

Cite this: *J. Mater. Chem. A*, 2014, 2, 11980

## Enhanced wetting properties of a polypropylene separator for a lithium-ion battery by hyperthermal hydrogen induced cross-linking of poly(ethylene oxide)<sup>†</sup>

Changzhen Man,<sup>a</sup> Peng Jiang,<sup>a</sup> Ka-wai Wong,<sup>a</sup> Yun Zhao,<sup>a</sup> Changyu Tang,<sup>\*a</sup> Meikun Fan,<sup>a</sup> Woon-ming Lau,<sup>a</sup> Jun Mei,<sup>a</sup> Shaomin Li,<sup>a</sup> Hao Liu<sup>\*a</sup> and David Hui<sup>b</sup>

Enhancing the electrolyte wetting of separators by surface modification is very critical to prepare high-performance lithium-ion batteries. Herein, we present a new approach named hyperthermal hydrogen induced cross-linking (HHIC) technology to increase the electrolyte-affinity of polypropylene (PP) separators by covalently cross-linking a thin layer of poly(ethylene oxide) (PEO) on surface-inert PP separators. With the HHIC treatment, the polar functionalities of PEO (e.g. –OH, C–O–C) can be preserved through selective cleavage of C–H bonds and subsequent cross-linking of resulting carbon radicals generated on PEO and PP chains. As proved by solvent rinsing tests, contact angle measurements and Fourier transform infrared spectroscopy, a PEO coating was found firmly fixed on the separator surface, which results in significantly improved wetting with the electrolyte. Electrochemical measurements on subsequent lithium-ion batteries with the modified separator by HHIC treatment exhibit a lower internal resistance but higher capacity retention when compared to the pristine separator. HHIC treatment is concluded to be a highly efficient and environmental-friendly approach for separator surface modification without need for other chemical additives (e.g. chemical cross-linkers, initiators, and catalysts) and can preserve the desired macroscopic material properties of separators such as pore structures and mechanical strength.

Received 16th April 2014

Accepted 21st May 2014

DOI: 10.1039/c4ta01870b

www.rsc.org/MaterialsA

### 1. Introduction

In the past few years, lithium-ion batteries (LIBs)<sup>1–4</sup> have been increasingly used as energy storage devices in various products such as portable electronic devices, mobile phones, electric vehicles, and in renewable energy storage because of their high energy density, low self-discharge rate and high open-circuit voltage. A typical LIB consists of an anode, a cathode, a collector, a separator, and the electrolyte.<sup>5–8</sup> The separator, which is usually a porous polymer membrane, serves to physically isolate the anode and the cathode in order to avoid an internal short-circuit. At the same time, it must allow enough ionic current flow to complete the circuit. It therefore plays a very important role in the reliability, stability and performance of the battery (e.g. capacitance, current and cycle life). An ideal separator must be chemically and thermally stable, and

mechanically robust. Commercially available polyolefin separators such as polypropylene (PP) and polyethylene (PE)<sup>9–12</sup> can basically meet the above requirements. However, these polyolefin separators have poor wettability towards electrolytes with high dielectric constant such as ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) because polyolefin has a low surface energy and is generally non-polar. It strongly hampers the ion transport, which in turn results in a high internal resistance.<sup>13–15</sup> This poor wetting of the separator becomes a serious concern against the strong demand for an energy storage device with high-power (e.g. battery for electric vehicle) because when the current flow is restricted, the performance of a lithium-ion battery cell will degrade accordingly.<sup>16</sup>

To overcome this problem, various surface modification processes have been tried to improve the wetting characteristic of polyolefin separators. In particular, much effort has been made to increase the surface polarity of polyolefin separators by either physical coating<sup>17</sup> or wet chemical modification<sup>18</sup> with organic molecules bearing specific polar groups such as poly(ethylene oxide) (PEO), methyl methacrylate, and acrylic acid onto the separator surface. Physical coating techniques are usually simple and low cost processes, and can maintain the

<sup>a</sup>Chengdu Green Energy and Green Manufacturing Technology R&D Center, Chengdu Development Center of Science and Technology, China Academy of Engineering Physics, Chengdu 610207, China. E-mail: sugarchangyu@163.com; mliuhao@gmail.com

<sup>b</sup>Department of Mechanical Engineering, University of New Orleans, New Orleans, USA

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta01870b

original mechanical strength of the polyolefin separator. However, the weak interfacial interaction (mainly van der Waal attraction) between the coating and polyolefin often raises an adhesion issue. The physically coated layers can easily delaminate from the separator surface when immersed in the liquid electrolyte. The poor durability also detrimentally affects the practical operation of cells.<sup>19–21</sup> In contrast, wet chemical modification can generate a stable coating on the separator by the formation of relatively strong covalent interaction between the coating and the separator or by cross-linking.<sup>22</sup> For instance, the target polar functionalities can be attached onto the separator surface by graft polymerization of monomers or by chemical coupling initiated by heating or ultraviolet light.<sup>23–25</sup> However, this approach requires a pre-engineering separator surface with reactive groups prior to grafting or chemical coupling, which often involves complex and costly multi-step treatments. Even worse, the usual ways of chemical initiation for grafting or coupling such as heating and ultraviolet light can lead to severe shrinkage and aging of the separator. Also, the initiators or catalysts needed will be inevitably introduced as impurities that can adversely degrade the electrochemical reactions during batteries operation. Cleaner techniques such as energetic particle radiation<sup>26,27</sup> (e.g. electron beams, plasma, and nuclear) are becoming attractive alternative approaches to separator modification because they can provide a “dry” and “green” chemical process to introduce only specific targeting functionalities onto the separator without unwanted chemical impurities. These approaches can generate a lot of active sites (carbon radicals) on backbones of organic materials to initiate the cross-linking between targeting molecules and separators, which also significantly simplify the steps for separator modification. However, the usual uncontrolled or high energy projectiles arising from these approaches such as electrons, ions, and radicals often lead to the degradation of the polymer backbone (C–C bond), the damaging of targeting molecules, and the formation of undesirable chemical functionalities simultaneously.

Therefore, a facile, low cost and green modification approach is needed for improving the wetting characteristics of separators. The hyperthermal hydrogen induced cross-linking (HHIC) technology recently developed can be a potential alternative to the radiation modification method for material surfaces.<sup>27–35</sup> This new technology involves bombardment of surfaces with energy-selected hydrogen molecule projectiles to selectively cleave C–H bonds but no other bonds. When such a light molecular hydrogen projectile collides with an organic or polymeric molecule, the transfer of the projectile kinetic energy to the target molecule is effective only if the projectile hits an hydrogen atom of the molecule. At the same time, the kinetic energy of the hydrogen molecular projectiles is selective and controlled to be just enough to break only the C–H bonds of organic or polymeric molecules. The adjacent carbon radicals then generated from the C–H bond cleavages will bond themselves, leading to an effective and efficient cross-linking of the organic or polymeric molecules. More importantly, keeping the desirable functionalities on these targeting molecules can be maximized during the chemical cross-linking due to the

selectivity of the energy-controllable hydrogen projectiles. With HHIC, the organic and polymeric molecules can be cross-linked quickly under mild conditions (e.g. room temperature) and without any damage to the substrate surface. In addition, it is an extremely clean process because no other additives such as chemical cross-linkers, initiators, catalysts and other reactive groups are required. These characteristics enable HHIC to functionally and greenly modify the separator surface with the desired wetting characteristics.

Here, we report the first application of HHIC technology for the surface modification of polypropylene (PP) separators for lithium-ion batteries. Poly(ethylene oxide) (PEO) was selected as the surface modifier due to its higher polarity and good affinity with the electrolyte. With HHIC treatment, the PEO thin layer can be firmly fixed onto the separator surface without any damaging effect to the desirable functionalities of PEO and underlying PP, nor any impurity incorporation. Both the originally poor wetting of the PP separator and the weak adhesion of the surface modifier observed in conventional modification processes can be overcome simultaneously. Improved battery performance of battery cells with the HHIC modified PEO on PP separators was demonstrated.

## 2. Experimental

### 2.1 Materials

Poly(ethylene oxide) (PEO,  $M_w = 100\,000$ ) and polypropylene (PP) separators (Celgard 2400) were purchased from Sigma-Aldrich Company (USA) and Celgard Company (USA), respectively. Chloroform was purchased from Changzheng Company (Chengdu, China) and purified before use. Benzophenone (BPO) used as an ultraviolet initiator was purchased from Xieli Company (Chengdu, China) for comparative studies.

### 2.2 Preparation of the PEO coating on the PP separator

4 mg mL<sup>-1</sup> of PEO solution was prepared by dissolving PEO powder in chloroform. The resultant solution was spin-coated on the surface of the PP separator at a speed of 6000 rpm for 30 s to create a thin PEO film.

### 2.3 Hyperthermal hydrogen induced cross-linking of the PEO-coated separator

A homebuilt system equipped with an electron cyclotron resonance (ECR) microwave plasma source (87.5 mT, 2.45 GHz) was used for HHIC cross-linking of PEO on PP. Fig. 1s† shows the schematic diagram of the system. In a typical HHIC process, the sample was placed on a stage located at the bottom of the reactor. After the sample was loaded, the whole system was pumped down to a base pressure of about  $3.0 \times 10^{-4}$  Pa. Afterwards, hydrogen gas was introduced inside the reactor until a pressure of  $\sim 9.9 \times 10^{-2}$  Pa was reached and the pressure was maintained throughout the whole experimental process. Protons in the hydrogen plasma were then partly extracted by using an applied potential difference of  $-100$  V with a current of  $\sim 160$  mA. The protons extracted were accelerated into the drift zone, which is a 60 cm long electric field-free compartment.

There, they underwent serial but random collisions with hydrogen molecules fed into the system. Through energy transfer from protons to molecular hydrogen during collisions, molecular hydrogen projectiles with appropriate kinetic energy capable of selectively breaking the C–H bonds were effectively generated. Residual electrons and positive ions were repelled by two grids immediately above the sample with an applied voltage of  $-150$  V and  $+200$  V, respectively. The sample was exposed to hyperthermal molecular hydrogen neutrals for 60 s. Based on these experimental parameters and operational processes, cross-linking within PEO chains and at the interfacial region between the PEO layer and the PP separator was realized.<sup>29</sup>

## 2.4 Characterizations

**Scanning electron microscope (SEM) observation.** The surface morphology of pristine and cross-linked PEO/PP separators was examined by scanning electron microscopy (SEM, S5200, Hitachi Company) under an acceleration voltage of 10 kV.

**Contact angle measurements.** The contact angles of the pristine and cross-linked separators were measured by a contact angle goniometer (JGW-360C, Chenghui Testing Machine Company, China). The sample is first loaded onto the stage and droplets of distilled water and the electrolyte (1 : 1 volume ratio mixture ethylene carbonate (EC)–dimethyl carbonate (DMC)) were delivered onto each specimen. The volume for each droplet is 5  $\mu$ L. The static contact angle was calculated by averaging the measurements from both the left and right sides of the droplet. And at least 10 measurements on each sample were made for each experimental condition to give the final reported value.

**Fourier transform infrared (FTIR) measurements.** The pristine and modified separators were studied by FTIR (Nicolet-iS10, Thermo Fisher Company, USA) in the range of 4000–400  $\text{cm}^{-1}$  under an ATR mode.

**X-ray photoelectron spectroscopy (XPS) measurement.** XPS (Axis Ultra DLD) was carried out using a focused monochromatized Al-K $\alpha$  radiation (1486.6 eV) to determine the change in carbon to oxygen ratio, and to confirm if PEO was successfully cross-linked on the PP separator surface.

**Mechanical properties test.** The stress–strain curves of the separators were measured on an electro-mechanical universal testing machine (WDW-10, Jinan New Century Company, China) at room temperature. The specimen size is 150 mm  $\times$  20 mm  $\times$  0.025 mm. The specimens were tested with a crosshead speed of 5 mm  $\text{min}^{-1}$ .

**Electrochemical property measurements of cells assembled with the separator.** The cross-linked PEO/PP separator was cut into a round disk of  $\phi$ 18 mm and then transferred into a glove box (MBraun Company, German) filled with argon gas after a thorough drying process. A LIB cell was assembled by sandwiching the separator between a lithium cobalt oxide (LiCoO<sub>2</sub>) anode and the Li cathode (electrode diameter:  $\phi$ 16 mm) in the glove box. The anode was prepared by coating the slurry consisting of 85 wt% LiCoO<sub>2</sub> (Sigma-Aldrich company, USA) with 10 wt% carbon black as a conducting agent and 5 wt%

polyvinylidene fluoride (PVDF) as a binder in a *N*-methyl pyrrolidone (NMP) solvent onto the aluminum foil. 1 M LiPF<sub>6</sub> in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volumetric ratio of 1 : 1 was employed as the electrolyte. The AC impedance measurement was determined using CHI 660D electrochemical workstation (Shanghai Chen Hua instruments Co., Ltd., China) over a frequency range from 0.1 Hz to 100 kHz. The cycling tests at different current densities including 0.1 C ( $C = 274 \text{ mA h g}^{-1}$ ) and 10 C were conducted in the voltage range of 3.0–4.2 V at room temperature using an Arbin multi-function measurement system (BT-2000, Arbin Company, USA).

## 3. Results and discussion

### 3.1 Coating and cross-linking of PEO on the separator

In this study, grafting of PEO onto the PP separator involves a simple procedure of spin casting a thin PEO layer on the PP separator from a PEO/chloroform solution, followed by HHIC treatment (Fig. 1). In the HHIC process,<sup>30</sup> the energy-controlled hydrogen projectiles collide with both PEO and PP chains to selectively cleave the C–H bonds but no other bonds. As a result, the generated carbon radicals on these molecules couple with each other to form a cross-linked PEO layer on the PP separator. Fig. 2 shows the SEM images of the surface morphology of a pristine PP separator and a PEO coated separator after HHIC treatment. Both of them exhibit the same porous structure and morphology. It indicates that the PEO layer on the PP separator is extremely thin and HHIC treatment basically does not change the pore size and structure. This result shows that the relevant properties of the porous structure offered by the PP separator could be nicely preserved. To verify if the PEO was successfully cross-linked on the surface, the PEO-coated PP separator was washed with chloroform and then subjected to ATR-FTIR and XPS measurements.

First, from the FTIR spectra shown in Fig. 3a and b, new peaks corresponding to the ether (C–O–C) and the hydroxyl of PEO (–OH) are clearly identified at 1120 and 3500  $\text{cm}^{-1}$  from the PEO-coated PP separator due to the formation of the PEO layer

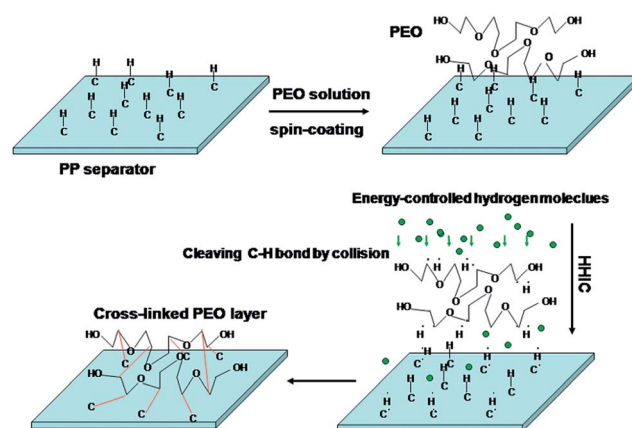


Fig. 1 Schematic illustration of grafting of PEO onto the PP separator by the HHIC process.

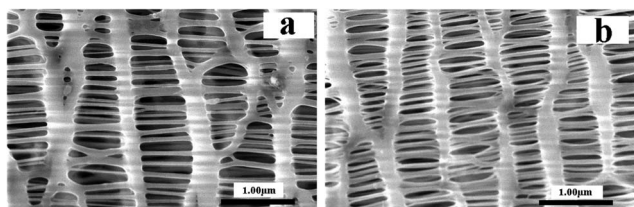


Fig. 2 SEM images of (a) the pristine separator and (b) the PEO-coated separator treated by HHIC.

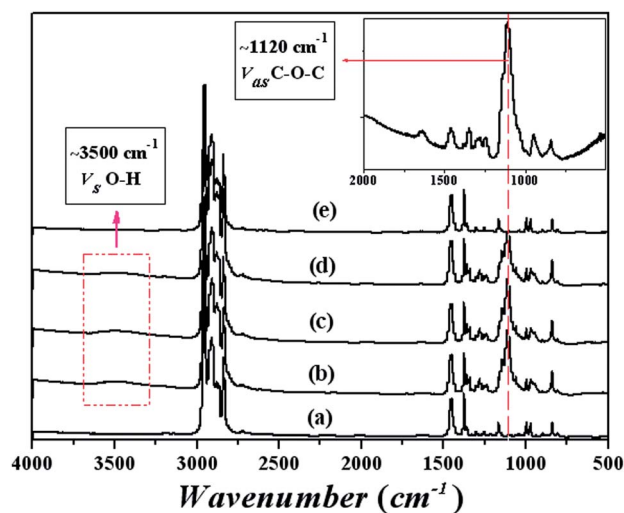


Fig. 3 FTIR spectra of (a) the pristine separator, the PEO-coated separator without any treatment (b), the PEO-coated separator treated by HHIC (c) before and (d) after chloroform washing for 12 h, and (e) the PEO-coated separator without HHIC treatment after chloroform washing for 12 h. The inset shows the spectrum of PEO.

on the PP separator. The characteristic peaks (C–O–C and –OH) of PEO (Fig. 3c) still remain on the PP separator after HHIC treatment. Further, it is found that even when the HHIC-treated PEO/PP separator was washed with chloroform, both –C–O–H and –C–O–C of PEO remain without change after washing for 12 h (Fig. 3d). However, all PEO was removed if it was not treated by HHIC (Fig. 3e). It implied that the PEO chains have effectively cross-linked themselves and also with the underlying PP (as illustrated in Fig. 1), so that the massive cross-linked PEO coating can withstand vigorous washing by chloroform that is known to dissolve PEO.

In addition, XPS spectra were used to quantitatively determine the effect of HHIC treatment on the PEO layer on the PP separator (Table 1 and Fig. 2S†). The pristine PP separator

Table 1 XPS analyses of the PP separator and PEO-coated PP separators before and after HHIC treatment

Sample	HHIC	Wash	C (%)	O (%)
PP separator	Not used	Not used	100	0
PEO-coated separator 1	Not used	Used	74.69	25.31
PEO-coated separator 2	Used	Not used	72.52	27.48
PEO-coated separator 3	Used	Used	72.37	27.63

mainly presents a strong C-peak (at 285.7 eV) without any O component in the XPS spectrum. The O-peak (at 535.6 eV) observed in the XPS spectrum of the PEO-coated separator corresponds to the oxygen-containing groups from PEO chains. The very weak peak at 846.2 eV was observed in the pristine and modified PP separators, which indicates the residual titanium-based initiator (for the polymerization of propylene into PP) from commercial PP materials. After HHIC treatment, there was no obvious change in C/O compositions on the surface of the PEO-coated PP separator. When the HHIC-treated PEO-coated PP separator was washed, the C/O compositions did not change significantly. These results indicate that HHIC treatment successfully cross-linked PEO on the PP separator without damaging the desired oxygen-containing groups from PEO chains. It facilitates to take full advantage of PEO to enhance the wetting of the PP separator.

Furthermore, it is observed that the original physical properties of the PP separator can be maintained even after HHIC treatment. The mechanical properties of the separators were evaluated before and after treatment. The stress–strain curves in Fig. 3S† show that the tensile strength of the cross-linked PEO-coated separator by HHIC treatment is almost the same as the pristine separator, suggesting that HHIC treatment did not damage the mechanical strength of the separator. For comparison, a commonly used UV irradiation was used to cross-link the PEO coating on the separator. It is found that both the tensile strength and strain at break in the UV-treated PEO-coated separator decrease sharply, a result which could be attributed to the degradation of the polymer chains under UV radiation arising from its high optical energy. The wrinkled and shrunken surface of the separator (Fig. 4S†) observed after UV treatment also indicates that the separator structure was destroyed under UV radiation. Once again, these results demonstrate that HHIC treatment is an effective method to graft PEO on the separator without destroying the bulk separator, which is of importance for the battery safety. This significant advantage over traditional radiation modification methods (*e.g.* UV and plasma treatments) is attributed to the unique design in the HHIC technology for selectively cleaving C–H bonds with energy-controllable hydrogen projectiles.<sup>30</sup>

### 3.2 Surface properties of modified separators

Contact angle measurements (Fig. 4) with water droplets were conducted to study the effect of the PEO coating on the surface properties of the PP separator after HHIC treatment. Compared to 108° for the pristine separator, the cross-linked PEO-coated separator shows a very low water contact angle of 27°, indicating that the separator surface becomes much more hydrophilic and provides a good surface for water wetting. This result further confirms that the hydrophilic PEO coating was successfully cross-linked on the separator without obvious degradation of hydrophilic functionalities. More importantly, the cross-linked PEO coating on the separator also decreases the less polar electrolyte solvent (mixture of EC and DMC) contact angle from 66° to 25°, indicating that the wetting ability of the modified separator toward electrolyte solvent was also significantly

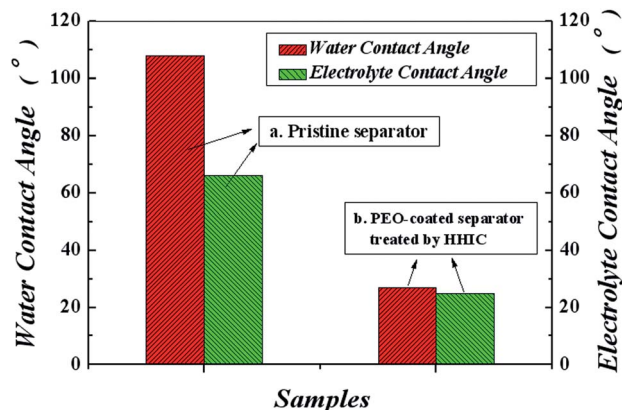


Fig. 4 Water and electrolyte contact angles of (a) the pristine separator and (b) the PEO-coated separator treated by HHIC.

enhanced due to the polar nature of the PEO coating. Thus the good wetting of the cross-linked PEO-coated separator with the electrolyte is expected to decrease the internal resistance and consequently improve the electrochemical performances of the lithium-ion battery cell (*e.g.* longer cycle life). It is noted that oxygen plasma was often used to improve the wetting properties of separators, but the wetting ability of modified separators with the electrolyte and water reported in the recent literature (*e.g.* water contact angles of more than  $40^\circ$  for modified separators)<sup>11,14,27</sup> are poorer than our separator modified by HHIC. It should be ascribed to two reasons: (1) oxygen plasma often introduces various oxygen-containing groups (*e.g.*  $-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $\text{CO}-\text{O}$ ), but some of them (*e.g.*  $\text{C}=\text{O}$ ) are not highly hydrophilic; (2) the amount of generated oxygen-containing groups on PP are limited, and they are unstable, which restrict the improvement in surface polarity and durability. However, our HHIC approach can effectively introduce the desirable functionalities such as  $-\text{OH}$  and  $\text{C}-\text{O}-\text{C}$  with a little loss by fixing the targeting molecules (PEO) on the PP surface.<sup>30</sup>

### 3.3 Electrochemical properties of cells assembled with modified separators

In order to evaluate the effect on the electrochemical properties of the HHIC-treated PEO layer on the separator, half-cells ( $\text{LiCoO}_2/\text{separator}/\text{lithium metal}$ ) were prepared. The AC impedance spectroscopy technique was employed to study the effect of improved wetting in the separator on the bulk resistance of the electrolyte through a porous separator. From AC impedance spectroscopic investigation,<sup>19,36</sup> the overlapping semicircles observed in the middle frequency range regions correspond to the charge accumulation process and the charge transfer process, both of which are related to the solid electrolyte interface (SEI) film impedance and the charge transfer process. As illustrated in Fig. 5, the total interfacial resistance ( $R_i$ ), that is the sum of the resistance of SEI ( $R_{\text{SEI}}$ ) and the charge transfer resistance ( $R_{\text{ct}}$ ), can be determined from the depressed semicircles. Evidently, the interfacial resistance of the lithium-ion cell assembled by sandwiching the pristine separator

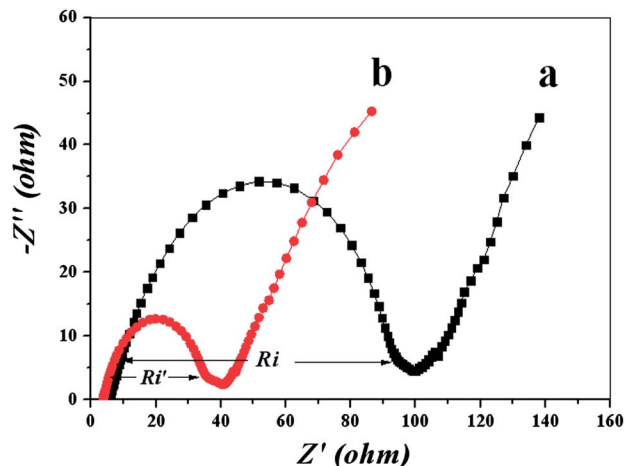


Fig. 5 A.C. impedance spectra of the lithium-ion cell assembled by sandwiching (a) the pristine separator and (b) the PEO-coated separator treated by HHIC after chloroform washing for 12 h.

( $\sim 100 \Omega$ ) is about 2.5 times higher than that with the cross-linked PEO-coated separator ( $\sim 40 \Omega$ ) after HHIC treatment. The cross-linked PEO-coated PP separator is shown to significantly decrease the interfacial resistance of the lithium-ion cell.

The discharge capacities of cells with the pristine and cross-linked PEO-coated separators are shown in Fig. 6. The discharge capacity of the cell slowly decreases with the increasing cycle number. This observation can be attributed to the deterioration of the interfacial contact of the electrodes and the physical changes in the active materials for the electrodes,<sup>12,37</sup> which leads to a gradual increase of internal cell resistance during repeated charge–discharge cycles. After 30 cycles, the cell with the cross-linked PEO-coated PP separator retained 84.1% of the initial discharge capacity, while the cell with the pristine separator showed 72.5%. Higher discharge capacity retention of the cell with the cross-linked PEO-coated separator is attributed to

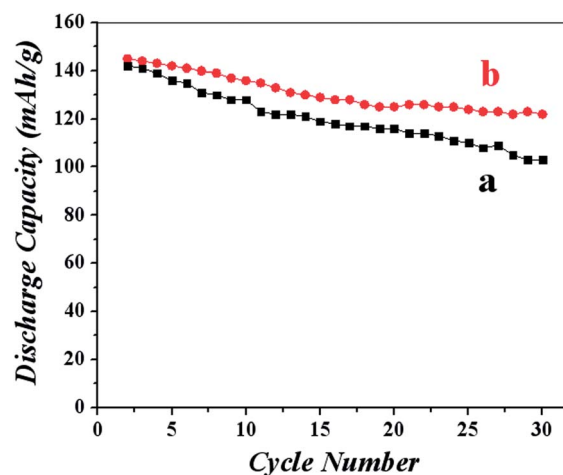


Fig. 6 Discharge capacity of lithium-ion cells assembled by sandwiching (a) the pristine separator and (b) the PEO-coated separator treated by HHIC after chloroform washing for 12 h.

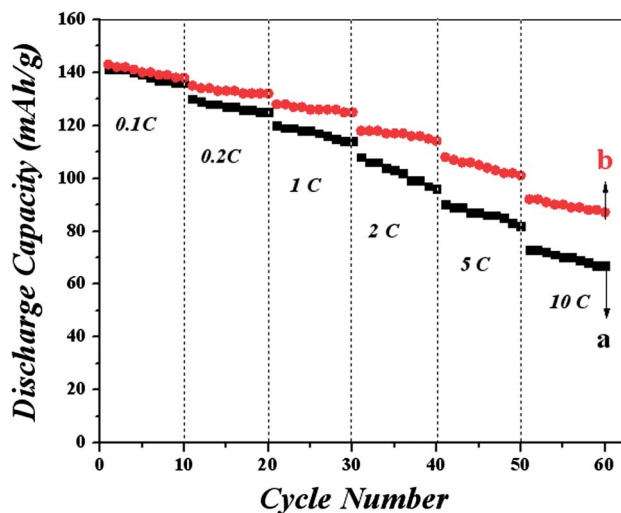


Fig. 7 Rate capability of lithium-ion cells assembled with (a) pristine and (b) PEO-coated separators treated by HHIC after chloroform washing for 12 h.

the enhanced wettability with the electrolyte and the reduced interfacial resistance.<sup>38</sup> This result suggests that the cross-linked PEO-coating on the separator surface by HHIC treatment plays a critical role in improving the cycle performance of the lithium-ion cell. The discharged capacities of cells at various current densities ranging from 0.1 C ( $C = 274 \text{ mA h g}^{-1}$ ) to 10 C are shown in Fig. 7. The cells with the pristine and the PEO-coated separators exhibit the capacity retentions of 85.1 and 89.5%, respectively, at 1 C rate, and then decreased clearly with increase in the current density. At higher current densities (5 and 10 C, respectively), the cell with the PEO-coated separator (80.0 and 70.0% capacity retentions, respectively) exhibits much higher capacity retention than that with the pristine separator (65.0 and 57.1% capacity retentions, respectively). That is, with the increase of current density, the difference in capacity drop at large current density between the pristine separator and the modified separator becomes more significant. It suggests that the modified separator with good electrolyte wettability facilitates ion transport through the separator at large current density, which contributes to the enhanced rate capacity.

## 4. Conclusion

Polar PEO was successfully cross-linked on the surface of the PP separator by short HHIC treatment of only 60 s at room temperature. The solvent wash test for the treated separator has proven that the PEO coating can be firmly fixed on the separator surface. Compared to the pristine PP separator with low surface energy, the modified separator exhibits an improved wetting with the electrolyte and low internal resistance without adversely affecting its polar characteristics. This leads to a lower internal resistance and higher capacity retention during battery cycling. Compared to conventional surface modification methods (such as UV curing, plasma radiation and high-temperature heating treatment), the HHIC treatment process is

shown to be a highly efficient and mild (room-temperature reaction) method for modifying separator surfaces without the undesired damage, which is extremely important for the battery safety. In addition, this approach is very environmental- and cost-effective for the battery manufacturing industry because extra thermal consumption and chemical additives such as chemical cross-linkers, initiators, catalysts and other reactive agents are not required.

## Acknowledgements

We would like to express our sincere thanks to financial support from National Natural Science Foundation of China (51103141 and 21105092), CAEP fund (2013B0302058), Sichuan technology innovation fund (20132039) and advanced functional polymer coating program.

## Notes and references

- 1 D. Aurbach, E. Zinigrad, Y. Cohen and H. Teller, *Solid State Ionics*, 2002, **148**, 405–416.
- 2 V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, **4**, 3243–3262.
- 3 B. Kang and G. Ceder, *Nature*, 2009, **458**, 190–193.
- 4 S. Yang, Y. Gong, Z. Liu, L. Zhan, D. P. Hashim, L. Ma, R. Vajtai and P. M. Ajayan, *Nano Lett.*, 2013, **13**, 1596–1601.
- 5 Y. Yao, M. T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W. D. Nix and Y. Cui, *Nano Lett.*, 2011, **11**, 2949–2954.
- 6 B. Jang, M. Park, O. B. Chae, S. Park, Y. Kim, S. M. Oh, Y. Piao and T. Hyeon, *J. Am. Chem. Soc.*, 2012, **134**, 15010–15015.
- 7 J. Hassoun, D. J. Lee, Y. K. Sun and B. Scrosati, *Solid State Ionics*, 2011, **202**, 36–39.
- 8 J. Hassoun, K. S. Lee, Y. K. Sun and B. Scrosati, *J. Am. Chem. Soc.*, 2011, **133**, 3139–3143.
- 9 N. S. Choi, Y. G. Lee, J. K. Park and J. M. Ko, *Electrochim. Acta*, 2001, **46**, 1581–1586.
- 10 X. Huang, *J. Solid State Electrochem.*, 2010, **15**, 649–662.
- 11 J. Y. Kim and D. Y. Lim, *Energies*, 2010, **3**, 866–885.
- 12 S. S. Zhang, *J. Power Sources*, 2007, **164**, 351–364.
- 13 X. Huang and J. Hitt, *J. Membr. Sci.*, 2013, **425**, 163–168.
- 14 C. Huang, C. C. Lin, C. Y. Tsai and R. S. Juang, *Plasma Processes Polym.*, 2013, **10**, 407–415.
- 15 X. Lv, H. Li, Z. Zhang, H. Chang, L. Jiang and H. Liu, *Phys. Procedia*, 2012, **25**, 227–232.
- 16 J. M. Ko, B. G. Min, D. W. Kim, K. S. Ryu, K. M. Kim, Y. G. Lee and S. H. Chang, *Electrochim. Acta*, 2004, **50**, 367–370.
- 17 J. Y. Sohn, J. S. Im, J. Shin and Y. C. Nho, *J. Solid State Electrochem.*, 2011, **16**, 551–556.
- 18 H. Ju, Z. Li, L. Ju and Y. Xu, *ECS Electrochem. Lett.*, 2012, **1**, A59–A62.
- 19 D. W. Kim, K. A. Noh, J. H. Chun, S. H. Kim and J. M. Ko, *Solid State Ionics*, 2001, **144**, 329–337.
- 20 Y. S. Chung, S. H. Yoo and C. K. Kim, *Ind. Eng. Chem. Res.*, 2009, **48**, 4346–4351.
- 21 J. L. Shi, L. F. Fang, H. Li, H. Zhang, B. K. Zhu and L. P. Zhu, *J. Membr. Sci.*, 2013, **437**, 160–168.

- 22 K. Gao, X. Hu, T. Yi and C. Dai, *Electrochim. Acta*, 2006, **52**, 443–449.
- 23 S. Hu, X. Ren, M. Bachman, C. E. Sims, G. P. Li and N. Allbritton, *Anal. Chem.*, 2002, **74**, 4117–4123.
- 24 J. Yuan, L. Chen, X. Jiang, J. Shen and S. Lin, *Colloids Surf., B*, 2004, **39**, 87–94.
- 25 D. L. Versace, P. Dubot, P. Cenedese, J. Lalevee, O. Soppera, J. P. Malval, E. Renard and V. Langlois, *Green Chem.*, 2012, **14**, 788–798.
- 26 I. Ishigaki, T. Sugo, K. Senoo, T. Okada, J. Okamoto and S. Machi, *J. Appl. Polym. Sci.*, 1982, **27**, 1033–1041.
- 27 J. Y. Kim, Y. Lee and D. Y. Lim, *Electrochim. Acta*, 2009, **54**, 3714–3719.
- 28 S. Karamdoust, B. Yu, C. V. Bonduelle, Y. Liu, G. Davidson, G. Stojcevic, J. Yang, W. M. Lau and E. R. Gillies, *J. Mater. Chem.*, 2012, **22**, 4881–4889.
- 29 D. B. Thompson, T. Trebicky, P. Crewdson, M. J. McEachran, G. Stojcevic, G. Arsenault, W. M. Lau and E. R. Gillies, *Langmuir*, 2011, **27**, 14820–14827.
- 30 C. V. Bonduelle, W. M. Lau and E. R. Gillies, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1740–1748.
- 31 Z. Zheng, K. W. Wong, W. C. Lau, R. W. Kwok and W. M. Lau, *Chem. –Eur. J.*, 2007, **13**, 3187–3192.
- 32 W. M. Lau, Z. Zheng, Y. H. Wang, Y. Luo, L. Xi, K. W. Wong and K. Y. Wong, *Can. J. Chem.*, 2007, **85**, 859–865.
- 33 Z. Zheng, W. M. Kwok and W. M. Lau, *Chem. Commun.*, 2006, 3122–3124.
- 34 Z. Zheng, X. D. Xu, X. L. Fan, W. M. Lau and R. W. M. Kwok, *J. Am. Chem. Soc.*, 2004, **126**, 12336–12342.
- 35 X. Wang, T. Zhang, B. Kobe, W. M. Lau and J. Yang, *Chem. Commun.*, 2013, **49**, 4658–4660.
- 36 Y. B. Jeong and D. W. Kim, *J. Power Sources*, 2004, **128**, 256–262.
- 37 P. Arora and Z. M. Zhang, *Chem. Rev.*, 2004, **104**, 4419–4462.
- 38 J. Y. Kim, S. K. Kim, S. J. Lee, S. Y. Lee, H. M. Lee and S. Ahn, *Electrochim. Acta*, 2004, **50**, 363–366.