminish dramatically with the elongated reaction time. Besides, a lower water contact angle is more likely to be obtained by using a solution of 5 mM catechol/tetraethylenepentamine than 2 mM after the same reaction time. Meanwhile, the separator after being modified by 5 mM catechol/tetraethylenepentamine for 24 h does not show an obvious change in thickness. (See Figure S2 in the Supporting Information.)

The change of the water contact angle of the separator can be ascribed to the composition variation of the separator surface after modification, since there is no obvious morphology change. The XPS spectra of the PP separator before and after modification can give a clear proof that the composition change is a result of the formation of polymers derived from the catechol/tetraethylenepentamine reaction (Figure 6a).[25] The initial PP separator only shows a single C peak, while after modification, N, O, and C peaks appear. The signal of N peak can only come from the polyamine moieties, and the XPS analysis of the surface of the modified separator shows that the molar ratio of carbonyl group to hydroxy is about 2.3. (See Figure S3 in the Supporting Information.) To study whether the bulk of the separator was also modified successfully, EDX was employed. As shown in Figure 6b, an oxygen peak obviously appears in the EDX spectrum, implying that the inside matrix of the separator has been coated by the derivatives of the reaction of catechol/polyamine as well.

To evaluate the efficiency of the modification, the water flux was also calculated according to the method reported elsewhere.[32] The separators were pretreated with alcohol to overcome the interfacial tension present between water and membranes.[33] The water flux of the modified PP separator is 102.1 L m^{-2} h^{-1} at 0.2 MPa, 1.5 times more than that of the bare PP separator. Meanwhile, the compatibility of the hydrophilic PP separator with the electrolyte solution was improved greatly. The contact angle of electrolyte on the hydrophilic separator surface is about 30°, much lower than that on the bare separator (Figure 7a,b). The uptake amount of electrolyte was tested by weighing the solution reserved after immersing the separator into electrolyte solution for 1 min. When the separator is taken out of the solution, a few droplets of electrolyte are always pinning on the surface, indicating a poor wettability of the surface by the liquid (Figure 7c). However, the modified separator is translucent and completely wetted by the electrolyte (Figure 7d). The relative uptake amount of the electrolyte by the separator increases from 80% to 270% after modification. The results demonstrated that the modified separator exhibited much better wettability and electrolyte uptake.[27]

Compared with the modification of PE separator using dopamine solution,[27] this method is much cheaper. For the preparation of 1 L of 10 mM solutions, the cost of dopamine is $11.81 while it is only $0.96 for the catechol and tetraethylenepentamine (according to the price of Aldrich, Supporting Information Table S1). Meanwhile, it is worth noting that the mechanical and thermal properties of the PP separator do not obviously show the change after the hydrophilic modification. (See the stress−strain curves in Figure S4 and the DSC results in Figure S5 in the Supporting Information.) The enhanced wettability of the modified PP separator without sacrificing the mechanical and thermal properties is expected to contribute to a better performance of Li-ion battery.

3.3. Electrochemical Properties of the Modified Separator.
To evaluate the effect of the modification on the separators' electrochemical properties, assembled batteries were examined by a galvanostatic charge−discharge test. Figure 8a shows the charge−discharge curves of the batteries in the first cycle at a current density of 0.1 C. In these curves, there are two distinguishable pseudoplateaus at 3.9 and 4.1 V which can be ascribed to the electrochemical behavior of the $LiMn_2O_4$ spinel.[34] From the first cycle charge−discharge test, the charge
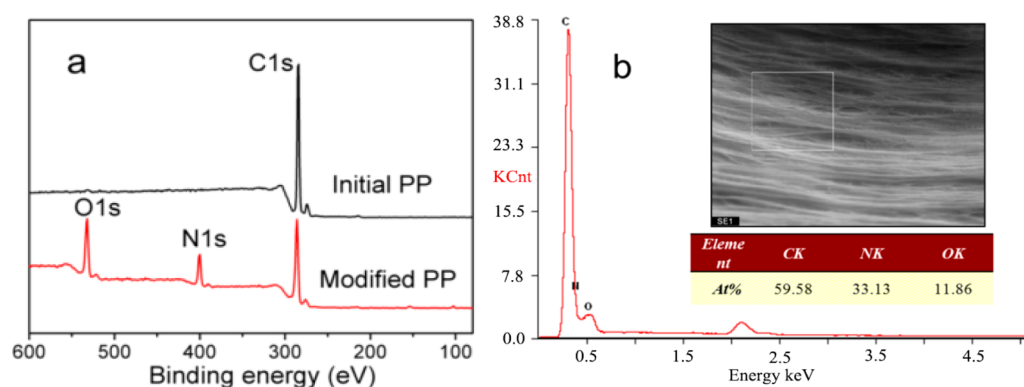
Figure 6. (a) XPS spectrum of the PP separator before and after catechol/tetraethylenepentamine modification. (b) EDX spectrum of the cross section of the modified PP separator. Inset in (b) is the corresponding SEM image of EDX investigation.
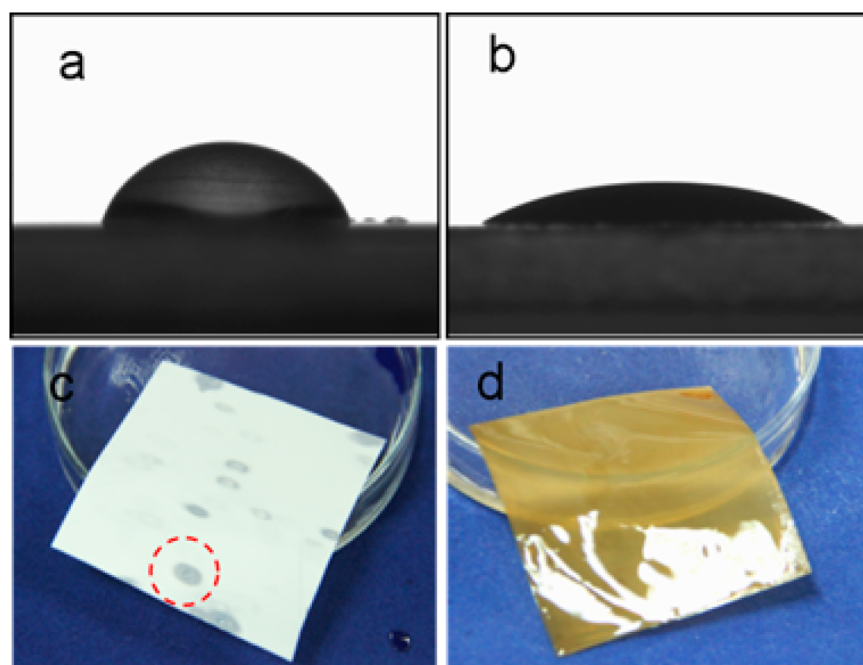

Figure 7. Profiles of electrolyte droplets on (a) the initial and (b) the modified PP separator and photographs of the initial (c) and modified (d) PP separators taken out of the electrolyte. The red circle in (c) indicates the electrolyte droplet remains on the surface of the initial separator.

and discharge capacity of the battery with the initial PP separator is 145.7 and 117.8 mAh g^{-1}, respectively, and the Coulombic efficiency is 80.9%. The battery using modified PP separator displays a better electrochemical behavior with a charge and discharge capacity of 141.8 and 120.9 mAh g^{-1}, respectively, and a Coulombic efficiency of 85.3%. The improvement of the discharge capacity and Coulombic efficiency may be due to the better wettability and retention ability of the modified separator in electrolyte.[5,27] There is a plateau in 3.0 V during the first cycle; it may be caused by the poor wettability of PP separator, and it disappears in the 2nd cycle. (See the Figure S6 in the Supporting Information.)

The data of discharging capacities at different discharging rates are shown in Figure 8b. When the discharging current densities increase from 0.1 to 15 C, the discharging capacities of the battery containing original PP separator rapidly decline from 117.8 to 12.3 mAh g^{-1}. In contrast, the battery with modified PP separator exhibits higher residual capacity, from 120.9 to 29.6 mAh g^{-1}. Although the reason why the battery with modified separator performed better at discharging under

large current was inexplicit, it was possible that lower electrolyte leakage arising from hydrophilic modification, which gave rise to a shorter path of ionic migration in the separator, might be responsible for this. In addition, the coulomb efficiency of the battery with unmodified separators is lower and more fluctuant than that of the battery using modified PP in the process of the charge−discharge cycle, especially after 100 cycles (Figure 8c). This result should also be related to the wettability between the PP separator and the electrolyte.[35] All in all, coulomb efficiency of the battery with modified separators shows better stability during the manifold cycles' test, demonstrating that catechol/polyamine modification is effective in improving the electrochemical cycle stability of the separators. Figure 8d shows typical Nyquist plots for the batteries using two different separators. The plots exhibit a semicircle at high frequencies corresponding to the charge-transfer resistances and a linear tail at low frequencies which is related to the diffusion process of Li ions. The significant reduction of bulk resistance resulted in a remarkable enhance-
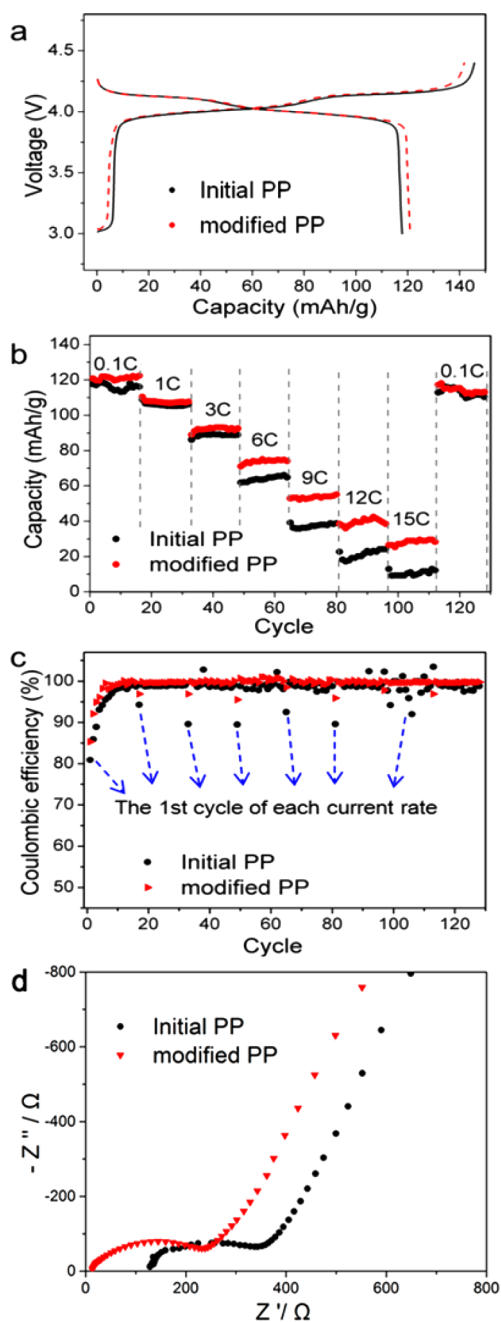
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Figure 8. (a) Voltage profiles of the batteries assembled by using initial and modified PP separator during the first cycle at a rate of 0.1 C. (b) Comparison of discharging capacities of the two types of batteries at different current densities. The voltage range for these measurements is between 3.0 and 4.5 V. (c) Coulombic efficiencies of the batteries based on the initial and modified PP separator during the power performance testing in (b) cycles. (d) The impedance spectra of the batteries with PP and modified PP separators.

ment of ionic conductivity through the separator in the battery, as a result of the increase of wettability and retention ability.

4. CONCLUSIONS

In summary, the high-performance separator of Li-ion battery was successfully fabricated by modifying PP separators with a low cost catechol/polyamine binary system. This method was an effective and versatile way to achieve hydrophilic modification on various substrates. With this method, PP

separator could be transformed from hydrophobic to hydrophilic without breakdown of pore structure and sacrifice of the mechanical properties. Meanwhile, the wettability of the separator in the electrolyte was improved significantly, which enhanced the battery performance. With high efficiency and low cost, the modified method we developed shows potential application in a large scale manufacturing high-performance separator for lithium ion battery or other porous membranes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Contact angle images, the cost of the reagents, SEM, XPS separate, stress−strain curves, DSC curves, and charge−discharge curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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