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Polypropylene Separators with Robust Mussel-inspired Coatings for High Lithium-ion Battery Performances

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 Electronic Supplementary Information

Abstract The performances of lithium-ion batteries (LIBs) are dependent on the wettability and stability of porous separators. Mussel-inspired coatings seem to be useful to improve the surface wettability of commercialized polyolefin separators. However, it is still a challenge to guarantee their stability under polar electrolytes. Herein, we report a facile and versatile way to enhance the wettability and stability of polypropylene separators by constructing robust polydopamine (PDA) coatings triggered with $\text{CuSO}_4/\text{H}_2\text{O}_2$. These coatings were conveniently deposited on the polypropylene separator surfaces and the PDA-coated separators exhibited the improved surface wettability and thermal stability. The electrolyte uptake increased nearly two folds from the pristine separator to the modified ones. Correspondingly, the ionic conductivity also rose from $0.82 \text{ mS} \cdot \text{cm}^{-1}$ to $1.30 \text{ mS} \cdot \text{cm}^{-1}$. Most importantly, the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings were very stable under strong polar electrolytes, endowing the cells with excellent cycle performance and enhanced C-rate capacity. Overall, the results unequivocally demonstrate that application of PDA coatings on polyolefin separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ is a facile and efficient method for improving the wettability and stability of separators for high LIBs performance.

Keywords Polypropylene separator; Lithium-ion battery; Surface wettability; Dopamine; Mussel-inspired coatings

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INTRODUCTION

The widespread proliferation of portable electronic devices and grid-scale energy storage systems into everyday life has occurred at an astonishing speed in recent years. Undoubtedly, lithium-ion batteries (LIBs) occupy a dominant position among numerous rechargeable power sources with many advantages, including high energy density at an affordable cost while providing sufficient cycle life.^[1–4] However, each of these performance attributes requires continued improvement and new functional materials for all cell components (e.g., electrode, electrolyte, and porous separator) offer one the best means to do so. As an important component of LIBs, the porous separators permit lithium ions transport between anode and cathode as well as prevent direct contact and shorting of the two electrodes.^[5–7] Therefore, these separators also play a critical role in high LIBs performance.

At present, polyolefin membranes have been widely applied as porous separators for LIBs due to their low cost, proper mechanical strength, and electrochemical stability.^[8]

However, one of the key issues is that these polyolefin separators demonstrate low surface energy resulting in a low affinity with polar electrolytes such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) to penetrate them.^[9,10] A series of strategies have been proposed to improve the surface wettability of polyolefin separators toward electrolytes, including dip-coating,^[11,12] plasma treatment,^[13] and UV-irradiation grafting.^[14] For example, Park *et al.* fabricated a polyimide coating on polyethylene separators to enhance their surface wettability and thermal stability by a simple dip-coating method.^[11] One challenge to employing a polyimide coating is low adhesion strength between the polar polyimide and the nonpolar polyethylene yielding poor separator stability. Another drawback when applying a coating to a porous separator is the resultant pore blocking and reduction in porosity. Zhang *et al.* reported that polypropylene nonwoven-based composites treated by plasma exhibited improved hydrophilicity, electrolyte uptake, cycle performance, and C-rate capability than conventional (*i.e.*, non-modified) separators.^[13] However, the plasma process that etches the separator structure results in damage and thereby compromises its mechanical integrity. In summary, low cost and improved microporous separators for LIBs require facile operation for the surface modification using large, scalable methods without the need of multistep procedures that employ complex

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instrumentation.

Mussel-inspired chemistry has been recognized as a facile and versatile method for surface modification since 2007.^[15–18] Inspired by this, Ryou and co-workers utilized polydopamine (PDA)-modified polyethylene membranes as LIBs separators. PDA coatings improved the surface wettability of polyethylene separators as well as electrolyte uptake tremendously, which aided in greater LIB performance.^[19] Subsequently, they investigated the roles of PDA coatings on polyethylene separators for LIBs and revealed that the excellent hydrophilicity and the strong adhesion of PDA coatings suppressed the growth of Li-dendrites and fostered greater battery cycle life.^[20] In addition, Cao *et al.* also fabricated PDA coatings on the electrospun poly(vinylene difluoride) nanofibrous membranes to improve the surface hydrophilicity, electrolyte uptake, and ionic conductivity of LIBs separators.^[21] Apart from PDA coatings, its derivatives have also been widely studied for the surface modification of separators, such as pyrogallol acid,^[22] tannic acid,^[23] and catechol.^[24,25] Overall, mussel-inspired chemistry has an excellent track record for the surface modification of LIBs separators. However, the aforementioned reports involve the deposition time of PDA of ten hours or longer (*e.g.*, a few days), which inhibits the large-scale production for practical applications. The most critical issue facing PDA coatings for LIB separators is their poor chemical stability. PDA coatings are unstable in extremely acidic and alkaline media as well as in polar organic solvents due to the presence of non-covalent assemblies.^[26] It is reasonable to expect that PDA coatings on polyolefin separators are also unstable under strong polar electrolytes, which may lead to elution from separators and directly compromise the performances of LIBs. Therefore, it is still a challenge to construct PDA coatings on LIBs separators with robust stability under polar electrolytes.

In our previous work, we have proposed a facile method for realizing the rapid deposition of PDA coatings by using $\text{CuSO}_4/\text{H}_2\text{O}_2$ as a trigger on polypropylene microfiltration membranes (PPMMs).^[27–29] The PDA coatings exhibited enhanced uniformity and hydrophilicity as compared to the ones prepared by air oxidation. It is worth noting that PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ provided remarkable stability in polar solvents, such as *N,N*-dimethylformamide and dimethyl sulfoxide. Inspired from these results, we used the same method to prepare PDA-coated PPMMs as LIBs separators. These PDA-coated separators undergoing $\text{CuSO}_4/\text{H}_2\text{O}_2$ triggering possessed improved wettability, electrolyte uptake, and stability towards the polar electrolytes compared with those prepared by conventional PDA deposition. In addition, the newly prepared and robust PDA coatings on separators endowed the corresponding LIBs with enhanced cycle performance, C-rate capacity, and safety properties.

EXPERIMENTAL

Materials

Polypropylene microfiltration membranes (PPMMs, thickness $\sim 70\ \mu\text{m}$ and porosity $\sim 47\%$) were kindly supplied by Beijing Key Laboratory of Energy Conversion and Storage

Materials, China. Samples were cut into rounds with a diameter of 2.5 cm, washed by acetone overnight to remove impurities adsorbed, and then dried in a vacuum oven at $50\ ^\circ\text{C}$. Dopamine hydrochloride, ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) were purchased from Sigma-Aldrich. Other reagents such as tris-(hydroxymethyl)aminomethane, copper(II) sulfate pentahydrate, hydrogen peroxide, ethanol, and hydrochloric acid were procured from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Water used in all experiments was deionized and ultrafiltrated to $18.2\ \text{M}\Omega$ with an ELGA LabWater system (France).

Fabrication of PDA-coated Separators Oxidized by $\text{CuSO}_4/\text{H}_2\text{O}_2$ and Air

$\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered fabrication of PDA coatings on PPMMs

The deposition process was executed according to our previous work.^[27] Dopamine hydrochloride ($2\ \text{mg}\cdot\text{mL}^{-1}$) was dissolved in Tris buffer solution ($\text{pH} = 8.5$, $50\ \text{mmol}\cdot\text{L}^{-1}$) with CuSO_4 ($5\ \text{mmol}\cdot\text{L}^{-1}$)/ H_2O_2 ($19.6\ \text{mol}\cdot\text{L}^{-1}$). PPMMs were prewetted by ethanol and then immersed in the Tris buffer solution for 40 min. Subsequently, the samples were washed with water and dried in a vacuum at $50\ ^\circ\text{C}$. Note that PPMMs were selected as representative polyolefin separators to elucidate the feasibility of our modification strategy, which can also be applied for the modification of Celgard or other type of polyolefin separators due to the universality of mussel-inspired PDA.

Air oxidized fabrication of PDA coatings on PPMMs

The conventional deposition was carried out according to typical procedure.^[30] Dopamine hydrochloride ($2\ \text{mg}\cdot\text{mL}^{-1}$) was dissolved in Tris buffer solution ($\text{pH} = 8.5$, $50\ \text{mmol}\cdot\text{L}^{-1}$). PPMMs were prewetted by ethanol and then immersed in the Tris buffer solution for 12 h. Subsequently, the samples were washed by water and dried in a vacuum at $50\ ^\circ\text{C}$.

Separator Characterization

Morphology of the samples was observed by a field emission scanning electron microscope (FESEM, Hitachi S4800, Japan). X-ray photoelectron spectra were collected by a spectrometer (XPS, PHI-5000C ESCA Perkin Elmer, USA) with Al $K\alpha$ excitation radiation ($1486.6\ \text{eV}$). Both static and dynamic contact angles were detected using a DropMeter A-200 contact angle system (MAIST VisionInspection & Measurement Co., Ltd. China). The pore size was measured by the capillary flow porometry method (CFP-1500AE, PMI) with the liquid (Surface tension: $20.1\ \text{mN}\cdot\text{m}^{-1}$). The thermal stability was evaluated by measuring the shrinkage rate of the separators after exposure to $150\ ^\circ\text{C}$ for 30 min. The chemical stability of PDA coatings on the separators was observed by immersing them into $1\ \text{mol}\cdot\text{L}^{-1}$ LiPF_6 in electrolyte (EC/DMC/DEC = 1/1/1, $V/V/V$) for 2 h. The electrolyte uptake was determined by comparing the mass change of the dry and the electrolyte-soaked separators, which is calculated by the following equation:

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

where W_1 and W_0 represent the weight of the electrolyte-

soaked separator and the dry separator, respectively.

Electrochemical Test

The electrolyte-soaked separators and two stainless steel (SS) electrodes were assembled into a blocking-type cell for the ionic conductivity measurement. AC impedance spectra from 0.1 MHz to 0.01 Hz were obtained on an electrochemical working station (Chenhua, CHI660E, China). The ionic conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{L}{A \times R_b} \quad (2)$$

where L and R_b are the thickness of separators and bulk resistance, respectively. A is the contact area between separators and SS electrodes. The impedance was measured by AC impedance spectra of the Li/electrolyte-soaked separator/Li cells from 0.1 MHz to 0.01 Hz at room temperature. The discharge/charge cycle tests of LiFePO₄/electrolyte-soaked separator/Li cells were conducted in the voltage range of 2.5–4.2 V at a current density of 0.2 C by LAND battery testing system. In addition, rate capacity of LiFePO₄/electrolyte-soaked separators/Li cells was measured at current densities of 0.2, 0.5, 1, 2, and 5 C by LAND battery testing system.

RESULTS AND DISCUSSION

Chemical Stability of PDA Coatings on the Separators

The performance of LIBs was influenced by the chemical stability of PDA coatings on the separators. As previously mentioned, PDA coatings are tremendously unstable under extreme chemical conditions such as low or high pH solutions and strong polar solvents. Furthermore, their stability is dependent on many factors, such as the coating composition, the coating uniformity, the coating morphology, and the substrate property.^[31] Electrolytes applied for LIBs typically consist of organic solvents with strong polarity and the se-

parator surfaces are directly immersed into and contacted with these electrolytes. Although PDA coatings improve solvent wettability of the separators, chemical stability needs to be addressed for moving this material from its nascent stage to commercial adoption. Fig. 1 compares the chemical stability of PDA coatings prepared by two deposition methods. The samples with PDA coatings triggered by CuSO₄/H₂O₂ appeared to be stable in the electrolyte solution of 1 mol·L⁻¹ LiPF₆ owing to the molecular structure of PDA with enhanced covalent parts and cross-linking sites.^[27] In contrast, the electrolyte solution gradually turned to yellow when a PDA-coated separator oxidized by air was immersed in the same electrolyte solution for more than 1 h. The yellow color means that PDA particles were eluted from the separator's surface into the liquid electrolyte solution in this case. These particles in the electrolyte solution altered the electrolyte properties and in turn compromised the performance of LIBs.^[32] To the best of our knowledge, it is the first time to point out and address the stability issue of PDA coatings on the electrolyte solution of 1 mol·L⁻¹ LiPF₆, and the enhanced stability holds great potential in the further development of mussel-inspired separators, especially their long-term service performance.

Thermal Stability of PDA-coated Separators

It is well known that the thermal stability of separators is another important consideration because of its influence on safety performance of LIBs.^[33–35] Polyolefin separators have relatively poor thermal stability, and high temperature causes thermal shrinkage. Serious thermal shrinkage leads to electrode shorting and potentially catastrophic cell explosion.^[36] We compared the thermal stability between non-modified and PDA-coated separators (Fig. 2). The non-modified separator showed poor thermal stability with a 41% shrinkage after heat treatment at 150 °C for 30 min. By contrast, only 25% thermal shrinkage occurred for the PDA-coated sepa-

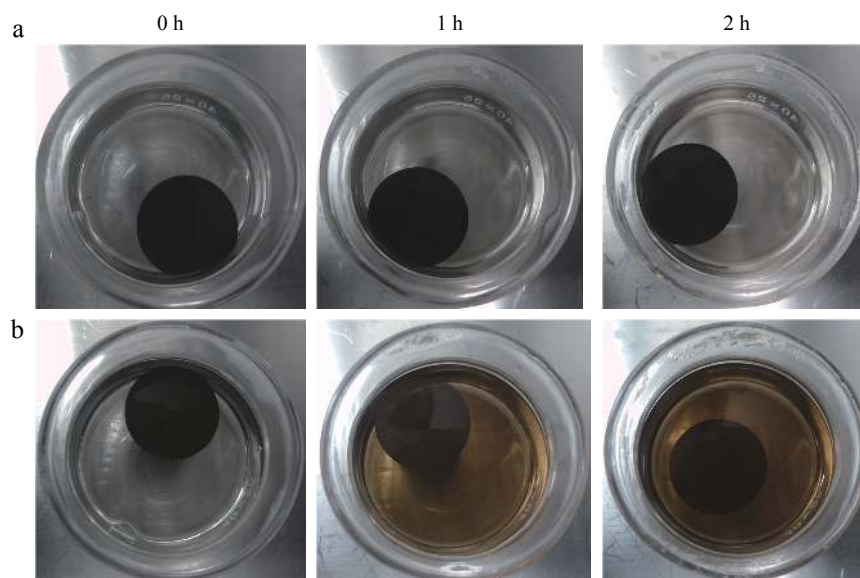


Fig. 1 Digital photographs of (a) PDA-coated separator triggered by CuSO₄/H₂O₂ and (b) PDA-coated separator oxidized by air after the immersion in 1 mol·L⁻¹ LiPF₆ in electrolyte (EC/DMC/DEC = 1/1/1) at different time points

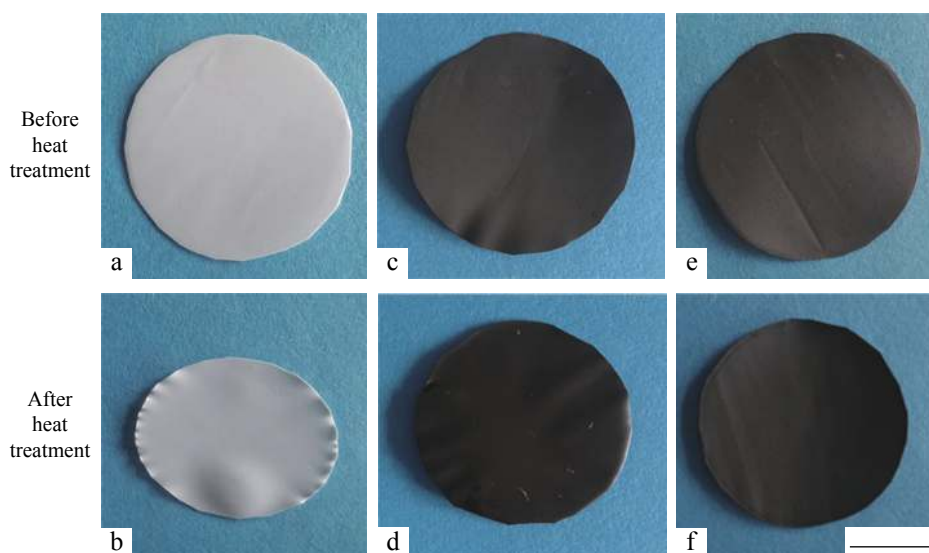


Fig. 2 Digital photographs of (a, b) non-modified separator, (c, d) PDA-coated separator oxidized by air, and (e, f) PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ (a, c, e) before and (b, d, f) after exposure to $150\text{ }^\circ\text{C}$ for 30 min. The scale bar is 1 cm.

rator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$, which was slightly better than PDA-coated separator through air oxidation ($\sim 27\%$). These results demonstrated that the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings improved the thermal stability of polypropylene separators to some extent.

Surface Wettability of PDA-coated Separators

Surface hydrophilicity is important for improving the wettability of separators toward electrolyte. Water contact angle (WCA) was measured to characterize the surface hydrophilicity of non-modified and PDA-coated separators (Fig. 3). WCA of the non-modified separator was 121° , which implies a very hydrophobic surface. WCA declined to $< 20^\circ$ for the PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$, which was substantially better than that of PDA-coated separator oxidized by air. These results indicate that the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings were a hydrophilic separator as opposed to the non-modified separator. Hence, the separators with $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings were preferential

to polar solvents, because more oxygen- and nitrogen-containing polar groups were introduced on the polypropylene separator surfaces (Fig. S1 and Table S1 in electronic supplementary information, ESI).

The surface wettability of separators was further evaluated by measuring the electrolyte contact angle and the electrolyte uptake.^[37] Figs. 4(a)–4(c) show that the electrolyte contact angle was $< 20^\circ$ on the PDA-coated separator, which was far less than that on the non-modified separator ($\sim 46^\circ$). From the experiments, we observed that the electrolyte drop permeated through the PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ in 7 s, while it took 30 s for an identical electrolyte drop to permeate the air-oxidized PDA coatings on the separators. Overall, the PDA coatings exhibited outstanding electrolyte wettability due to the presence of more polar functional groups. Similarly, the surface wettability was further confirmed by the electrolyte uptake, which was $(289.8 \pm 10.8)\%$ (Fig. 4d). This value was much greater than that of the non-modified separator ($(157.5 \pm 12.3)\%$).

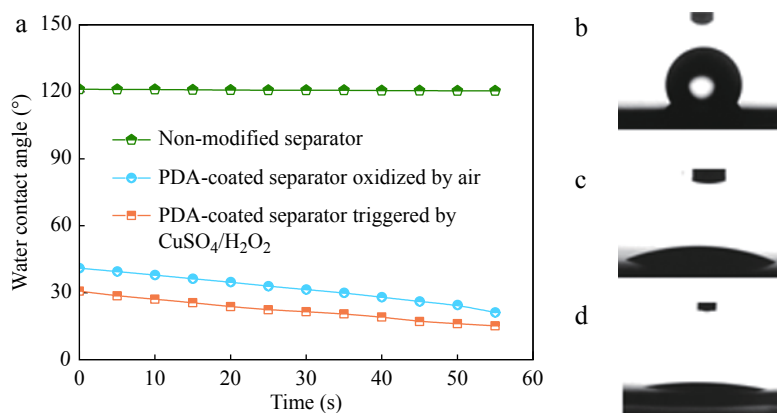


Fig. 3 (a) Water contact angle of the non-modified and PDA-coated separators with different preparation methods; Images of water contact angle of different samples: (b) non-modified separator, (c) PDA-coated separator oxidized by air, and (d) PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$

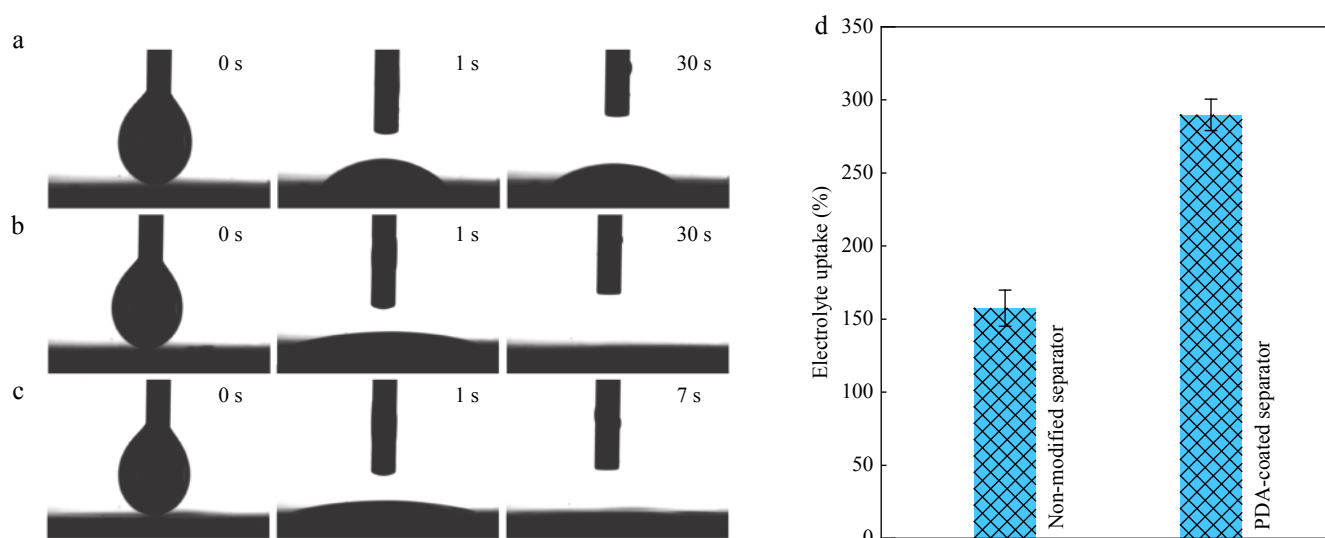


Fig. 4 Images for the electrolyte (EC/DMC/DEC = 1/1/1) contact angle of different samples: (a) non-modified separator, (b) PDA-coated separator oxidized by air, and (c) PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$; (d) Electrolyte uptake (%) of the non-modified separator and the PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$. Electrolyte uptake of PDA-coated separator oxidized by air was not measured because of unstable PDA coatings in the electrolyte.

In general, the electrolyte uptake will directly impact the through-plane resistance and the ion conductivity of separators. AC impedance spectroscopy determined that the high frequency resistance (HFR) decreased from 4.87Ω to 3.07Ω when using separators with PDA-coating triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$. HFR represents the ohmic resistance of the electrolyte. The reduction in the resistance corresponded to an increase in the ion conductivity from $0.82 \text{ mS}\cdot\text{cm}^{-1}$ to $1.30 \text{ mS}\cdot\text{cm}^{-1}$ after the deposition of PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$. The ionic conductivity of the separators in electrolyte with PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ was higher than that of air-oxidized PDA coatings on the separator ($1.20 \text{ mS}\cdot\text{cm}^{-1}$) (Fig. S2 and Table S2 in ESI).

Structure of PDA-coated Separators

Another issue that warrants investigation by the surface modification of the separator is pore blocking and porosity decrease.^[38] Pore blocking and porosity decreases of the separators have adverse effects on LIB performance.^[22] PDA coatings oxidized by air usually produce a large number of particles on the separator surface,^[39] which block solvent penetration into the separator pores or solvent transport within the pores and thereby lead to an undesirable decrease in porosity (Fig. 5). FESEM images show that the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings exhibited high uniformity with

practically no visible PDA particles on the separator surface, attributed to the conformality of rapid deposition. To further evaluate the change of separator pore size, capillary flow porometry was performed to measure the separator pore size (Fig. S3 in ESI). The mean pore size of PDA-coated separator was 553 nm, which was close to that of the non-modified separator (mean pore size: 563 nm). Therefore, the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA deposition process had a minor influence on the separator structure. To recap briefly, the $\text{CuSO}_4/\text{H}_2\text{O}_2$ -triggered PDA coatings provided better chemical stability, hydrophilicity, electrolyte wettability, conformality, and ionic conductivity compared to the conventional air-triggered PDA deposition processes.

Cell Performance of PDA-coated Separators

Cells ($\text{LiFePO}_4/\text{separator}/\text{Li}$) were assembled with different electrolyte-soaked separators to evaluate the influence of PDA coatings on the performances of LIBs. Fig. 6 shows the discharge potential profiles for the cells under a voltage of 2.5–4.2 V at various rates ranging from 0.2 C to 5 C. It was observed that the discharge capacity and voltage gradually decayed with the increase of current density. However, the decay was more pronounced for the non-modified separator than the PDA-coated one. In addition, the discharge capacity also decreased gradually with the increase of discharge rate

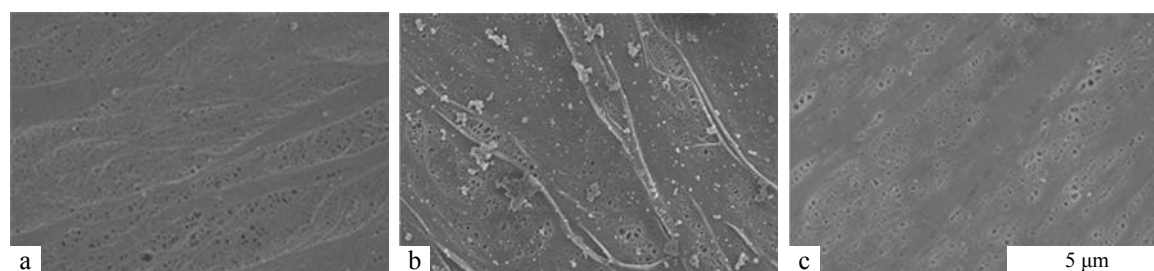


Fig. 5 SEM images of (a) non-modified separator, (b) PDA-coated separator oxidized by air, and (c) PDA-coated separator triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$

from 0.2 C to at 5 C (Fig. 7a). It is noteworthy that the discharge capacity of cells assembled with those PDA-coated separators was much higher than that with the non-modified separator at different discharge current densities. When the discharge rate was kept at 5 C, the discharge capacity was $56.2 \text{ mAh}\cdot\text{g}^{-1}$ for cells assembled with the non-modified separator, which was 41.7% of their discharge capacity at 0.2 C. Comparatively, cells assembled with PDA-coated separator exhibited much higher discharge capacity retention at 5 C ($73.9 \text{ mAh}\cdot\text{g}^{-1}$, 48.9% of discharge capacity at 0.2 C). The discharge capacity maintained a plateau value at 5 C at larger capacity values, which was attributed to the high stability of PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$. To further demonstrate the promise of the separators with PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$, the air oxidized PDA-coated separators were also assembled into cells and their discharge C-rate capacities were measured for comparison (Fig. S4 in ESI). It is worthy pointing out that the discharge capacity dropped drastically at 5 C for the air oxidized PDA-coated separators, even lower than that of the cells assembled with nascent separators. We ascribed such discharge capacity decay to the poor chemical stability of PDA coatings, because the polar electrolyte dissolved non-covalent part of their molecule structure to detach them from the separator into electrolyte. Due to the presence of electrophoresis phenomenon, these detached PDA particles tended to move to the surface of electrodes, especially at the high rate charge/discharge, posing a great influence on with Li-ion migration.^[40]

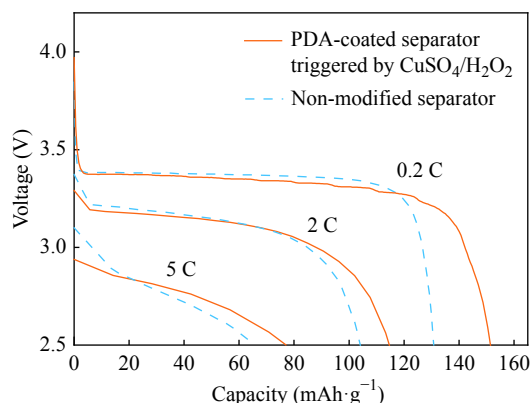


Fig. 6 Discharged profiles of the LiFePO_4 /separator/Li cells assembled with non-modified separator and PDA-coated separator at different current densities during the power capability tests. The data are every first cycle of different current densities.

The impedance of the separators was further measured with results shown in Fig. 7(b) and Table 1. The Nyquist plots from the AC impedance spectra contained two semi-circles in high-middle frequency regions and a straight line in low frequency region.^[41] The high, middle, and low frequencies represent Li-ion migration through the solid electrolyte interphase (SEI) layer (R_{SEI}), the charge transfer between electrode and electrolyte (R_{ct}), and Li-ion diffusion in the electrodes, respectively. Additionally, R_b represents the bulk resistance of the cell.^[19] It is worth noting that the values of R_{SEI} and R_{ct} in the cells assembled with the PDA-coated separators triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ were smaller

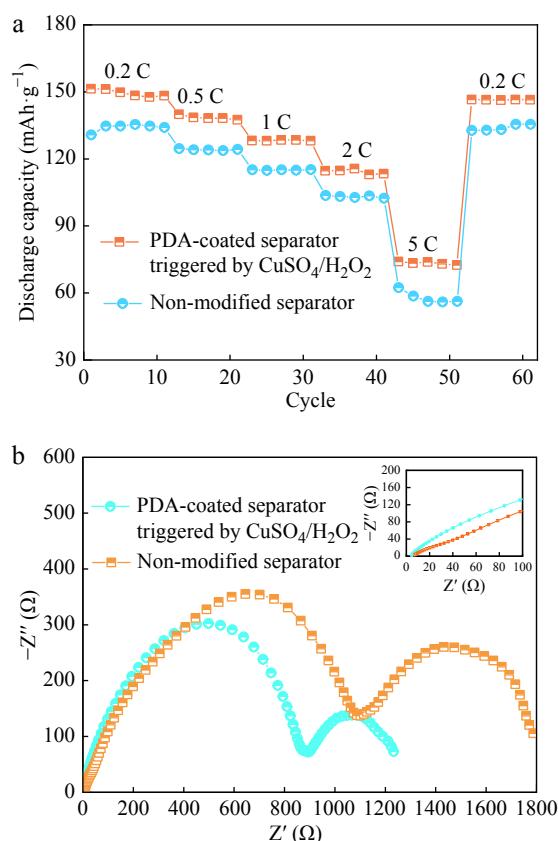


Fig. 7 (a) Discharge C-rate capacity of the LiFePO_4 /separator/Li cells; (b) Nyquist plots of the Li/separator/Li cells

Table 1 Resistance of the Li/separator/Li cells assembled with different separators

Separator	R_b (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	R (Ω)
Non-modified separator	7.3	1081.7	712.5	1801.5
Separator with PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$	4.6	871.9	367.3	1243.8

than the respective resistance values for the non-modified membrane, indicating that the former modified separators displayed lower interfacial resistance ($R_{\text{SEI}} + R_{\text{ct}}$) and better compatibility with the lithium electrode. Similarly, the bulk resistance (R_b) of the cells assembled with PDA-coated separator was 4.6Ω , which was smaller than that of the non-modified separator (7.3Ω). PDA coatings oxidized by air, on the other hand, resulted in large interfacial resistance and bulk resistance (Fig. S5 and Table S3 in ESI), which was in accordance with the results of C-rate capacity. The results unequivocally demonstrate that PDA coatings triggered by $\text{CuSO}_4/\text{H}_2\text{O}_2$ exhibited robust stability on the separators and reduced the interfacial resistance to enhance C-rate capacity of the LIB cells.

The final set of experiments characterized the cycling stability of LIBs with the separators. Cycling stability is an essential prerequisite for long-life battery.^[42,43] Fig. 8 shows the cycling stability and coulombic efficiency of the LiFePO_4 /separator/Li assembled cells with different separators at a constant current density of 0.2 C under a voltage range of 2.5–4.2 V. The discharge capacity of cells assembled with the non-modified separator was around $128 \text{ mAh}\cdot\text{g}^{-1}$ after

100 cycles. By contrast, the discharge capacity of cells assembled with the PDA-coated separator reached 147.8 mAh·g⁻¹ after 100 cycles (94.2% of its initial discharge capacity). The latter exhibited the much higher coulombic efficiency than that of the former group. Such improved battery cyclability was ascribed to the fact that the PDA coatings triggered by CuSO₄/H₂O₂ exhibited superior surface wettability and chemical stability, so as to impart the modified separators with enhanced and robust electrolyte wettability.

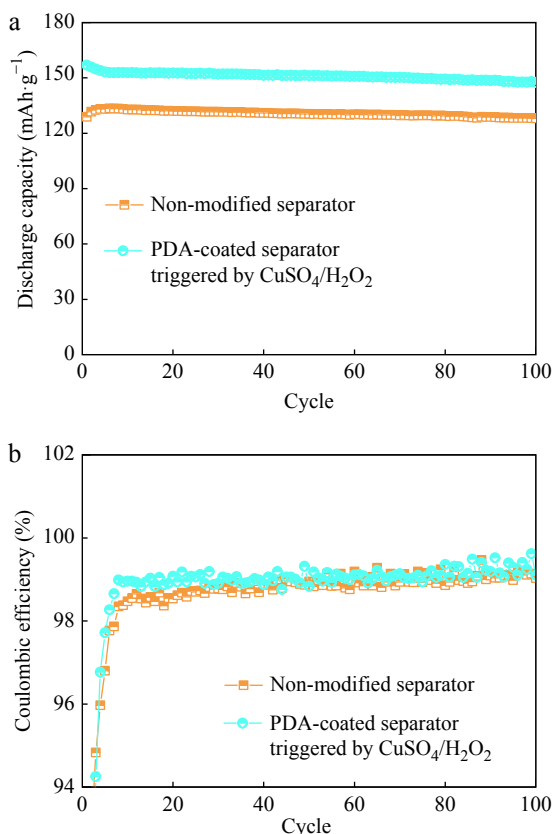


Fig. 8 (a) Cycling stability and (b) coulombic efficiency of the LiFePO₄/separator/Li cells (0.2 C for both charge and discharge)

CONCLUSIONS

In conclusion, we demonstrate a facile and rapid method for fabricating robust PDA coatings on the surfaces of LIBs separators. PDA coatings triggered by CuSO₄/H₂O₂ exhibited the high stability under strong polar electrolyte, which is significantly beneficial to long-term service performance of modified separators. The presence of more functional groups in the PDA coatings endowed the separator with improved properties including thermal stability, surface wettability, electrolyte uptake, and ionic conductivity, which are distinct progresses over the conventional PDA deposition method. Furthermore, cells assembled with these PDA-coated separators showed enhanced C-rate capacity and the batteries with these modified separators gave excellent cycle performance (*i.e.*, only a 6% reduction of discharge capacity after 100 cycles was observed). This work, to the best of our knowledge, is the first time that robust PDA coatings on

polyolefin separators were developed *via* a rapid deposition process for tremendous improvement to LIB performance.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes the details of XPS spectra FTIR/ATR spectra, and the pore size distribution of the non-modified separator and PDA-coated separator, resistance and conductivity of the cells assembled with PDA-coated separator triggered by CuSO₄/H₂O₂, and discharge C-rate capacity and Nyquist plots of the cells assembled with PDA-coated separator oxidized by air, is available free of charge in the online version of this article at <https://dx.doi.org/10.1007/s10118-019-2310-4>.

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