

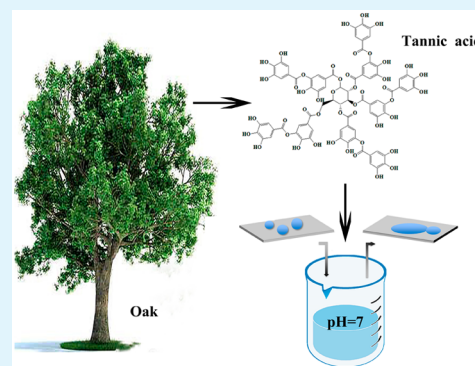
Tannic-Acid-Coated Polypropylene Membrane as a Separator for Lithium-Ion Batteries

Lei Pan, Haibin Wang, Chaolumen Wu, Chenbo Liao, and Lei Li*

Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China

ABSTRACT: To solve the wetting capability issue of commercial polypropylene (PP) separators in lithium-ion batteries (LIBs), we developed a simple dipping surface-coating process based on tannic acid (TA), a natural plant polyphenol. Fourier transform infrared and X-ray photoelectron measurements indicate that the TA is coated successfully on the PP separators. Scanning electron microscopy images show that the TA coating does not destroy the microporous structure of the separators. After being coated with TA, the PP separators become more hydrophilic, which not only enhances the liquid electrolyte retention ability but also increases the ionic conductivity. The battery performance, especially for power capability, is improved after being coated with TA. It indicates that this TA-coating method provides a promising process by which to develop an advanced polymer membrane separator for lithium-ion batteries.

KEYWORDS: tannic acid, separator, lithium-ion battery, wetting capability, power capability



1. INTRODUCTION

The development of high-performance lithium-ion batteries (LIBs) for application in portable electronics, plug-in hybrid and electric vehicles, and energy storage systems has attracted more attention in recent years.^{1,2} In the construction of LIBs, a separator is placed between the cathode and anode electrodes, which prevents the physical contact of electrodes while allowing Li⁺ ion transport during the charge and discharge processes. The separator as a critical component of LIBs directly affects the battery performance, especially for cycling stability and power capability.^{3,4} Now, commercial separators used for LIBs are typically microporous polyolefin polymer films (polyethylene (PE) and polypropylene (PP)) due to their high mechanical strength, good electrochemical and chemical stability, low cost, and thermal shutdown property.^{3,4} Although the polyolefin separators are generally reliable for portable application, there are still some major issues with vehicular storage. One of these major issues is that these polyolefin separators have hydrophobic surface properties and low surface energy, which will result in their poor compatibility with conventional liquid electrolytes.^{3,4} The poor wetting capability issue will cause the pores or tunnels in the polyolefin separators to be not completely filled with liquid electrolytes, which then results in high ionic resistance between the separator and the electrodes. It will not only directly affect the battery performance, including the cycling stability and power performance, but also bring additional disadvantages in the manufacturing costs and speeds because the electrolytes soaking into separators is one of the slowest steps in battery manufacturing processes.^{2–6}

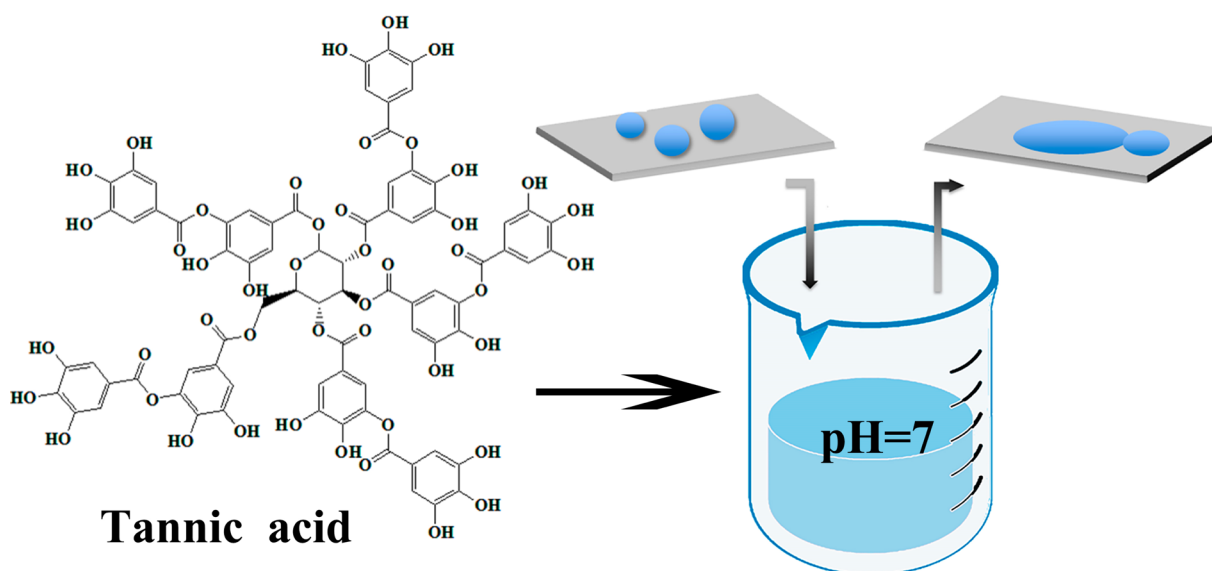
To solve the poor wetting capability issue of these polyolefin separators, various modification methods have been used. Grafting hydrophilic monomers onto the polyolefin separator surfaces is a simple and effective method for solving this issue.^{6–14} Some hydrophilic monomers such as acrylonitrile (AN),⁶ acrylic acid (AA),⁷ methyl methacrylate (MMA),⁸ glycidyl methacrylate (GMA),⁹ diethylene glycol–dimethacrylate (DEGDM),⁷ poly(ethylene glycol) borate acrylate (PEGBA),¹⁰ and 2,4,6,8-tetramethyl–2,4,6,8-tetravinylcyclotrisiloxane,¹¹ have been grafted onto the polyolefin separators by using various grafting techniques including ultraviolet irradiation grafting,^{12,13} plasma grafting,⁶ gamma irradiation grafting,¹⁴ and electron-beam-irradiation grafting processes.^{7–11} Polymer coating is another method normally used to modify these microporous polyolefin separators.^{15–18} Different polymer-coated separators such as poly(ethylene oxide) (PEO)-coated PP,¹⁵ poly(methyl methacrylate) (PMMA)-coated PE,¹⁶ PMMA/poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP)-coated PE,¹⁷ and polyimide (PI)-coated PE separators¹⁸ have been prepared. In addition, other modification methods including the physical adsorption of hydrophilic protein¹⁹ and the atomic layer deposition (ALD) coating of inorganic materials such as Al₂O₃ and TiO₂^{20–22} have also been reported. Despite the fact that these above-mentioned methods can be effective in improving the hydrophilic surface of the polyolefin separators, it also suffers from some drawbacks regarding their multiple or complex operations, microporous

Received: May 15, 2015

Accepted: July 15, 2015

Published: July 15, 2015

Scheme 1. Tannic Acid Surface Modification Using a Simple Dip-Coating Process in a Bis-Tris Buffer Solution at pH 7.0 and the Resultant Hydrophilic Tannic-Acid-Coated Surface



structure of separators, or environmental problems.²³ For example, the grafting method requires sophisticated and expensive equipment.^{6,8} A high irradiation dose will lead to the deterioration of the separator mechanical strength. In addition, the grafting process can only modify the polyolefin separator surfaces. For the polymer- or inorganic-material-coating methods, it is a big challenge to obtain uniform and thin coating layer onto or inside the microporous separators. The coated layer will block pores or tunnels inside the separators, thus decreasing the porosity and liquid electrolyte uptake of the separators, which will finally result in a decrease in the battery performance, especially the power capability.^{23,24} In addition, the coating methods will also cause some environmental issues because some toxic organic solvents need to be used. Therefore, it is important to develop a new coating method to avoid destroying the microporous structure of the polyolefin separators for LIBs.

Recently, Choi et al. reported polydopamine-coated PE separators through dopamine self-polymerize in weak alkaline aqueous solution.²⁵ Although the microporous structure and porosity of the PE separators were not changed by the polydopamine coating, the coated separators became more hydrophilic, which not only increased liquid electrolyte uptake and ionic conductivity but also improved the battery performance. However, this coating process is not suitable for practical applications because dopamine is too expensive. Herein, we developed a simple, green, and cheap coating process (Scheme 1) to obtain modified PP separators with hydrophilic surface by using tannic acid (TA) as the sole coating precursor. TA, one kind of plant polyphenol, can be directly extracted from lots of plants including tea, wood (including oak), and Chinese galls. The cost of TA is then much lower than that of dopamine (see Table 1). Similar to the coatings derived from dopamine self-polymerization, TA coatings also can be formed spontaneously in a bis-Tris buffer aqueous solution at room temperature. Because there are large multiples of phenol structural units (hydrophilic units) in the chemical structure of TA, as shown in Scheme 1, the TA coating will make the polyolefin separator surface more hydrophilic. This coating process not only retains many of the advantages of polydopamine coatings but also is a

Table 1. Cost of Reagents

material	dosage in 1 L of solution (g)	unit price ^a (per 100 g)	total
dopamine	1.9	\$354.26	\$6.73
tannic acid	1	\$14.34	\$0.14

^aBoth of the reagents are calculated according to the price in Aladdin.

“green and cheap” modification technology due to tannic acid being much less costly than dopamine. To the best of our knowledge, however, this new coating process, based on TA to modify the commercial polyolefin separators for LIBs, has never been reported.

2. EXPERIMENTAL SECTION

2.1. Preparation of Tannic-Acid-Coating PP Separators. For the tannic acid coating, commercial microporous PP separators (Celgard 2400) were immersed in bis-Tris buffer (100 mM buffer and 600 mM NaCl) aqueous solution of tannic acid (1 mg mL⁻¹ and pH 7.0) at room temperature for 24 h. After being coated, the separators were washed with deionized water several times to remove the residual tannic acid. Finally, the resultant separators were dried at 60 °C for 24 h. In our experiments, the weight content of the tannic acid on the PP separators was about 1.2 ± 0.2 wt %.

2.2. Characterization. The chemical composition of the separators was measured by using X-ray photoelectron spectroscopy (XPS) using a RBD upgraded AXIS ULTRA DLD system with Mg K α radiation ($h\nu = 1253.6$ eV) and attenuated total reflection-infrared spectra (ATR-IR) with an FT-IR spectrophotometer (Bruker, EQUINOX 55) using a ZnSe crystal at the resolution of 4 cm⁻¹ and 64 scans, respectively. The pressure was equal in all ATR-IR measurements to eliminate any possible effect on the penetrating depth of the IR beam. Morphology of the samples was measured by using field emission scanning electron microscopy (FESEM, JEOL Ltd.). The water contact angles of the samples were carried out by using a contact angle measuring system (SL200C, USA KINO Industry) at room temperature. The porosity of the microporous separators was determined by a

gravimetric method.²⁶ For the thermal shut-down characterization, thermal analyses were conducted by using DSC (TA Instruments Q20) with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

2.3. Electrochemical Characterization. Battery-grade LiPF₆, ethylene carbonate (EC), and dimethyl carbonate (DMC) were purchased from Shenzhen Capchem Chemicals Co., Ltd. and used without further purification. Samples of 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte were prepared in an argon-filled glovebox in which both the water and oxygen content were less than 1 ppm.

For the liquid electrolyte uptake measurements, the separators were soaked in 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte for 1 h at room temperature and then taken out. Subsequently, the excessive liquid electrolyte on the separator surfaces was removed away with waterleaf paper prior to measuring the weight. The final liquid electrolyte uptake was calculated from the equation $(M2 - M1)/M1 \times 100$, where $M1$ and $M2$ represent the weights of the samples before and after the immersion in the liquid electrolyte, respectively.

Before the ionic conductivity measurements, the separators were soaked in 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte for 24 h at room temperature in an argon-filled glovebox. The ionic conductivity of the samples was determined between two stainless steel (SS) electrodes by AC impedance measurement on Autolab PGSTAT302 (Eco Chemie) electrochemical test system over a frequency range from 10⁻² to 10⁶ Hz at room temperature.

The electrochemical stability of the separators was measured by cyclic voltammetry on Autolab PGSTAT302 (Eco Chemie) electrochemical test system. Before measurements were taken, the separators were first soaked in 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte for 24 h at room temperature. After that, the separators were assembled into lithium/separator/stainless steel cells. In our experiments, lithium foil was used as both the counter and reference electrodes, and stainless steel was used as the working electrode, respectively. All of the test cells were assembled and sealed in the glovebox. The experiments were performed with a sweep rate of 10 mV sec⁻¹ at room temperature.

The LiMn₂O₄ cathode materials were purchased from Hunan Reshine New Material Co., Ltd. The LiMn₂O₄ cathode electrodes were prepared by casting a slurry containing LiMn₂O₄ powder (80 wt %, as active material), carbon black (10 wt %, as conductive additive) and PVDF (10 wt %, as binder) onto aluminum foil. The weight-loading of active material was about 5 mg cm⁻². A 2016-coin-type cell was assembled in an argon-filled glovebox with oxygen and moisture level below 1 ppm. Metallic lithium foil (1.56 cm diameter and 0.45 mm thick) was used as the anode, and the PP separators with and without TA coating were employed as the separators. Samples of 1 M LiPF₆ in EC/DMC (1:1, wt:wt) were used as the liquid electrolyte in our experiments for both test cells using the PP separators with and without TA coating. The cell performance testing, including cycling stability and rate capability, was carried out on a Land CT2001A tester (Wuhan, China) at the constant current mode over the range of 3.0–4.6 V (versus Li⁺/Li). Furthermore, electrochemical impedance spectroscopy (EIS) of the cells was measured by using an Autolab frequency response analyzer over the frequency range from 0.1 to 10⁶ Hz with an amplitude of 10 mV.

3. RESULTS AND DISCUSSION

Tannic acid is weakly acidic (pK_a around 10) due to large multiples of phenol groups in the chemical structure (see Scheme 1). The pH of TA aqueous solution was thus kept at 7.0 with a bis-Tris buffer solution (100 mM buffer and 600 mM NaCl) at room temperature for the TA-coating experiments. Unlike the dark color of the polydopamine coating reported in the literature,²⁵ we found that there were no color changes for the TA-coated PP separator compared with the results from the original PP separator, even after 24 h of coating. To confirm the presence of the TA coating on the PP separator, we carried out ATR-IR measurements in our experiments. From the ATR-IR spectra shown in Figure 1, it

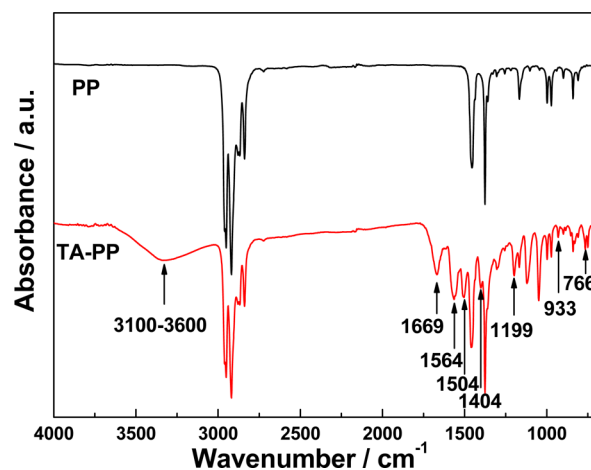


Figure 1. ATR-IR spectra of PP separators without (PP) and with tannic acid coating (TA-PP).

can be found that some new peaks appeared in the TA-coated PP separator compared to the results from the original PP separator. A broad new peak between 3600 and 3100 cm⁻¹ was ascribed to the -OH stretching vibration due to the large multiples of phenol groups in TA.^{27,28} Other new peaks include ones at 1669 cm⁻¹ (the C=O stretching vibration of the carboxylic acid group),²⁸ 1564 cm⁻¹ (the C=C stretching vibration of the aromatic ring),²⁹ 1504 cm⁻¹ (the C-O-H in the plane bend of the hydroxyl group),²⁸ 1404 cm⁻¹ (the C-O stretching on the acid functionality in tannic acid),²⁸ 1199 cm⁻¹ (the C-O stretching vibration of polyols),^{30,31} 933 cm⁻¹ (the C-O-C bending mode)^{30,31} and 758 cm⁻¹ (the C-H out-plane bend of the phenyl group),²⁷ respectively. The TA coating was further confirmed by XPS measurements. As shown in Figure 2, a new peak of O 1s appeared in the TA-coated separator. In addition, the intensity of the C 1s peak was also increased compared to that of the original PP separator. Both the FT-IR and XPS results indicate that the tannic acid has been successfully coated on the PP separator.

Although the TA coating was confirmed on the PP separator, it can be found that the microporous structure of the PP separators with and without the TA coating remained almost the same, as indicated by SEM images shown in Figure 3A,B. The porosity of the separators before and after the TA coating were also not changed. These results indicate that the TA coating did not destroy the microporous structure of the PP separator.

For the safety of lithium-ion batteries, most commercial polymer separators must have thermal shutdown (fuse)

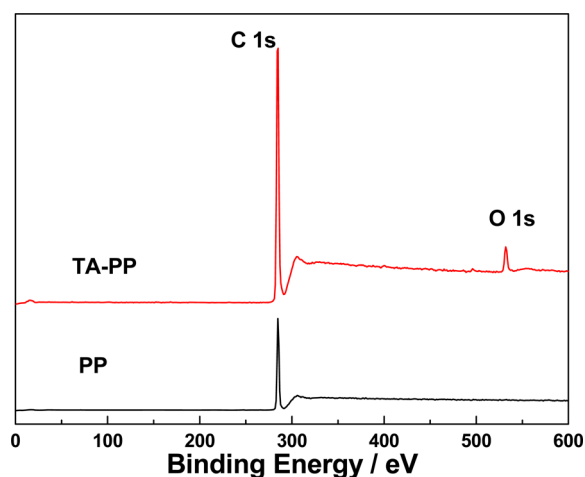


Figure 2. XPS spectra of PP separators without (PP) and with tannic acid coating (TA-PP).

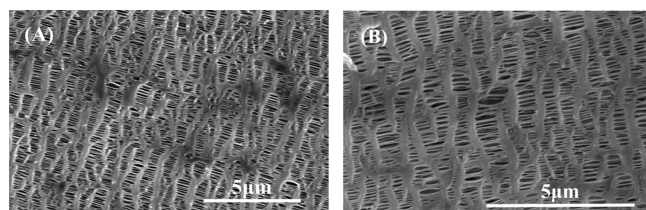


Figure 3. SEM images of PP separators without (A) and with (B) tannic acid coating.

capability.^{4,32,33} Close to the melting temperature of the polymer separators, the separators will fuse, and the pores in the separators will collapse to form a nonporous film that will not only minimize the ionic conduction between the electrodes but also protect the lithium-ion batteries from overcharging or electrically shorting.^{32,33} In general, the melting temperature of the PP separator is about 165 °C.³³ Figure 4 shows DSC thermograms of the PP separators with and without the TA coating. It can be found that the TA-coated PP separator showed DSC thermograms almost identical to that of the original PP separator, and the melting temperature was also around 165 °C. This indicates that the thermal shutdown

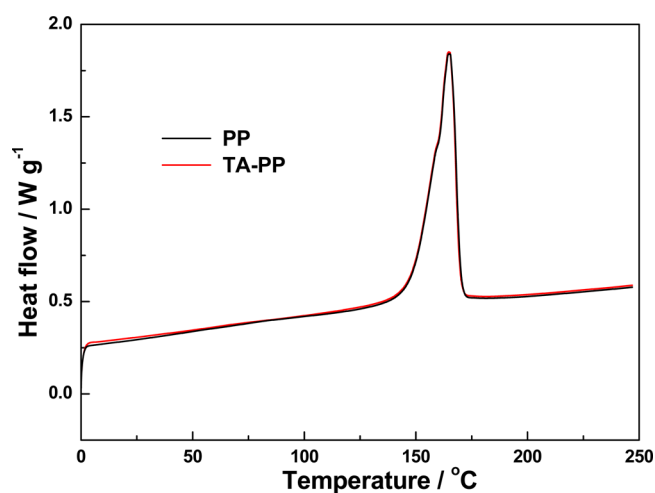


Figure 4. DSC heating curves of PP separators without (PP) and with tannic acid coating (TA-PP).

property of the separators is well maintained even after the TA coating.

The surface properties of the PP separators before and after the TA coating are shown in Figure 5. As shown in Figure 5A,

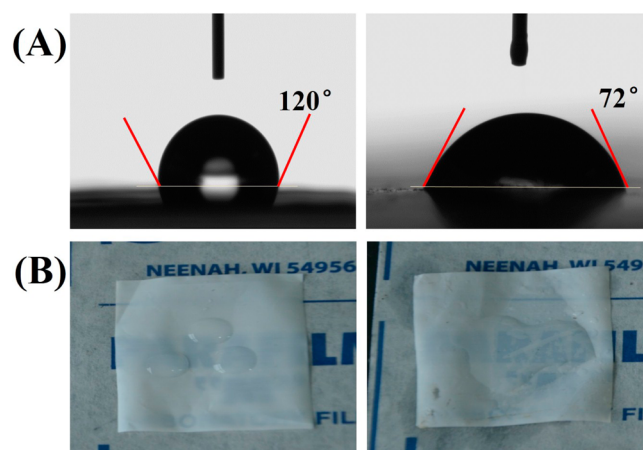


Figure 5. (A) Contact angle images of PP separators without (left) and with (right) tannic acid coating. (B) A wetting test of PP separators without (left) and with (right) tannic acid coating. 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte was poured on the separator surfaces.

the contact angle of water decreased from $120^\circ \pm 2.5^\circ$ for the original PP separator to $72^\circ \pm 1.3^\circ$ for the TA-coated PP separator. This indicates that the PP separator, after the TA coating, becomes more hydrophilic. The wetting testing of the liquid electrolyte on the separators was carried out by pouring 1 M LiPF₆ in EC/DMC (1:1, wt:wt) liquid electrolyte onto the surfaces of the separators with and without the TA coating. As shown in Figure 5B, the original PP separator showed poor compatibility with the liquid electrolyte, and we only observed liquid drops on the separator surfaces. After being coated with TA, the separator exhibited better compatibility with the liquid electrolyte and completely wetted the surfaces. Then, the liquid electrolyte (1 M LiPF₆ in EC/DMC, 1:1, wt:wt) uptake increased from 90 wt % \pm 2.1 wt % of the original PP separator to 125 wt % \pm 2.1 wt % of the TA-coated PP separator. In general, ionic conductivities are expected to depend mainly on the uptake amount of liquid electrolyte in the separators.^{24,34} In addition, the ionic conductivity of the liquid electrolyte (1 M LiPF₆ in EC/DMC, 1:1, wt:wt) used in our experiments was about 10 mS cm⁻¹. The ionic conductivity then also increased from 0.23 ± 0.01 mS cm⁻¹ for the original PP separator to 0.46 ± 0.01 mS cm⁻¹ for the TA-coated PP separator due to the enhanced liquid electrolyte uptake.

The electrochemical stability of the PP separators with and without the TA coating was tested by using cyclic voltammetry in lithium/separators/stainless steel cells. As shown in Figure 6, it can be observed that there is no significant decomposition in either of the PP separators between 1 to 5 V versus Li/Li⁺. This indicates that the TA-coated PP separator shows good electrochemical stability for LIBs applications.

The influence of the TA-coated PP separator on the electrochemical performance was evaluated in Li/LiMn₂O₄ coin-type half cells in the potential range of 3.0–4.6 V (versus Li⁺/Li). Figure 7a shows the first charge–discharge profiles of the cells with the PP separators with and without the TA coating at a current density of 1 C. It can be found that there

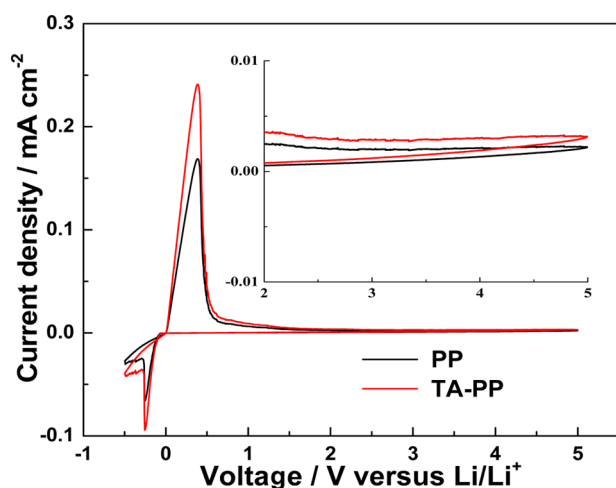


Figure 6. Cyclic voltammety curves of PP separators with and without tannic acid coating with stainless steel as the working electrode, Li foil as the reference, and counter electrodes at room temperature. Scan rate: 10 mV sec⁻¹.

are two pseudoplateaus at around 3.9 and 4.1 V in both the charge and discharge curves, which is the typical electrochemical behavior of the spinel LiMn_2O_4 .³⁵ Both the specific capacity and the Coulombic efficiency of the cell with the TA-coated PP separator (charge-specific capacity: 101.9 mAh g⁻¹, discharge-specific capacity: 101.0 mAh g⁻¹, Coulombic efficiency: 99.11%) show slightly higher values than those of the cell with the original PP separator (charge-specific capacity: 99.7 mAh g⁻¹, discharge-specific capacity: 98.0 mAh g⁻¹, Coulombic efficiency: 98.20%). The reason maybe that the TA-coated PP separator has a higher liquid electrolyte retention ability than that of the original PP separator, resulting in higher ionic conductivity. The cycling performance of both cells was tested at a 1 C rate under constant current conditions. From Figure 7b, it can be observed that both cells show good stable cycling performance and display about 9% capacity loss after 200 cycles. The cell with the TA-coated PP separator shows a slightly higher discharge specific capacity than that of the cell with the original PP separator during the cycling test. After 200 cycles, the specific capacity of the cell with the TA-coated separator (92.0 mAh g⁻¹) was still slightly higher than that of the cell with the original PP separator (89.8 mAh g⁻¹).

The good wetting capability of the TA-coated PP separators on the power performance was confirmed by measuring the discharge specific capacities at different current densities in the range of 0.5–9 C in our experiments. As shown in Figure 7c, it can be observed that the cell with the TA-coated separator shows a better rate capability than that of the cell with the original PP separator. The discharge-specific capacities of the cell with the original separator were reduced significantly with an increase in the current densities from 0.5 C (98.0 mAh g⁻¹) to 9 C (28.2 mAh g⁻¹, 28.8% of the discharge capacity at 0.5 C). In contrast, the cell with the TA-coated separator showed higher specific-capacity retention from 0.5 C (101.0 mAh g⁻¹) to 9 C (53.5 mAh g⁻¹, 53.0% of the discharge capacity at 0.5 C). The discharging potential profiles of both cells at various current densities were shown in Figure 8. It can be found that the discharging potentials of the cell using the original PP separator shifted downward more significantly with increasing current densities compared to that of the cell using the TA-coated separator. This indicates that the voltage drop of the

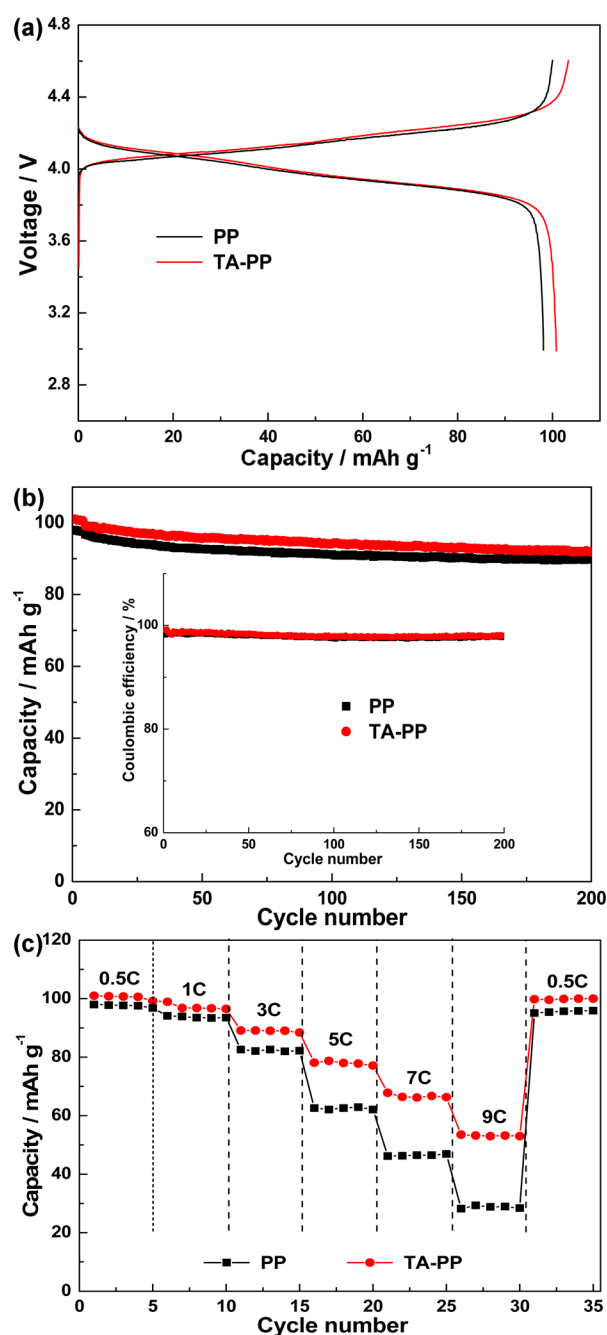


Figure 7. Electrochemical characterizations for the Li/separator/ LiMn_2O_4 cells using PP separators with and without tannic acid coating. (a) Charge–discharge profiles at the 1st cycle for the cells with different separators (1 C for both charge and discharge). (b) Cycling stability and Coulombic efficiency with different separators. Rate: 1 C. (c) Discharge capacity profiles of the cells at various rates. Charge rate: 0.5 C.

original PP cell is more significant than that of the TA-coated PP cell. We can then know that the rate capability of LIBs was more enhanced by the TA coatings on the PP separator. As reported in the literature, the rate capability of the LIBs is directly affected by the ionic conductivity.^{36–38} After being coated with TA, the PP separator becomes more hydrophilic. Thus, it increases the liquid electrolyte retention within the separator, which gives rise to a shorter path of ionic migration in the separators, finally resulting in the increased ionic

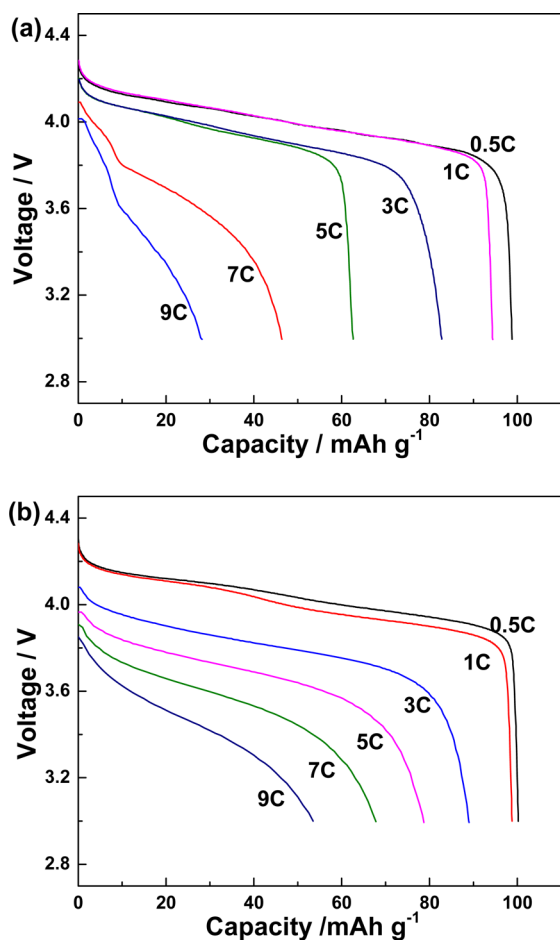


Figure 8. Discharged profiles of the cells using PP separators without (a) and with (b) tannic acid coating at different current densities during the power capability tests shown in Figure 7c. The data shown in this Figure were selected from every first cycle of each discharged rate (i.e., 1st cycle for 0.5 C, 6th cycle for 1 C, 11th cycle for 3 C, 16th cycle for 5 C, 21st cycle for 7 C, and 26th cycle for 9 C, respectively).

conductivity. To further investigate the effect of improved wetting capability of the separators, we carried out AC impedance measurements for both cells using the PP separators with and without the TA coating. The AC impedance was measured after the 1st and 35th cycles, when the cells were discharged to 3.0 V. From Figure 9, it can be found that all impedance spectra consist of one depressed semicircle at high frequencies and a straight line at low frequencies. The equivalent circuits of the LMO electrodes are also shown in Figure 9. R_s , R_{ct} , Z_W , and CPE are denoted in the equivalent circuit as solution resistance, charge transfer resistance, Warburg impedance and constant phase elemental, respectively. It can be found that the R_s resistance of both cells were not markedly changed; the original PP separator increased from 3.68 Ω in the 1st cycle to 3.91 Ω in the 35th cycle, and the TA-coated separator increased from 2.67 Ω in the 1st cycle to 3.78 Ω in the 35th cycle. However, the R_{ct} resistance of the cell with the TA-coated separator was smaller than that of the cell with the original PP separator. After the first cycle, the R_{ct} resistance values of both cells with the original and TA-coated PP separators were about 79.6 and 70.7 Ω , respectively. After the 35th cycle, the R_{ct} resistance values of both cells with the original and TA-coated PP separators were increased to 358.0 and 262.8 Ω , respectively. The lower charge-transfer-resistance

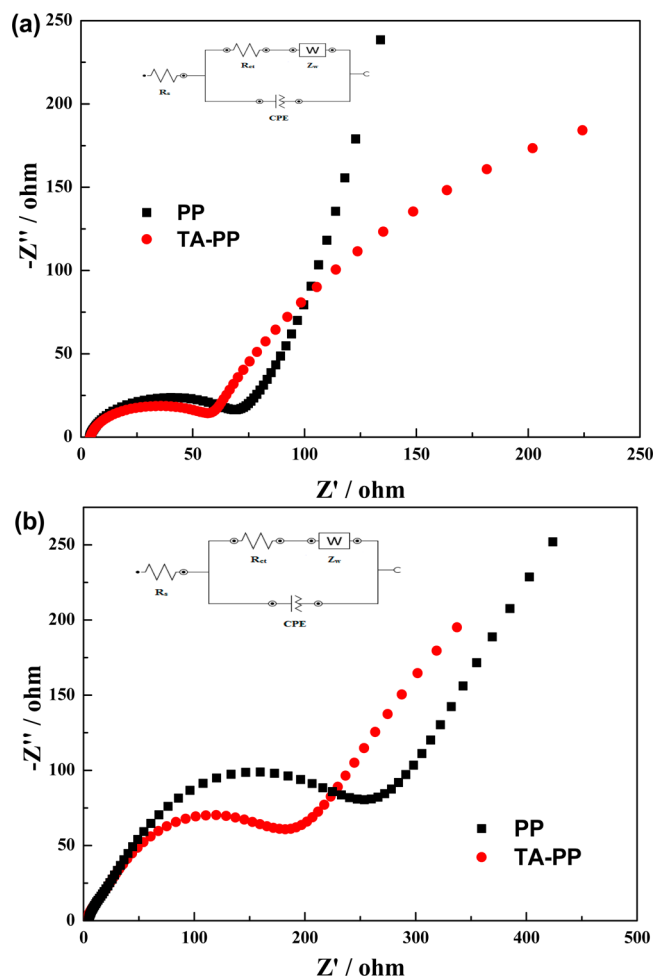


Figure 9. Impedance spectra of the cells using PP separators with and without tannic acid coating after (a) the 1st and (b) the 35th cycles. Rate: 1 C. Temperature: 25 $^{\circ}\text{C}$. Frequency range: 0.1– 10^6 Hz.

of the TA-coated PP separator was due to the hydrophilic surface and higher electrolyte uptake.^{36–38} According to the results mentioned above, it indicates that the TA-coated PP separator with the hydrophilic surface can significantly enhance the battery performance, especially the power capability. In addition, it is worth noting that the TA-coating method is much cheaper compared with the cost of the polydopamine-coating method.²⁵ According to the price from Aladdin, as shown in Table 1, the cost of 1 L of 10 mM dopamine solution (used in the literature)²⁵ is about \$6.73; however, the cost of 1 L of 1 mg mL⁻¹ tannic acid solution (used in our experiments) is only about \$0.14.

4. CONCLUSIONS

In summary, we demonstrated that the natural plant polyphenol surface-coating process can solve the wetting capability issue of separators for LIB applications. The tannic acid coatings make the surface of PP separators more hydrophilic, which then increases the electrolyte retention ability and ionic conductivity of the TA-coated separators. The increased ionic conductivity enhances the battery performance, especially for rate capability. We expect that this “green” surface-coating process is quite versatile and thus is applicable for developing other separators and membranes for various energy storage devices (such as lithium-ion batteries, super-

capacitors, and flow batteries), fuel cells, and membrane separations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lilei0323@sjtu.edu.cn.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

This research was supported by the National Key Basic Research Program of China (no. 2014CB932303), the Natural Science Foundation of Shanghai (14ZR1422100), the Science and Technology Commission of Shanghai Municipality (14DZ2250800), and the Shanghai Key Lab of Electrical Insulation and Thermal Ageing (Shanghai Key Lab of Electrical and Electronic Polymer Materials). We thank the Instrumental Analysis Center of Shanghai Jiaotong University.

REFERENCES

- (1) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414*, 359–367.
- (2) Scrosati, B.; Hassoun, J.; Sun, Y.-K. Lithium-Ion Batteries. A Look into the Future. *Energy Environ. Sci.* **2011**, *4*, 3287–3295.
- (3) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4417.
- (4) Arora, P.; Zhang, Z. J. Battery Separators. *Chem. Rev.* **2004**, *104*, 4419–4462.
- (5) Daniel, C. Materials and Processing for Lithium-Ion Batteries. *JOM* **2008**, *60*, 43–48.
- (6) Kim, J. Y.; Lee, Y.; Lim, D.-Y. Plasma-Modified Polyethylene Membrane as a Separator for Lithium-Ion Polymer Battery. *Electrochim. Acta* **2009**, *54*, 3714–3719.
- (7) Gineste, J. L.; Pourcelly, G. Polypropylene Separator Grafted with Hydrophilic Monomers for Lithium Batteries. *J. Membr. Sci.* **1995**, *107*, 155–164.
- (8) Gao, K.; Hu, X.; Yi, T.; Dai, C. PE-g-MMA Polymer Electrolyte Membrane for Lithium Polymer Battery. *Electrochim. Acta* **2006**, *52*, 443–449.
- (9) Ko, J. M.; Min, B. G.; Kim, D.-W.; Ryu, K. S.; Kim, K. M.; Lee, Y. G. S. H.; Chang, S. H. Thin-film Type Li-Ion Battery, Using a Polyethylene Separator Grafted with Glycidyl Methacrylate. *Electrochim. Acta* **2004**, *50*, 367–370.
- (10) Lee, J. Y. B.; Bhattacharya, B.; Park, Y. C. J. K.; Nho, Y.-C. New Separator Prepared by Electron Beam Irradiation for High Voltage Lithium Secondary Batteries. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2009**, *267*, 2390–2394.
- (11) Lee, J. Y.; Lee, Y. M.; Bhattacharya, B.; Nho, Y. C.; Park, J. K. Separator Grafted with Siloxane by Electron Beam Irradiation for Lithium Secondary Batteries. *Electrochim. Acta* **2009**, *54*, 4312–4315.
- (12) Jeong, K. U.; Chae, H. D.; Lim, C. I.; Lee, H. K.; Ahn, J. H.; Nah, C. Fabrication and Characterization of Electrolyte Membranes Based on Organoclay/Tripolypropylene glycol Diacrylate/Poly(vinylidene fluoride) Electrospun Nanofiber Composites. *Polym. Int.* **2010**, *59*, 249–255.
- (13) Song, M. K.; Kim, Y. T.; Kim, Y. T.; Cho, B. W.; Popov, B. N.; Rhee, H. W. Thermally Stable Gel Polymer Electrolytes. *J. Electrochem. Soc.* **2003**, *150*, A439–A444.
- (14) Kim, K. J.; Kim, Y. H.; Song, J. H.; Jo, Y. N.; Kim, J. S.; Kim, Y. J. Effect of Gamma Ray Irradiation on Thermal and Electrochemical Properties of Polyethylene Separator for Li Ion Batteries. *J. Power Sources* **2010**, *195*, 6075–6080.
- (15) Li, H.; Ma, X. T.; Shi, J. L.; Yao, Z. K.; Zhu, B. K.; Zhu, L. P. Preparation and Properties of Poly(ethylene oxide) Gel Filled Polypropylene Separators and Their Corresponding Gel Polymer Electrolytes for Li-Ion Batteries. *Electrochim. Acta* **2011**, *56*, 2641–2647.
- (16) Shi, J. L.; Fang, L. F.; Li, H.; Zhang, H.; Zhu, B. K.; Zhu, L. P. Improved Thermal and Electrochemical Performances of PMMA Modified PE Separator Skeleton Prepared via Dopamine-initiated ATRP for Lithium Ion Batteries. *J. Membr. Sci.* **2013**, *437*, 160–168.
- (17) Sohn, J. Y.; Im, J. S.; Shin, J.; Nho, Y. C. PVDF-HFP/PMMA-coated PE Separator for Lithium Ion Battery. *J. Solid State Electrochem.* **2012**, *16*, 551–556.
- (18) Song, J.; Ryou, M. H.; Son, B.; Lee, J. N.; Lee, D. J.; Lee, Y. M.; Choi, J. W.; Park, J. K. Co-polyimide-coated Polyethylene Separators for Enhanced Thermal Stability of Lithium Ion Batteries. *Electrochim. Acta* **2012**, *85*, 524–530.
- (19) Schroen, C. G. P. H.; Wijers, M. C.; Cohen-Stuart, M. A.; Vander Padt, A.; Van't Riet, K. Membrane Modification to Avoid Wettability Changes Due to Protein Adsorption in An Emulsion/Membrane Bioreactor. *J. Membr. Sci.* **1993**, *80*, 265–274.
- (20) Jung, Y. S.; Cavanagh, A. S.; Gedvilas, L.; Widjonarko, N. E.; Scott, I. D.; Lee, S. H.; Kim, G. H.; George, S. M.; Dillon, A. C. Improved Functionality of Lithium-Ion Batteries Enabled by Atomic Layer Deposition on the Porous Microstructure of Polymer Separators and Coating Electrodes. *Adv. Energy Mater.* **2012**, *2*, 1022–1027.
- (21) Xu, Q.; Yang, J.; Dai, J.; Yang, Y.; Chen, X.; Wang, Y. Hydrophilization of Porous Polypropylene Membranes by Atomic Layer Deposition of TiO₂ for Simultaneously Improved Permeability and Selectivity. *J. Membr. Sci.* **2013**, *448*, 215–222.
- (22) Chen, H.; Lin, Q.; Xu, Q.; Yang, Y.; Shao, Z.; Wang, Y. Plasma Activation and Atomic Layer Deposition of TiO₂ on Polypropylene Membranes for Improved Performances of Lithium-Ion Batteries. *J. Membr. Sci.* **2014**, *458*, 217–224.
- (23) Lee, H.; Yanilmaz, M.; Toprakci, O.; Fu, K.; Zhang, X. A Review of Recent Developments in Membrane Separators for Rechargeable Lithium-Ion Batteries. *Energy Environ. Sci.* **2014**, *7*, 3857–3886.
- (24) Zhang, S. S. A Review on the Separators of Liquid Electrolyte Li-Ion Batteries. *J. Power Sources* **2007**, *164*, 351–364.
- (25) Ryou, M.-H.; Lee, M.; Park, J.-K.; Choi, J. W. Mussel-Inspired Polydopamine-Treated Polyethylene Separators for High-Power Li-Ion Batteries. *Adv. Mater.* **2011**, *23*, 3066–3070.
- (26) Krishnamoorthy, L.; Arif, P. M.; Ahmedkhan, R. Separation of Proteins from Aqueous Solution Using Cellulose Acetate/Poly (vinyl chloride) Blend Ultrafiltration Membrane. *J. Mater. Sci.* **2011**, *46*, 2914–2921.
- (27) Aromal, S. A.; Philip, D. Facile One-Pot Synthesis of Gold Nanoparticles Using Tannic Acid and Its Application in Catalysis. *Phys. E* **2012**, *44*, 1692–1696.
- (28) Cumberland, S. L.; Strouse, G. F. Analysis of the Nature of Oxyanion Adsorption on Gold Nanomaterial Surfaces. *Langmuir* **2002**, *18*, 269–276.
- (29) Shankar, S. S.; Rai, A.; Ahmad, A. M.; Sastry, M. Rapid Synthesis of Au, Ag and Bimetallic Au Core-Ag Shell Nanoparticles Using Neem (Azadirachta Indica) Leaf Broth. *J. Colloid Interface Sci.* **2004**, *275*, 496–502.
- (30) Shen, D. S.; Mathew, J.; Philip, D. Phytosynthesis of Au, Ag and Au-Ag Bimetallic Nanoparticles Using Aqueous Extract and Dried Leaf of Anacardium Occidentale. *Spectrochim. Acta, Part A* **2011**, *79*, 254–262.
- (31) Philip, D.; Unni, C. Extracellular Biosynthesis of Gold and Silver Nanoparticles Using Krishna Tulsi (Ocimum Sanctum) Leaf. *Phys. E* **2011**, *43*, 1318–1322.
- (32) Venugopal, G.; Moore, J.; Howard, J.; Pandalwar, S. Characterization of Microporous Separators for Lithium-Ion Batteries. *J. Power Sources* **1999**, *77*, 34–41.
- (33) Huang, X. Separator Technologies for Lithium-Ion Batteries. *J. Solid State Electrochem.* **2011**, *15*, 649–662.

(34) Kim, J. Y.; Lee, Y.; Lim, D. Y. Plasma-Modified Polyethylene Membrane as a Separator for Lithium-Ion Polymer Battery. *Electrochim. Acta* **2009**, *54*, 3714–3719.

(35) Lee, H.-W.; Muralidharan, P.; Ruffo, R.; Mari, C. M.; Cui, Y.; Kim, D. K. Ultrathin Spinel LiMn_2O_4 Nanowires as High Power Cathode Materials for Li-Ion Batteries. *Nano Lett.* **2010**, *10*, 3852–3856.

(36) Levi, M. D.; Salitra, G.; Markovsky, B.; Teller, H.; Aurbach, D.; Heider, U.; Heider, L. Solid-State Electrochemical Kinetics of Li-Ion Intercalation into $\text{Li}_{1-x}\text{CoO}_2$: Simultaneous Application of Electro-analytical Techniques SSCV, PITT, and EIS. *J. Electrochem. Soc.* **1999**, *146*, 1279–1289.

(37) Lee, Y. S.; Jeong, Y. B.; Kim, D. W. Cycling Performance of Lithium-Ion Batteries Assembled with a Hybrid Composite Membrane Prepared by an Electrospinning Method. *J. Power Sources* **2010**, *195*, 6197–6201.

(38) Zhang, S. S.; Xu, K.; Jow, T. R. Electrochemical Impedance Study on the Low Temperature of Li-Ion Batteries. *Electrochim. Acta* **2004**, *49*, 1057–1061.