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Facile and Nonradiation Pretreated Membrane as a High Conductive Separator for Li-Ion Batteries

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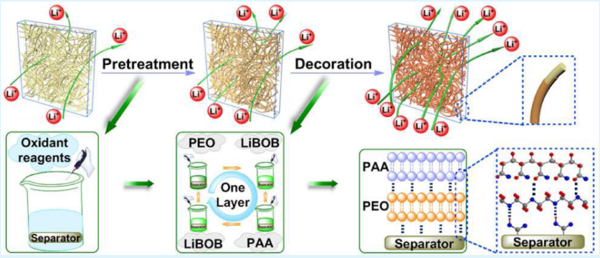
S *Supporting Information*



ABSTRACT: Polyolefin membranes are widely used as separators in commercialized Li-ion batteries. They have less polarized surfaces compared with polarized molecules of electrolyte, leading to a poor wetting state for separators. Radiation pretreatments are often adopted to solve such a problem. Unfortunately, they can only activate several nanometers deep from the surface, which limits the performance improvement. Here we report a facile and scalable method to polarize polyolefin membranes via a chemical oxidation route. On the surfaces of pretreated membrane, layers of poly(ethylene oxide) and poly(acrylic acid) can easily be coated, thus resulting in a high Li-ion conductivity of the membrane. Assembled with this decorated separator in button cells, both high-voltage ($Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$) and moderate-voltage ($LiFePO_4$) cathode materials show better electrochemical performances than those assembled with pristine polyolefin separators.

KEYWORDS: *polyolefin membranes, nonradiation, separator, high lithium-ion conductivity, lithium-ion battery*

INTRODUCTION

Polyolefin membranes are widely used as separators in commercialized Li-ion batteries and may be promising for other types of batteries, such as lithium−air, Li−S, and Na-ion batteries, in the future.[1−5] Microporous polyolefin membranes, such as polyethylene, polypropylene (PP), or their blends and copolymers, are the most favorable separators due to their good mechanical robustness, excellent chemical stability, and well-tailored physical properties.[6,7] However, polyolefin separators deliver a poor wettability in high polarized solvent, such as ethylene carbonate (EC), propylene carbonate, and dimethyl carbonate (DMC). Accordingly, such poor wetting state of the polyolefin membranes causes an increase in internal resistance of the cells and thus has negative effects on their electrochemical performances.[5,8,9]

Activating and subsequently grafting certain functional groups on the inert surfaces of polyolefin membranes are essential to improve the wettability of such membranes.[6,9−11] Radiation pretreatment methods, such as plasma,[12−14] electron beam,[15−17] and photons,[18−22] are widely used to activate the inert surfaces of polyolefin membranes. However, radiation pretreatments can only activate several nanometers deep from the surface of the membrane. In addition, radiation pretreatments are costly and thus are difficult to scale up.

Here, a facile and nonradiation method is proposed for polyolefin membrane surfaces pretreatment. For grafting certain functional groups, layers of ion-conductive polymers are subsequently integrated to the pretreated membrane to enhance the Li-ion conductivity of polyolefin separators (Figure 1). Typically, the pristine polyolefin membrane is immersed in

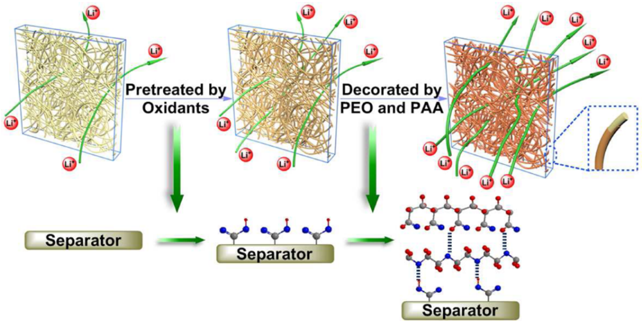


Figure 1. Schematic illustration of the strategy to treat and decorate the pristine polyolefin separator.

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a complex solution which contains different oxidants to obtain a hydrophilic surface (also high affinity to the electrolyte). Then polarized layers of poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) can easily be coated on the surfaces of pretreated polyolefin membranes through hydrogen bonds to enhance their ionic conductivity. In this work, the pretreatment method is nonradiative, facile, and low in cost. As such, it is promising to prepare the preferred separators with a high Li-ion conductivity in a large scale.

EXPERIMENTAL SECTION

Materials. All reagents are of analytical grade without further purification. PEO [average molecular weight (MW) 100 000], PAA (average MW 3000), H_2O_2 (30% ∼ 32%), $K_2S_2O_8$ (99.5%), and lithium bis(oxalato)borate (LBOB, >99%) were purchased from Aladdin Industrial Corporation. HNO_3 (98% and 65%) and $KMnO_4$ (99.5%) are from Sinopharm Chemical Reagent Co. Ltd.

Modification and Decoration of Separators. To polarize the surfaces of the polyolefin membrane and facilitate the decoration of PEO and PAA, a series of experiments were designed to optimize technical processes. Polypropylene membrane was suspended and fixed at the bottom of a beaker with a small glass strip. The mixture of oxidants was poured into the beaker at 25 °C, which was sealed with polyethylene membranes. Then the beaker was kept at 25 °C for 48 h. After that, the PP membrane was immersed in the deionic water for 1 h, three times. Finally, the pretreated membrane was naturally dried at room temperature, followed by a vacuum drying at 40 °C overnight.

Decoration of polyolefin membranes are performed as follows: the pretreated polyolefin membrane was orderly immersed into the following solutions: (1) 10 mM LiBOB and 20 mM PEO; (2) 10 mM LiBOB; (3) 10 mM LiBOB and 20 mM PAA; (4) 10 mM LiBOB (mM = mmol/L). Then the PP membrane with “1” decoration layer was obtained. The 2-layer PP membrane can be obtained by repeating the above process one more time, the “3” layers by repeating the process twice, and so on. LiBOB was dissolved in all polymer solutions to increase the ionic conductivity and uniformity of the decoration layers.[10] The pH values of all the above solutions were adjusted to 2.5 with HCl.[10] Before subsequent tests, all modified polyolefin membranes were dried in a vacuum oven at 40 °C for 48 h and then stored in an Ar atmosphere glovebox for 2 weeks.

Morphology and Contact Angle. The morphological characterizations of membranes were carried out on an Hitachi SU8010 with a working voltage of 5 kV and working distance of 10 mm. Experiments of contact angle were performed on a contact angle tester (DCH Huajia Commercial Co., DSA20). Before the tests, all the PP membranes must be dried thoroughly as follows: first, natural drying in room temperature for at least 8 h, and second, vacuum drying at 40 °C for 8 h. The solution volume for deionic water and electrolyte was 5 μL. The final value of the contact angle was an arithmetic mean value of six tests.

Electrochemical Characterizations. CR2025-type button cells were assembled in a glovebox filled with Ar. The general process of cell assembly is as follows: cathode materials, acetylene black, and polyvinylidenefluoride were blended at a ratio of 75:15:10. The mixture was made into a slurry with *N*-methyl-2-pyrrolidone as solvent, and then the slurry was pasted on aluminum foil followed by vacuum drying at 80 °C for 24 h. The electrolyte was $LiPF_6$-dissolved in DEC/EC/DMC (1:1:1 volume ratio, Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd., China.). Galvanostatic charge/discharge tests were performed between 2.3 and 4.2 V (for $LiFePO_4$ from Xinxiang Qixin Advanced Power Source Materials) or 2.0−4.6 V (for $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$, homemade) on a Land CT2001A battery tester (Wuhan Jinnuo Electronics Co. Ltd., China).

Electrochemical impedance spectroscopy (EIS) tests were carried out on a Bio-Logic VMP3 instrument with a frequency range between 0.1 and 10^5 Hz. Button cells were assembled with polyolefin membranes sandwiched between two stainless steel electrodes to examine the Li-ion conductivity with different numbers of decorated layers. Otherwise, button cells were assembled with membranes sandwiched between two metal lithium plates to test Li-ion conductivity and interface performance between the separator and electrodes.

RESULTS AND DISCUSSION

Activating the surfaces of the pristine polyolefin membrane is a necessary step to facilitate the subsequent grafting or coating with functional groups. The surface activation method adopted here is facile via chemical oxidation by immersing the PP membrane into an aqueous solution which contains certain oxidant reagents at room temperature for 48 h. To optimize the experimental conditions of the oxidants, water and electrolyte contact angles were selected to examine the wettability of pretreated PP membranes. Results of contact angles for the corresponding oxidants are numbered and shown in Table 1.

Table 1. Contact Angles of Pretreated Separators and Corresponding Experimental Conditions

		contact angles (deg)	
no.	type of oxidants	deionic water	electrolyte
1	H_2O (contrast test)	89.2 ± 3.2	33.5 ± 3.8
2	65% HNO_3 + H_2O_2	68.6 ± 2.8	33.5 ± 3.3
3	98% HNO_3 + H_2O_2	85.1 ± 3.4	30.6 ± 3.5
4	65% HNO_3 + H_2O_2 + $K_2S_2O_8$	87.3 ± 3.7	31.8 ± 2.9
5	98% HNO_3 + H_2O_2 + $K_2S_2O_8$	71.3 ± 2.2	26.2 ± 3.2
6	65% HNO_3 + $KMnO_4$	73.2 ± 3.5	36.6 ± 4.0
7	65% HNO_3 + $K_2S_2O_8$	71.9 ± 2.9	34.4 ± 3.6
8	98% HNO_3 + $KMnO_4$	71.7 ± 2.2	27.8 ± 3.2
9	98% HNO_3 + $K_2S_2O_8$	75.2 ± 3.0	26.4 ± 3.8

Low value of water contact angle means favorable water affinity, which will be beneficial to the subsequent decoration process because grafting and coating are carried out in water solution in most cases. As observed in Table 1, the no. 2 experiment results in the lowest value of water contact angle (only to deionic water) among all control groups. However, it is found that this value gradually increases with time. We attribute this phenomenon to the adhesion of H_2O_2 molecules on the surfaces of pretreated membranes, speculated from the low value for water contact angle and high value for electrolyte contact angle. The interaction force between H_2O_2 molecule and molecule of electrolyte is slightly weaker than that between H_2O_2 molecule and H_2O molecule (strong hydrogen bonds). Furthermore, H_2O_2 molecules adhered on the surfaces would gradually volatilize and result in lower and lower value of contact angles, where as carboxyl groups on the surfaces of membrane would not disappear very soon using the chemical oxidation method [see Fourier transform infrared (FT-IR) spectra in Figure S2, Supporting Information]. The no. 5 oxidant has the best results among the rest of the experiments. Figure 2 shows the contact angles of pristine, pretreated (by no. 5 oxidants) and decorated (with four layers of PEO and PAA) PP membranes.

Notably, the result for the no. 8 experiment is also good, close to that of no. 5. However, in this case $KMnO_4$ is reduced into small particles of MnO_2 adhering to the surface of the separator. It is difficult to get rid of these MnO_2 particles from the surface of the membrane. These particles are detrimental to the separator because MnO_2 can be reduced into metal Mn on the surface of the anode and then takes part in electrode

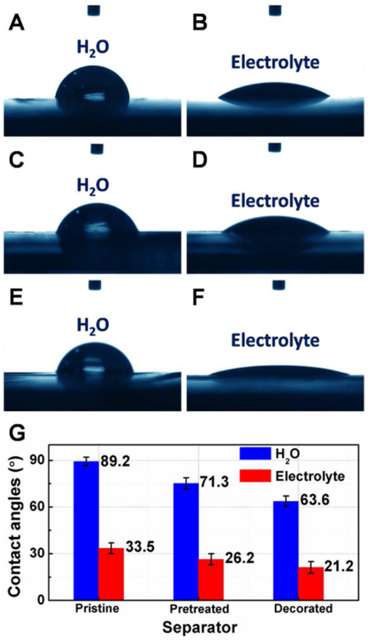

Figure 2. Pictures of contact angles of pristine (A and B), pretreated (C and D), and decorated (E and F) polyolefin membranes and their corresponding contact angle values (G).

reactions as shuttles in cells. Therefore, the no. 5 oxidant was selected to treat PP membranes in the subsequent experiments.

Moreover, to compare the pretreating effects of our chemical oxidation approach with a traditional method, X-ray treatment was selected as the contrast method. The results of contrast experiments show that there are no obvious differences in pretreating effects between the two methods. The values of water (81.4 ± 1.6°) and electrolyte contact angles (31.7 ± 1.2°) for membranes treated by X-ray are higher than those of membranes treated by chemical oxidation. By process optimization, the method of X-ray pretreatment could be improved. Similar conclusions can also be drawn from the results of electrochemical tests (see Supporting Information).

PEO and PAA are known as ionic conductive polymers. They can remarkably enhance the Li-ion conductivity of polyolefin separators.[10,23−25] To decorate the pretreated polyolefin membrane with PEO and PAA, the same strategy as in the literature[10] was adopted. The pretreated membranes were coated with 2, 4, 8, or 12 layers of PEO and PAA. Characteristic peaks of PEO and PAA were detected on the FT-IR spectra of decorated membranes with 12 layers (see Figure S2).

EIS is an effective way to examine the ionic conductivity of polyolefin membranes. Button cells were assembled with polyolefin membranes as separators sandwiched between two stainless steel electrodes. Then ionic conductivities of membranes coated with different layers of PEO and PAA were measured by a Bio-Logic VMP3 instrument in a frequency range from 0.1 Hz to 100 kHz. The obtained Nyquist plots are almost linear (see Figure S3A), implying that the conductivity mainly comes from ion conduction.[26−28]

The intercept on the real axis can provide us the information on electrolyte bulk resistance.[26−28] Thus, the conductivity can approximately be calculated based on the area and thickness of the membranes. The membrane area comes from the type of button cells (CR2025 with a diameter of ∼1.8 cm) and the membrane thickness can be adopted as 25 μm, almost the same thickness as the pristine membrane (see Figure S4). The resistances measured from the intercept are 5.3, 3.6, 3.0, 6.3, and 10.6 Ω for the PP membranes decorated with 0, 2, 4, 8, and 12 layers of PEO and PAA, respectively (see Figure S3B). Accordingly, the corresponding Li-ion conductivities of the above decorated membranes are 0.19, 0.27, 0.33, 0.16, and 0.09 mS·cm^{-1}, respectively. These results are reliable as a value of 0.21 mS·cm^{-1} has been reported for commercial separators (Celgard 2730) in the literature.[26] So decoration with 4 layers of PEO and PAA obtains the highest Li-ion conductivity from the results of EIS.

Why 4-layers' decoration is better than 8- and 12-layers' decoration? Scanning electron microscopy (SEM) provides us a much more intuitive comparison of the surface of the decorated PP membranes. Figure 3 shows SEM images of the pristine, pretreated, 4-layer-decorated and 12-layer-decorated PP membranes. Compared to pristine and pretreated membranes, a large proportion of the decorated surface is covered by ionic conductive polymers for decorated membranes. The coverage gets worse for the 12-layer-decorated PP membrane in comparison with that for the 4-layer-decorated membrane. From the magnified image of Figure 3D, almost no holes can be found on the surface of the decorated membranes. This explains why the Li-ion conductivity decreases even after membrane decoration with more layers of PEO and PAA. Notably, the surface is uniform after chemical oxidation pretreatment (Figure 3A,B).

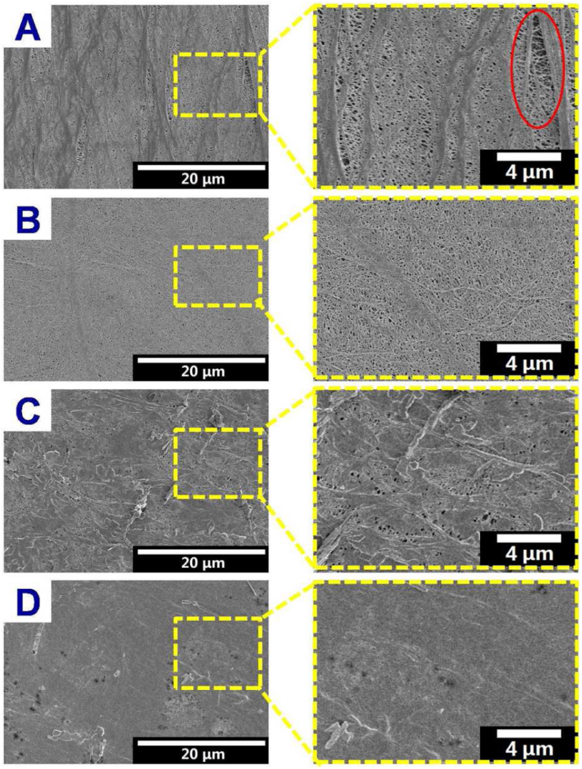

Figure 3. SEM images of pristine (A), pretreated (B), 4-layer-decorated (C), and 12-layer-decorated PP membranes (D). Right-side images show the corresponding enlarged parts.

Permeability is one of the most important parameters for the usage of a separator in Li-ion batteries. The electrolyte permeability was tested using modified membranes with

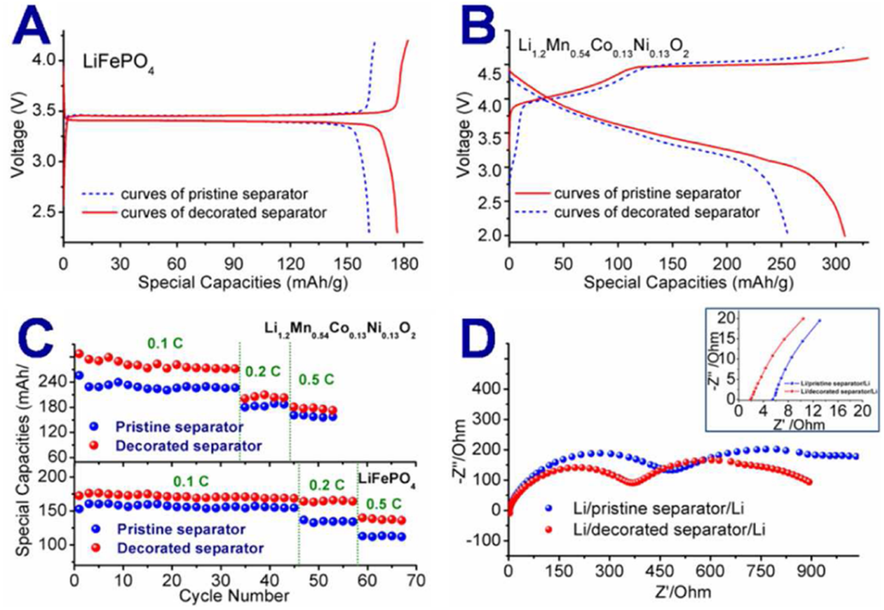

Figure 4. Charge/discharge curves of $LiFePO_4$ (A) and $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ (B), cycle capacities of $LiFePO_4$ and $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ (C), and EIS of Li/separator/Li cells (D). Insert of D is the EIS over the high-frequency range.

different layer numbers, according to the literature.[10] The values of our results are different from those reported in the literature as the support membrane was discounted during the calculation of the electrolyte permeability. However, the values are on the same order of magnitude and have a similar tendency to those from the literature[10] (see Figure S5 in the Supporting Information).

Half cells were assembled with a high-voltage ($Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$) and moderate-voltage ($LiFePO_4$) cathode material to test electrochemical performances of the decorated PP membranes. Figure 4 shows the profiles of the charge/discharge, cycle capacities, and EIS of the above two types of cells. The specific capacity of the $LiFePO_4$ electrode, assembled with a decorated separator, is 176.2 mA·h/g, while it is only 161.4 mA·h/g for the pristine separator (Figure 4A,B). The rate of increment is ca. 9.2%. The specific capacity exceeds the theoretical value (170 mA·h/g), which may come from the doped elements (Sn for instance) added by the manufacturer (Xinxiang Qixin Power Source Material Co. Ltd.). Such element can afford more than one electron transfer during the discharge process.

$Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ (LMCNO for short) is deemed one of the promising materials for the next-generation Li-ion batteries. However, this high-voltage material requires the matched separator and electrolyte. With our decorated separator the LMCNO shows a specific capacity of 307.9 mA·h/g, in comparison with 255.8 mA·h/g for the same material with pristine membranes. The rate of increase is ca. 20.4%, higher than that for $LiFePO_4$. Compared with $LiFePO_4$, a moderate-voltage cathode material, high voltage of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ consumes a little more electrolyte to form the solid electrolyte interface (SEI) layer during the charge process, so the latter has a higher increase rate as the decorated separator can "afford sufficient electrolyte" to the interface of the LMCNO cathode.

Cycle capacities confirm the above theory of "affording sufficient electrolyte" (Figure S6 also gives supporting proof.). The cycle capacity curve of the $LiFePO_4$ electrode is almost a horizontal line at different charge/discharge rates (Figure 4C). Interestingly, the increase in capacities at a high discharge rate is greater than that at a low discharge rate. The difference of discharge capacity between cells with decorated and pristine separators is 15 mA·h/g at 0.1 C (1C = 170 mA/g), while the values become 30 and 25 mA·h/g at 0.2 and 0.5 C, respectively. The high rate performance with decorated separators comes from the high Li-ion transformation between the two electrodes by "affording sufficient electrolyte". For the high-voltage cathode material, the results are not as positive as the moderate-voltage cathode material. Also, the increase in discharge capacities at a high rate is not so obvious in comparison with that at a low discharge rate. This result may relate to the continual formation and reformation of the SEI layer on the surface of cathode materials.[29] More studies on this issue are in progress using decorated separators.

Electrochemical impedance spectra, as shown in Figure 4D, provide us more direct proof for the theory of "affording sufficient electrolyte". As such, Li/separator/Li cells were assembled and tested. Different from stainless steel sandwiched cells, electrochemical reactions (forming the SEI layers) in the Li/separator/Li cells take place on the surface of the electrodes. A typical EIS spectrum of this type of cell is shown in Figure 4D. The intercept with the x-axis in the high-frequency region refers to the ohmic resistance (insert of Figure 4D). Two semicircles in the intermediate frequency region represent the resistance associated with the formation and charge-transfer process of the SEI (commercial anodes of lithium wafer are with a cover layer of Li_2CO_3, LiF, or an analogous SEI layer). Theoretically, the line in the low-frequency region refers to the diffusion process in the electrodes. Unfortunately, the lower frequency limit of the instrument cannot detect such diffusion process.

In the high-frequency region, the intercepts on the real axis are 1.9 and 5.5 Ω, respectively. Similarly, the conductivity can approximately be calculated based on the area and the thickness of the membranes (CR2025 button cell). The corresponding Li-ion conductivities of the above cells are 0.52 and 0.18 mS·

cm^{-1}, respectively. The high conductivity of the decorated membrane comes from its higher electrolyte uptake. There are two semicircles in the intermediate-frequency region, referring to the interfacial resistance associated with the electrochemical process of the SEI.[30] The SEI film plays an important role in the electrochemical reactions of electrodes in lithium batteries. From Figure 4D, it can be seen that the electrode with a decorated separator shows a lower interfacial resistance than that with a pristine membrane (red line: smaller radius in the high-frequency semicircular portion). The former has an interfacial resistance of about 400 Ω while the latter has a resistance of about 550 Ω. Thus, the introduction of PEO and PAA to the surface of the separator facilitates the electrons' transfer on the surface of the electrodes, due to the good affinity of PEO and PAA to the electrolyte.

CONCLUSION

Traditional radiation treatments activate only several nanometers from the polyolefin membranes' surface and therefore are limited for a large-scale production. As such, a facile, nonradiation treatment method is proposed in this work to modify the membrane surfaces. PEO and PAA have easily been integrated to the pretreated membrane surfaces to enhance the Li-ion conductivity of the membrane. Decorated polyolefin membranes by PEO and PAA have smaller values of water and electrolyte contact angle, which means decorated membrane having a good affinity to water and electrolyte. Results from EIS and SEM show that chemical oxidation pretreatment facilitates obtaining uniform surfaces for polyolefin membranes, and the 4-layer coating has proved to be the best for PP membrane decoration. With use of high- and moderate-voltage cathode materials, electrochemical performances of cells with a 4-layer decorated membrane are proved to be excellent. The increased discharge capacities and improved cycle performances are attributed to the good affinity of PEO and PAA to the decorated polyolefin membranes and electrolyte, and the high Li-ion transformation in decorated membranes. The proposed method in this work is promising to polarize the surface of polyolefin membranes in a facile way.

ASSOCIATED CONTENT

Supporting Information

Experimental details and additional characterization data, such as EIS, FT-IR, and SEM are shown in Figures S1–S6. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05718.

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Notes

The authors declare no competing financial interest.

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