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Short Communication

Membrane Separators Coated by TiO_2-PMMA with Low Thermal Shrinkage Rate for Lithium-Ion Batteries

Yangyang Xi, Peng Zhang, Haining Zhang, Zhaohui Wan, Wenmao Tu, Haolin Tang[*]

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China, 430070
[*]E-mail: thln@whut.edu.cn

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Composite membrane separators are fabricated by coating one side of microporous polyethylene membrane with poly(methyl methacrylate) modified titanate nanoparticles that are synthesized through emulsifier-free emulsion polymerization of methacrylate-functionalized titanate nanoparticles. The formed composite membrane separators exhibit great thermal-shrinking resistance due to the introduction of thermal resistant titanate nanoparticles. After immersed into electrolyte solution, the swelling poly(methyl methacrylate) microspheres leads to the formation of gel electrolyte, thus stabilizing the electrolyte. Moreover, the porous structure of the coated layer can facilitate the swelling of electrolyte and the transport of lithium ions. The thus-assembled lithium ion battery shows an improved cycle performance and rate capability.

Keywords: Lithium ion battery, composite membrane separator, titanate nanoparticles, surface modification, ionic conductivity

1. INTRODUCTION

Lithium ion batteries have been widely applied for portable electronic devices and electric vehicles due to their high energy density and long cycling performance[1]. As one of the key components, membrane separator functions not only as the separation materials between anode and cathode to avoid short circuit, but also as the medium for lithium ion transport from anode to cathode after filled with electrolyte solutions. Currently, the often used and commercially available membrane separators are made of polyolefins including polyethylene (PE), polypropylene (PP), and the composites of PE and PP [2]. However, the relatively low thermal stability of polyolefins can lead to the short circuit between anode and cathode at elevated temperature during battery operation, which in turn results in the safety issue due to the thermal runaway, more seriously causing fire or explosion

[3,4]. Thus, development of membrane separator with high thermal stability is of great importance for safe operation of lithium ion batteries.

One effective way to address the low thermal stability of polyolefin membrane separators is to coat the surface either with polymeric materials having low shrinkage ratio or with ceramic nanoparticles. It has been reported that the temperature for 5% shrinkage ratio of PE membrane increased from 122 ^{o}C to 132 ^{o}C after surface coating with carboxymethyl cellulose [5]. Shi et al. reported that both thermal stability and electrochemical performance improved for the battery assembled from aluminum oxide nanoparticles coated PE membrane using emulsion of carboxymethyl cellulose/styrene-butadiene rubber (SBR) as binder [6]. In another example, Ruey et al. demonstrated that coating titanate dioxide nanoparticles on PP/PE/PP composite membrane separator can significantly enhance the thermal stability and cycling performance of aeembled batteries [7].

Apart from the membrane separator, the leakage of electrolyte solution from the membrane is also a great concern to the safe operation of lithium ion battery since flammable gas might be emitted [8]. Gel polymer electrolyte (GPE) has been realized as potential membrane electrolyte to protect leakage of electrolyte solution from the membrane as it has great electrolyte retention capability. For instance, Park et al. reported the enhanced wettability of membrane separator with electrolyte solution after coated the PE surface with poly(methyl methacrylate) microspheres[9]. Accordingly, both ionic conductivity of membrane separator and the rate capability of battery are improved compared to the pristine PE membrane separators[10]. Jun et al. found that after grafting of PMMA chains on the surface of PE using surface-initiated polymerization, the ionic conductivity of the electrolyte filled membrane separator reached 1.19 mScm^{-1} at room temperature[9]. Although GPE exhibits high ion conductivity and great compatibility to the electrode, the relatively weak mechanical strength hinders their further practical applications[11].

In this paper, we report the fabrication of composite membrane separators by coating the surface of PE membranes with PMMA modified titanate dioxide nanospheres. The idea behind this design is to improve the thermal stability of the membrane separator and the wettability with electrolyte solution. The TiO_2-PMMA nanospheres are synthesized by emulsion polymerization of methacrylate modified TiO_2 nanospheres and methyl methacrylate (MMA) monomer. The physicochemical properties of the formed composite membrane separator with 5 μm TiO_2-PMMA layer was investigated in detail and the electrochemical performance of thus-assembled lithium ion batteries was evaluated.

2. EXPERIMENTAL

2.1 Synthesis of TiO_2-PMMA nanospheres

To a suspension of 10g TiO_2 (100nm, Aladdin) in 250ml absolute ethanol, 13ml deionized water, 6.8g aqueous ammonia, 6.2g γ-methacryloxy propyl trimethoxyl silane (MPS/KH570, 98%, Aldrich) were added sequentially. After sonication for 1h, the above mixture was stirred for 48h. The products of MPS modified TiO_2 (TiO2-MPS) nanospheres were collected by centrifugation, thoroughly washed with deionized water, and finally dried under vaccum at 60 ^oC.

To from TiO_2-PMMA nanospheres, 1.0g TiO_2-MPS was dispersed in 90ml deionized water in a 250ml three-neck flask under protection with nitrogen atmosphere. 3.0g methyl methacrylate (MMA, purified with 5 wt% NaOH aqueous solution) and 0.05g potassium persulfate (KPS) in 10ml deionized water were added to the suspension. The mixture was refluxed for 6h. The resultant was centrifuged and washed with deionized water for three times to remove the remained monomers and initiators. The final products were dried under vacuum at 60 ^oC for 12h.

2.2 Fabrication of TiO_2-PMMA/PE composite membrane separator

0.95g TiO2-PMMA, 0.03g SBR emulsion (50 wt%), 0.02g carboxymethyl cellulose were mixed with 5ml absolute ethanol and 5ml deionized water to form the white slurry for coating. The slurry was then coated on onside of PE membrane (20 μm, wet-processing method, Toray) using concave scraper. The TiO_2-PMMA/PE composite membrane separator was finally dried under air flow at 60 ^oC for 6h.

2.3 General characterization

Flourier transformation infrared spectroscopy (FTIR, Nicolet 6700) was applied to determine the surface modification of TiO_2 with MPS and PMAA in the range of 400 to 4000cm^{-1} with resolution of 4cm^{-1}. The morphology of the membrane was investigated using field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra Plus). Thermal shrinkage rate was calculated by the variation of area of the membrane (initial size: 4.5cm×4.5cm) before and after keeping the sample at different temperatures for 30min. The electrolyte uptake was estimated from the weight change of membrane after immersed the membrane into 1M LiPF6 solution in mixed solvent of ethylene carbonate/dimethylcarbonate (EC/DMC, 1:1 in volume) for 30min. Before weighing the sample with electrolyte, the electrolyte solution at the surface was rapidly wiped off using filter paper. Contact angle measurements were carried out to investigate the wettability of membrane with electrolyte solution. To determine the ion conductivity of membrane separators after electrolyte uptake, the sample was sandwiched between two stainless steel and assembled in a CR2032 cell in glovebox. The AC impedance was measured on an electrochemical working station (CHI604D, Chenhua) in the frequency range of 10 – 105 Hz and the ion conductivity (σ) was calculated using $\sigma = L/(R\times A)$, where L is the thickness of membrane, R is the resistance obtained from AC impedance measurement, and A is the effective contact area of electrode (2.13cm^2 in this work).

2.4 Lithium ion battery assembly and electrochemical performance

To evaluate the potential application of the designed composite membrane separator, button cells (CR2016) was assembled in a glovebox filled with argon using $LiFePO_4$ as cathode, lithium foil as anode, and 1M $LiPF_6$ solution in EC/DMC mixed solvent (1:1 in volume) as electrolyte. To prepare the cathode, the mixture of $LiFePO_4$, acetylene black, and polyvinylidene fluoride (PVDF) (weight ratio of 8:1:1) was dispersed in N-methylpyrrolidone (NMP) to form the slurry. The slurry was homogeneously coated on aluminum foil and dried with blowing air for 2h at 80 ^oC, followed by drying in vacuum at 100 ^oC for 12h. The cathode was finally obtained by punching the coated aluminum to circle shape for assembly of CR2016 cells. Prior to the measurements of battery performance, the assembled cell kept at room temperature for 24h. The charge/discharge cycling tests were performed on CT2001A (LAND Electronics) under constant current mode at 0.5C in the voltage range of 2.5 – 3.8V. The rate capability of the assembled battery was tested under 0.2, 0.5, 1 and 2C, respectively.

3. RESULTS AND DISCUSSION

To fabricate the TiO_2-PMMA/PE membrane separators, TiO_2-PMMA nanospheres were first synthesized through emulsion polymerization of TiO_2-MPS and MMA monomer. FTIR spectra of pristine TiO_2, TiO_2-MPS, and TiO_2-PMMA were recorded to monitor the surface modification process, as shown in Figure 1. For pristine TiO_2, the absorption band at around 700 cm^{-1} is typical Ti-O-Ti vibration and absorption bands around 3400cm^{-1} and 1635cm^{-1} are assigned to surface hydroxyl groups and adsorbed water molecules. The absorption bands from 1200cm^{-1} to 1400cm^{-1} result from the residue alkoxyl groups at the surface due to incomplete hydrolysis during TiO_2 formation. After surface modification of TiO_2 with MPS, the appeared absorption band at 1723 cm^{-1} is corresponded to the stretching vibration of C=O groups[12]. The significantly increased absorption band at 1723 cm^{-1} ($\upsilon_{C=O}$) and the observed new absorption bands at 2993 cm^{-1} (υ_{C-H}) and in the fingerprint region of 1200-1400 cm^{-1} clearly suggest the successful polymerization at surface of TiO_2.

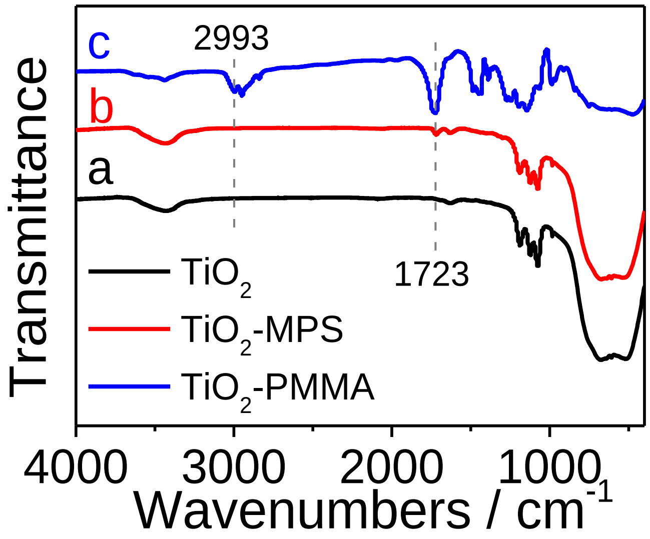

Figure 1. FTIR spectra of pristine TiO_2 (a), TiO_2-MPS (b), and TiO_2-PMMA (c).

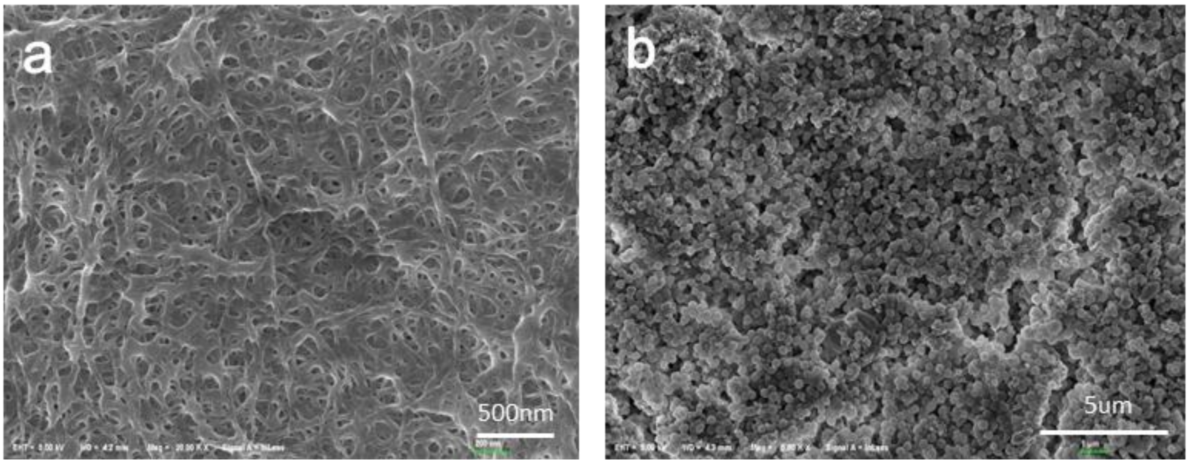

Figure 2. SEM images of PE membrane separator (a) and TiO_2-PMMA/PE composite membrane separator (b).

Figure 2 displays the SEM images of PE membrane separator and the formed composite membrane separator of TiO_2-PMMA/PE. It is obvious that the PE membrane has microporous structure with homogeneous pore distribution (Figure 2a). After surface coating with TiO_2-PMMA microspheres (Figure 2b), it can be clearly seen that the spherical particles are homogeneously distributed on the surface and no obvious aggregation was observed. It is evident that the formed voids among coated nanospheres provide porous structure of the coating layer. Such porous structure is beneficial for storage of electrolyte solution and for lithium ion conduction[13].

The wettability of membrane separator with electrolyte solution was investigated by photographs and contact angle measurements. Figure 3 shows the photographs of PE membrane separator and TiO_2-PMMA/PE composite membrane separator in contact with electrolyte solution. It can be seen that the electrolyte solution does not wet the pristine PE membrane and it however spread out the surface of TiO_2-PMMA/PE composite membrane rapidly, suggesting the high electrolyte uptake for TiO_2-PMMA/PE composite membrane.

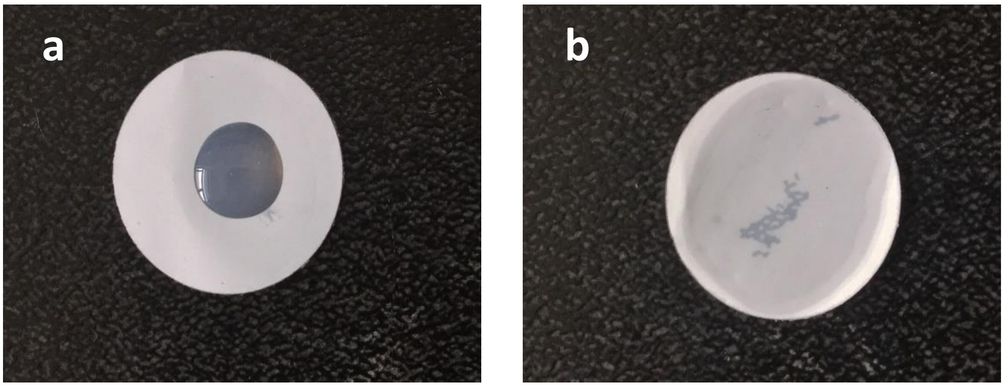

Figure 3. Photographs of PE membrane separator (a) and TiO_2-PMMA/PE composite membrane separator (b) in contact with electrolyte solution.

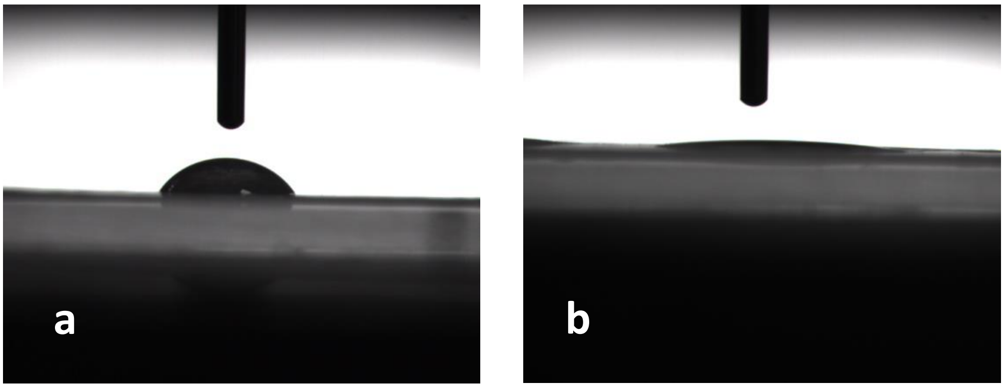

Figure 4. Photographs of electrolyte solution drop in contact with PE membrane separator (a) and iO_2-PMMA/PE composite membrane separator (b) for contact angle measurements.

Contact angles were further applied to quantitively evaluate the wetting behavior of membrane separators, as shown in Figure 4. The contact angle for pristine PE membrane separators is observed to be about 52.5^o whereas it is only about 5^o for TiO_2-PMMA/PE composite membrane separator, indicating the great electrolyte uptake for the formed composite membrane separator. Such enhancement is probably caused by two reasons. Firstly, the coating layer possesses nanosized porous structure, and the electrolyte solution can infiltrate facilely through the well-connected interstitial voids possibly driven by capillary force [10,14,15]. Secondly, PMMA molecules have a high affinity with the applied solvent because both solvent and PMMA contain carbonyl groups [10,16].

The electrolyte uptake of separator is closely related to the electrochemical performance of the lithium ion batteries[17].After immersed in electrolyte solution for 30min, the electrolyte uptake reaches 201.8% for TiO_2-PMMA/PE composite membrane separator which is much higher than that for pristine PE membrane separator (97.4%). For the composite separator, electrolyte solution can be stored in the pore of PE membrane and the porous structure of the coating layer. On the other hand , the PMMA can swell after absorbing electrolyte solution, improving the electrolyte uptake of separator[10,11,18].

Thermal stability of the membrane separator is closely related to the safety of the lithium ion batteries. The thermal shrinkage of the formed composite membrane separator was investigated at different temperature. Table 1 shows the shrinkage rate of PE and composite membrane separators at different temperature. It can be clearly seen that the formed TiO_2-PMMA/PE composite membrane separator exhibits much lower shrinkage rate than PE membrane separator does under the same conditions. For PE membrane separator, the shrinkage rate dramatically increased at temperature above 130 ^oC since the melt point of PE is about 135 ^oC. The shrinkage rate reaches about 48% for PE membrane separator at 140 ^oC and it is only about 29% for TiO_2-PMMA/PE composite membrane separator. Figure 5 shows the photographs of the membrane separators before and after placed in an oven at 140 ^oC for 30 min, provide more obvious evidence for the shrinkage of two membrane separators. For PE membrane separator (Figure 5a), the membrane after thermal treatment becomes more transparent compared to the initial sample as the melting of polymers can leads to the pore closed and the scattering of the light by porous structure was accordingly vanished.

Table 1. Shrinkage rate of membrane separators at different temperatures.

Temperature	Shrinkage rate	
	PE membrane	Composite membrane
110℃	1.25%	0
120℃	5.48%	2.22%
130℃	21.04%	10.81%
140℃	47.9%	29.6%

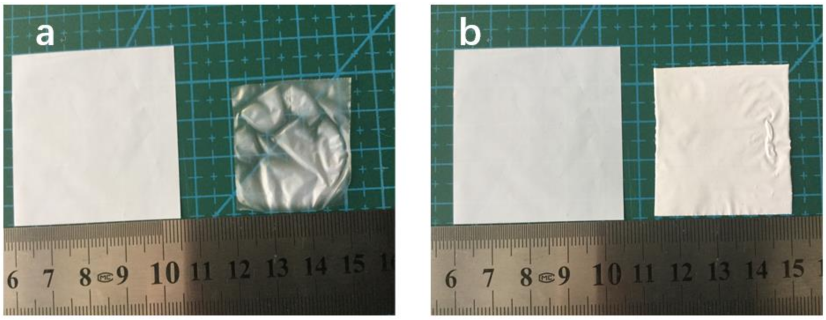

Figure 5. Photographs of PE membrane separator (a) and TiO_2-PMMA/PE composite membrane separator before (left) and after (right) placed in oven at 140°C for 30 min.

Although the shrinkage of TiO_2-PMMA/PE composite membrane separator was also observed (Figure 5b), the shrinkage rate is obviously much less than that of PE membrane separator. The enhanced thermal stability after coated PE membrane with TiO_2-PMMA nanospheres is attributed to the introduction of the highly stable TiO_2 nanoparticles [7,19,20]. In addition, the SBR-CMC mixed binder with high heat resistance can also improve the thermal stability of composite membrane [6,15]. Compared to other binders such as PVDF and PVDF-HFP [21,22], the SBR-CMC mixed system is water soluble, environmental friendly, and cost-effective whereas PVDF and PMMA must dissolve in organic solvents. The improvement of thermal stability using ceramic composite coatings has been reported by different research groups. For example, Park et al. reported that the thermal shrinkage of membrane separator of PE reached only 10% at 120 °C in 30 mins after coating with SiO_2/PMMA binary nanoparticles without any other binders [14]. Yang et al. prepared core-shell structured SiO_2-PMMA sub-microspheres, and coated it on one side PE separator. The according thermal shrinkage is 12.9% at 130℃ for 30min, which is similar to TiO_2-PMMA/PE composite membrane separator [15].

Ion conductivity is one of the key parameters for membrane separators and it determines the electrochemical performance of the assembled battery. Figure 6 shows the impedance spectra of PE and TiO_2-PMMA/PE composite separators operated at 25 °C. It can be seen that the resistance of TiO_2-PMMA/PE composite separator is lower than that of PE membrane separator. The calculated ion conductivity of TiO_2-PMMA/PE composite separator is about 0.87 $mScm^{-1}$, about two times higher than that of PE membrane separator (0.43 $mScm^{-1}$), attributed to the high electrolyte uptake induced great ion conduction [13, 23].Although the thickness increased after surface-coating, the voids formed between coated nanospheres can increase the electrolyte uptake, which leads to the high transport ability for lithium ions. Accordingly, the TiO_2-PMMA/PE composite separator exhibits an increased ion conductivity compared to pristine PE membrane separator.

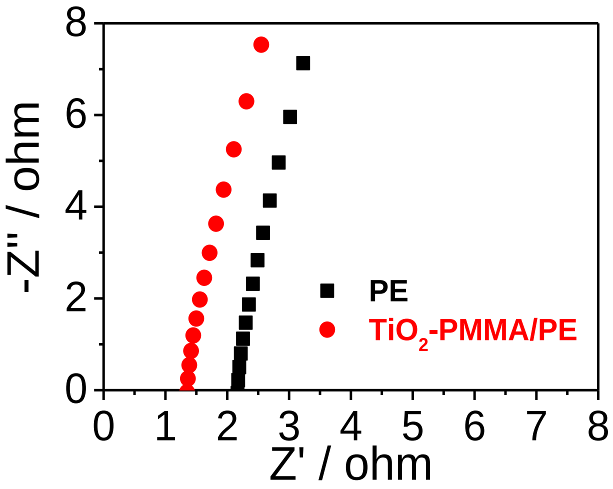

Figure 6. AC impedance spectra of PE and TiO_2-PMMA/PE composite separators operated at 25 °C after immersed in electrolyte solutions.

Figure 7 displays the comparison of cycling performance of half-cells assembled from PE and TiO_2-PMMA/PE composite separators operated at 25 °C, respectively. It is evident that both cells exhibit similar discharge capacity in the first 30 cycles. However, the performance for the cell assembled from pristine PE membrane separator decreased significantly whereas it remains almost stable for the cell assembled from TiO_2-PMMA/PE composite separator with the further increase in cycle numbers. For instance, the cell assembled from pristine PE membrane separator retains about 64.5% of its initial discharge capacity after 100 cycles and the discharge capacity retention rate is about 97.8% for the cell assembled from TiO_2-PMMA/PE composite separator. We believe that the high discharge capacity retention ability for the cell assembled from TiO_2-PMMA/PE composite membrane separator results from the high lithium ion transport capability induced by high wettability of the composite membrane separator and high electrolyte uptake.

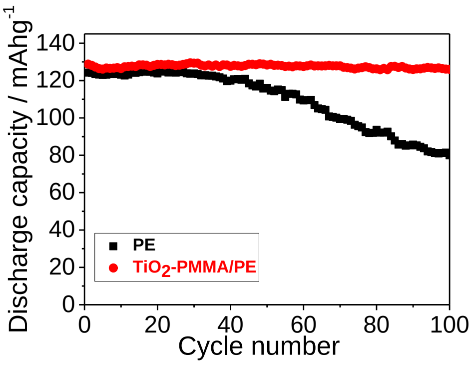

Figure 7. Cycle performance of assembled coin cells from PE (black squares) and from TiO_2-PMMA/PE composite (red circles) separators under 0.5C at 25 °C.

The rate capability of the assembled cells from pristine PE and TiO_2-PMMA/PE composite membrane separators is shown in Figure 8. It can be seen that the specific capacitance of the cell assembled from TiO_2-PMMA/PE composite membrane separator is higher than that of the cell assembled from pristine PE membrane separator within the tested ranges. While discharged below 0.5C, the difference in discharge capacity between cells assembled from pristine PE and TiO_2-PMMA/PE composite membrane separator is less significant whereas the difference becomes more pronounced while discharged at 1C and 2C. This result indicates that coating of membrane separator with TiO_2-PMMA has positive effect on the battery performance. The enhancement of rate capability results from the improved wettability and the increased electrolyte uptake, which allow more lithium-ion transport during cycling.

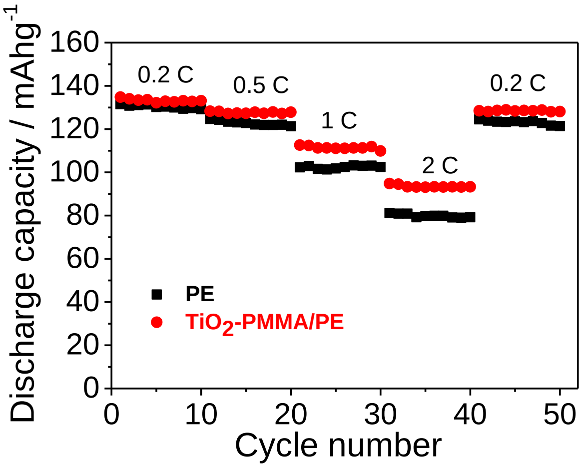

Figure 8. Comparison of rate capability of cells assembled from PE and TiO_2-PMMA/PE composite membrane separators.

4. CONCLUSION

In this paper, we demonstrated that coating of polyethylene membrane separator with poly(methyl methacrylate) grafted titanate nanospheres is an effective way to enhance the thermal stability and electrochemical performance of assembled lithium ion batteries. Owing to the highly thermal-stable ceramic nanospheres and binders, the thermal stability of membrane separators is significantly improved. Surface modification of ceramic nanoparticles with poly(methyl methacrylate) can improve the compatibility of electrode with After coating the membrane surface with modified ceramic nanospheres, large numbers of voids are generated in the coated layer and thus improve the electrolyte uptake and ion conductivity. Accordingly, the electrochemical performance is also improved for the cell assembled from the designed composite membrane separators. The results described here demonstrate that coating of the commercial membrane separator with modified ceramic nanoparticles is an effective way to improve the thermal stability and the according safety issues related to the lithium ion batteries.

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