Electronic supplementary information

Trifunctional Multi-walled Carbon Nanotubes/Polyethylene Glycol (MWCNT/PEG)-coated Separator through a Layer-by-layer Coating Strategy for High-energy Li-S Batteries

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Experimental

Preparation of layer-by-layer MWCNT/PEG-coated Separators

The MWCNT/PEG slurry was prepared by mixing 50 wt.% multi-walled carbon nanotubes (MWCNT: 10 mg, NanoTechLabs, Inc.) with 50 wt.% polyethylene glycol (PEG: 10 mg, average molecular weight = 300 g mol^{-1}, Aldrich) in isopropyl alcohol (IPA). After ultra-sonication for 30 min, the slurry was coated onto one side of a polypropylene membrane (Celgard 2500) through the vacuum-filtration process, followed by drying in a vacuum oven at 50 °C overnight to form a standard one-layer MWCNT/PEG-coated (MWCNT/PEG#1) separator. For preparing a MWCNT/PEG#2-coated separator, another batch of MWCNT/PEG mixtures was vacuum-filtered onto the dried MWCNT/PEG#1-coated separator. This process creates a layered configuration that has a "buffer zone" in between the two MWCNT/PEG coating layers. For preparing a MWCNT/PEG#3-coated separator, one more batch of the MWCNT/PEG mixtures was vacuum-filtered onto the dried MWCNT/PEG#2-coated separator, resulting in two buffer zones in between the three MWCNT/PEG coating layers. The diameter of the coating is 1.9 cm. The weights of the layer-by-layer MWCNT/PEG#1, MWCNT/PEG#2, and MWCNT/PEG#3 coatings are, respectively, *c.a.* 0.039, 0.078, and 0.117 mg cm^{-2} (Fig. S1b). As a control experiment,

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MWCNT/PEG mixtures containing 20 mg of MWCNT and 20 mg of PEG as well as 30 mg of MWCNT and 30 mg of PEG were directly vacuum-filtered onto a Celgard membrane as, respectively, the non-layer-by-layer MWCNT/PEG#2- and MWCNT/PEG#3-coated separators. The MWCNT/PEG-coated separators were configured with the coating layer facing toward the cathode so that the MWCNT/PEG coating could filter out the diffusing polysulfides before they diffuse out from the cathode region of the cells. In order to assess the polysulfide-filtering capability, a liquid-uptake rate was calculated as [1,2]

$$\text{Liquid-uptake rate (\%)} = \frac{W - Wo}{Wo} \times 100$$

where W_0 and W are the respective weights before and after absorbing the electrolyte solution. The surface accumulation of electrolyte solution was avoided, which could present a fair data comparison. Fig. S5 indicates that the bare Celgard separator itself has a liquid-uptake rate of 300% due to its porous structure, assuring a high electrolyte flux. Therefore, the liquid electrolyte could quickly spread throughout the membrane and smoothly migrate through the open pores of the Celgard membrane, resulting in a high ionic conductivity. This is the reason why the Celgard membrane is commonly used separator in many different battery research. On the other hand, after adding the MWCNT/PEG coating layers, the separator exhibits a higher liquid uptake rate. As the number of coating layer increases, the liquid-uptake rate of the separator increases from 300% to 500%. This implies that the MWCNT/PEG coating layer has a synergistic effect with the Celgard membrane on enhancing the electrolyte flux, further improving the ionic conductivity. Moreover, due to the unblocked electrolyte pathway and the strong tortuosity of the MWCNT/PEG coating, the MWCNT/PEG-coated separator functions well as a filter to filter out just the diffusing polysulfides.

Regular pure sulfur cathode preparation

A mixture of 80 wt.% precipitated sulfur, 10 wt.% Super P (TIMCAL), and 10 wt.% polyvinylidene fluoride (PVDF, kureha) was dispersed in N-methyl-2-pyrolidone (NMP), and stirred for 2 days to form uniform active material slurry. The obtained viscous slurry was coated onto an aluminium foil current collector by the doctor blade method and dried at 50 °C for 12 h in a vacuum oven, followed by roll-pressing and cutting into circular disks. The sulfur content (including the weight of coating additives) is identical (78 wt.%). The sulfur loadings of the cells employing the MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators are, respectively, 1.3, 2.6, and 3.9 mg cm^{-2}. All the capacity values were calculated on the basis of sulfur mass and the theoretical capacity.

Cell assembly

CR2032-type coin cells were assembled inside an argon-filled glove box. A commercial Celgard 2500 PP membrane was used as the pristine separator. The electrolyte solution was 1.85 M $LiCF_3SO_3$ salt (Acros Organics) in a mixed solvent of 1,2-Dimethoxyethane (DME; Acros Organics) and 1,3-Dioxolane (DOL; Acros Organics) (1 : 1 by volume) with 0.1 M $LiNO_3$ as an additive. The electrolyte/sulfur (E/S) ratio was controlled to be 15 in all examined cells. The assembled Li-S cells were placed to rest for 10 h before conducting the cycling test.

Electrochemical and Microstructural Analyses

The electrochemical impedance spectroscopy (EIS) data of the cells before and after cycling were collected with a potentiostat (VMP3, Bio-logic) in the frequency range of 1 MHz to 100 mHz. Discharge/charge curves, Q_H/R_{QH}, and cycling performance were recorded with a cell test system (Arbin Instruments) in a potential window of 1.8 - 2.8 V at various cycling rates (C/5 ~ 1C). Cyclic voltammetry (CV) tests were performed using a universal potentiostat (VoltaLab PGZ 402, Radiometer Analytical) at a scan rate of 0.075 mV s^{-1} with a potential range of 1.8 - 2.8 V. Microstructure analyses were carried out with an automated gas sorption analyzer (AutoSorb iQ2, Quantachrome Instruments), and a field emission scanning electron microscope (Quanta 650 FE-SEM, FEI) with an energy-dispersive X-ray spectrometer (EDX) for elemental mapping. The shuttle factor was calculated based on the relationship between the Coulombic efficiency and the shuttle factor as[3,4]

$$C_{eff} = \frac{Q_{DH} + Q_{DL}}{Q_{CH} + Q_{CL}} = \frac{2f + ln(1 + f)}{2f - ln(1 - f)}$$

where C_{eff} refers to the Coulombic efficiency and f refers to the shuttle factor.

The average Coulombic efficiency of the cell with a bare Celgard separator is 65 % after 150 cycles. In contrast, the cells with MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators retain very high average Coulombic efficiencies of, respectively, 96.3 %, 97.5 %, and 98.2 % after 300 cycles at C/5 rate. Thus the shuttle factors of the cells with a bare Celgard separator and MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators are, respectively, 0.84, 0.11, 0.08, and 0.05, as shown in Fig. S6. With the coating of MWCNT/PEG, the shuttle factor is significantly reduced. Furthermore, with an increase in number of coating layers, the shuttle factor further decreases, indicating that the multi-layered separator is better at suppressing the shuttle effect in the cell.

Supporting figures

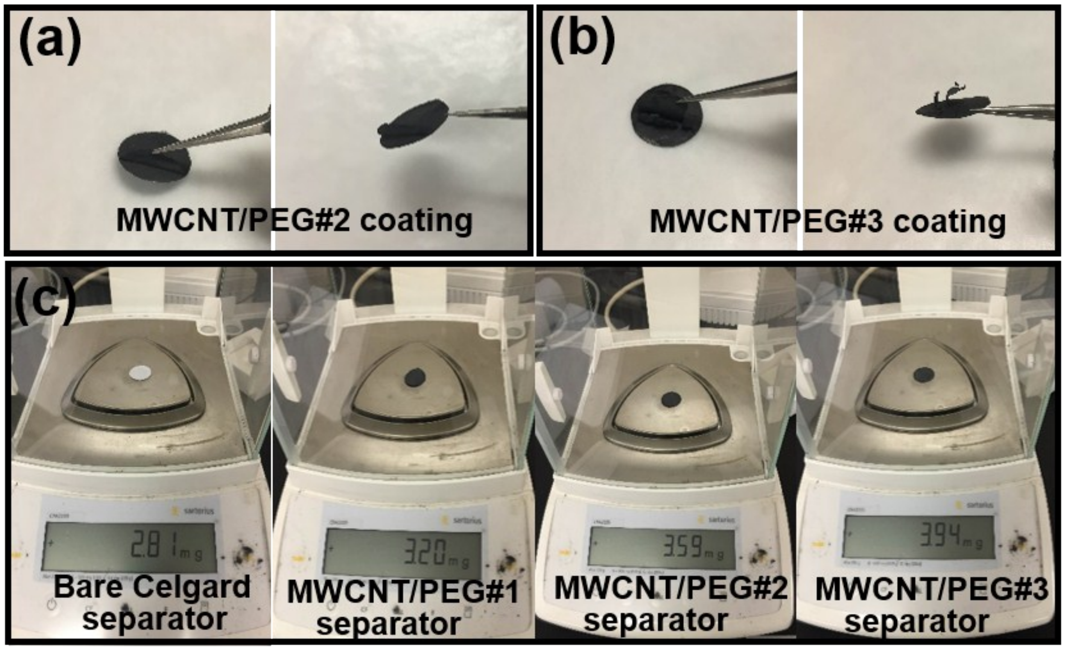

Fig. S1 Illustration of the layer-by-layer structure for the (a) MWCNT/PEG#2- and (b) MWCNT/PEG#3-coated separators. (c) The weights of the bare Celgard, MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators (from left to right) are indicated.

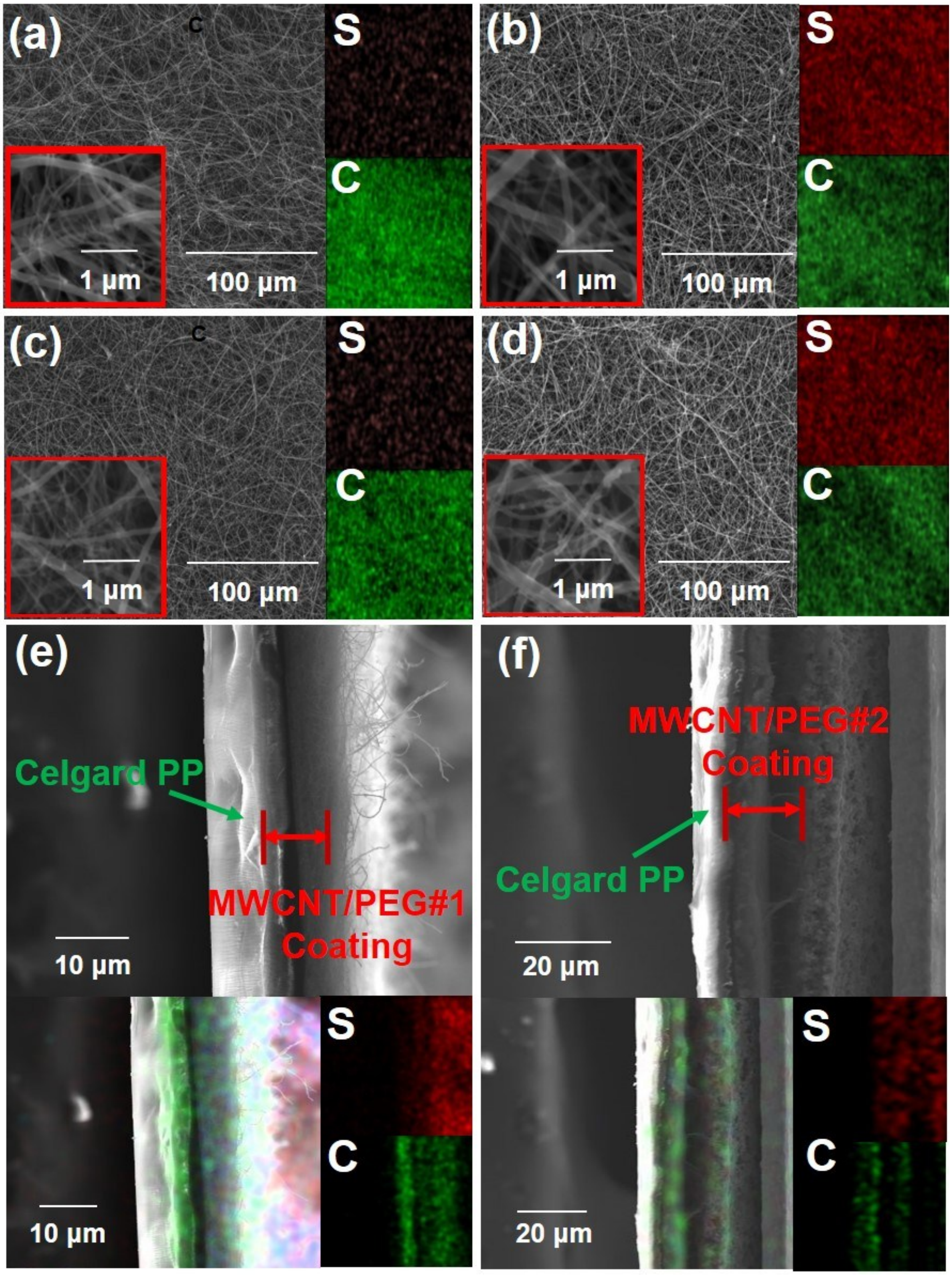

Fig. S2 SEM images and elemental analysis of the separators with (a) uncycled and (b) cycled MWCNT/PEG#1 coatings and (c) uncycled and (d) cycled MWCNT/PEG#2 coatings. Cross-sectional SEM images of cycled separators with (e) MWCNT/PEG#1 and (f) MWCNT/PEG#2 coatings.

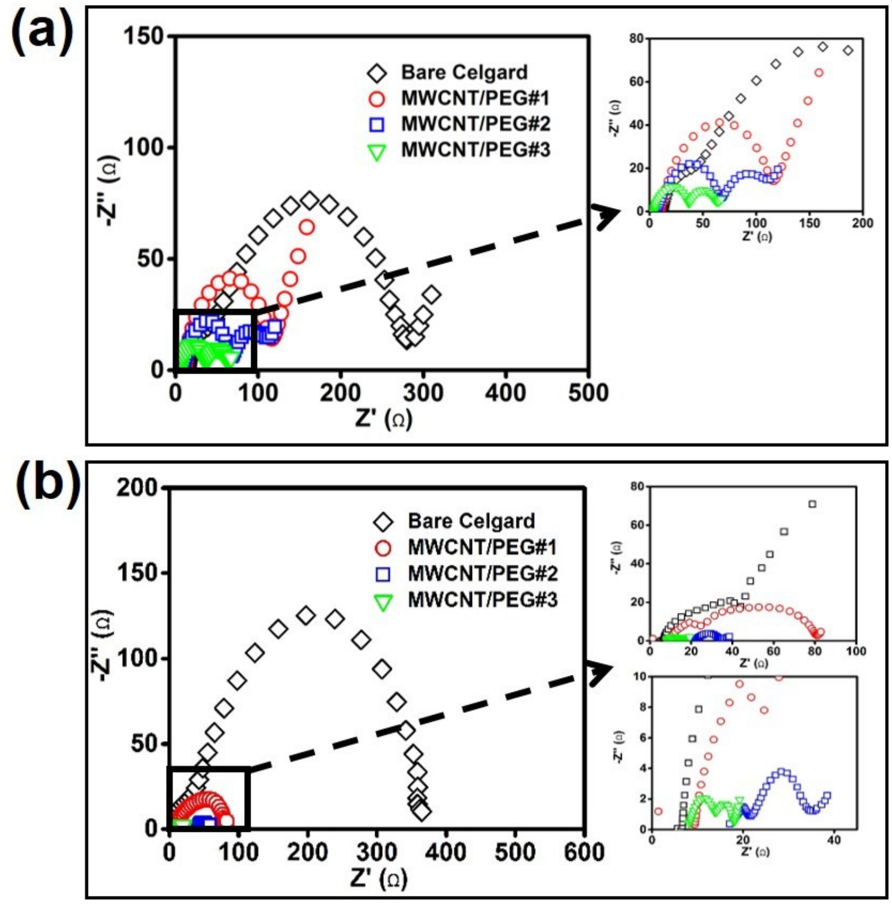

Fig. S3 EIS of cells with the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator (a) before and (b) after 300 cycles.

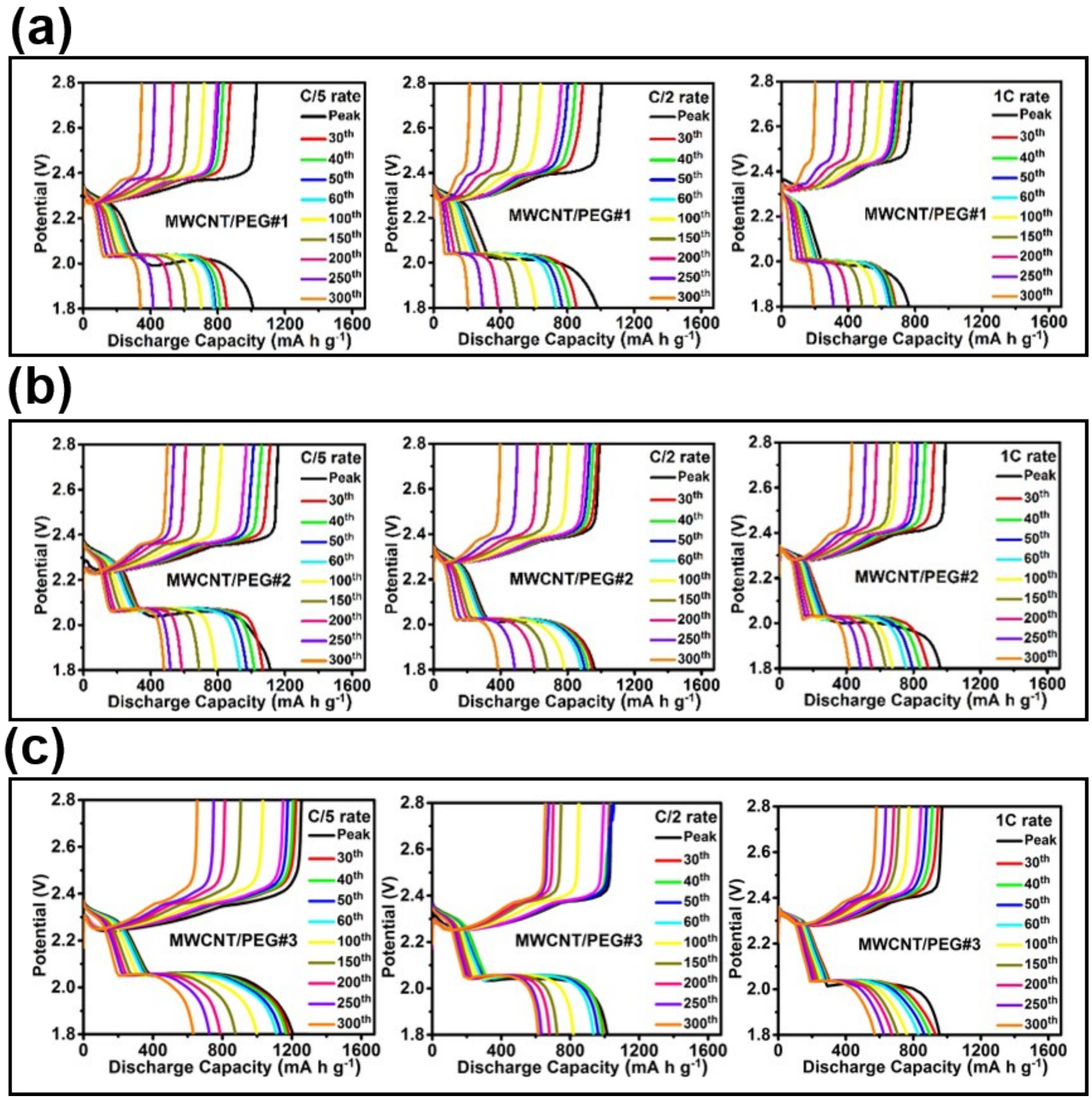

Fig. S4 Discharge/charge curves of cells with separators containing (a) MWCNT/PEG#1, (b) MWCNT/PEG#2, and (c) MWCNT/PEG#3 coatings at various cycling rates.

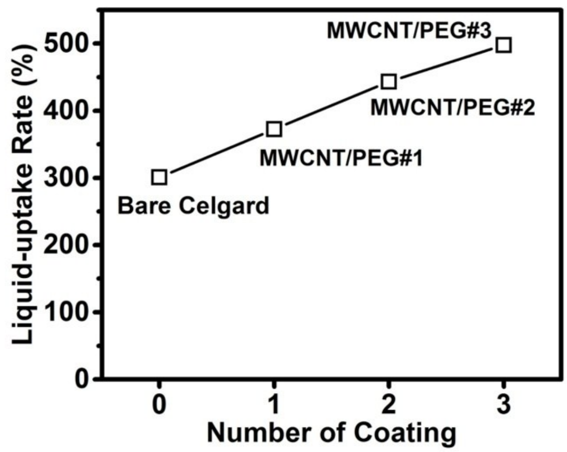

Fig. S5 Liquid-uptake rate of the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator.

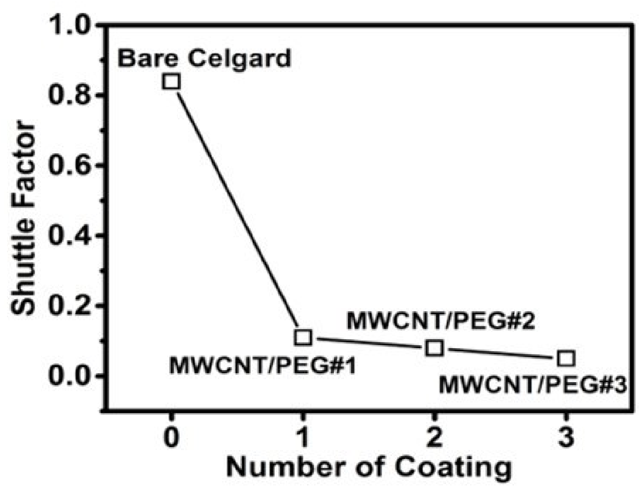

Fig. S6 Shuttle factor of the cells with the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator at C/5 rate.

References

1. Z. Li, G. Su, D. Gao, X. Wang and X. Li, *Electrochem. Acta*, 2004, **49**, 4633-4639.

2. F. Lian, Y. Wen, Y. Ren and H. Guan, *J. Membr. Sci.*, 2014, **456**, 42-48.

3. Y. V. Mikhaylik and J. R. Akridge, *J. Electrochem. Soc.*, 2004, **151**, A1969-A1976.

4. J. Q. Huang, Q. Zhang, S. M. Zhang, X. F. Liu, W. C. Zhu, W. Z. Qian and F. Wei, *Carbon*, 2013, **58**, 99-106.