

Effect of SiO₂ Content on Performance of Polypropylene Separator for Lithium-Ion Batteries

Hongyu Liu,¹ Jun Xu,¹ Baohua Guo,¹ Xiangming He²

¹Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

²Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence to: B. Guo (E-mail: bhguo@mail.tsinghua.edu.cn)

ABSTRACT: Composite separators are prepared by introducing SiO₂ nanoparticles on both sides of polypropylene separator with various SiO₂ contents through a dip-coating process, where polyvinylidene fluoride-hexafluoropropylene is used as binder. Coated layers have highly porous structure, which is quantitatively analyzed by air permeability. Compared to pristine separator, composite separators show significant lower Gurley value, reduced thermal shrinkage, higher liquid electrolyte uptake, better mechanical properties, and better cell performance such as discharge C-rate capability and cycle performance. The influence of SiO₂ content on these properties is also studied, and the best SiO₂ content is given. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41156.

KEYWORDS: composites; membranes; porous materials

Received 3 March 2014; accepted 12 June 2014

DOI: 10.1002/app.41156

INTRODUCTION

Currently, the most widely used separators for lithium-ion batteries are polyolefin porous separators, predominantly polyethylene (PE) and polypropylene (PP), due to their excellent chemical/electrochemical stability, proper porosity, easy processing, and low cost.^{1–3} Although they have many advantages, their poor thermal stability will lead to thermal shrinkage when abnormally heated and low mechanical properties will lead to mechanical rupture during battery assembly or penetration in service.^{4–12} Furthermore, their poor compatibility with liquid electrolyte will lower cycle life of the battery.^{13–16}

In order to solve these problems, the introduction of nanoparticles (such as silica (SiO₂),¹⁷ titania (TiO₂),¹⁸ alumina (Al₂O₃)¹⁹) on the surface of the separator to prepare composite separator attracts much attention.²⁰ With proper nanoparticles, the composite separator shows excellent thermal stability, wettability, and better mechanical properties.²¹ Many composite separators have been prepared in recent years, but few discussed the influence of nanoparticles content on the performance of separators although the thickness and the morphologies of the coated layers are greatly influenced by nanoparticles content.

In this article, SiO₂ composite separators are prepared with polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) as binder. The influence of SiO₂ content on the separator surface and cross-section morphology, air permeability, thermal shrinkage, electrolyte uptake, mechanical properties, and cell

performances such as discharge C-rate capability and cyclability are investigated, and compared with those obtained with pristine PP separator.

EXPERIMENTAL

Preparation of Separators

Dissolved 0.4 g PVDF-HFP (Kynar Flex 2801) in 60 mL mixed solvent (dimethylacetamide (DMAC)/propylene glycol monomethyl ether acetate (PMA) = 3/1, vol/vol). Then various content (wt %, the mass of SiO₂/the total mass of the solution) of SiO₂ (50 nm, Hangzhou Wanjing New Material Co., Ltd, China) was added into the solution with vigorous stirring for 10 min, followed by a continuous agitation for 5 h.

Both sides of PP separator (Celgard 2400) were coated with a simple immersion of the separator into the prepared suspension liquid. The coated separators were then dried at room temperature to evaporate solvents.

Characterization of Separators

The surface and cross-section morphologies of coated layer were investigated using a scanning electron microscope (SEM, JSF7401). The air permeability was examined by the Gurley value with a permeometer (BTY-B2P, Labthink, China). Thermal shrinkage was observed by measuring dimensional change after the separator was subjected to 170°C for 10 min. Liquid electrolyte uptake was examined by measuring the weight gain after the separator was immersed in mixed solvent (ethylene carbonate (EC)/diethyl carbonate (DEC) = 1 : 1 (vol/vol)) for 1

min. Mechanical properties were determined using a universal tensile machine (UTM-1432, Chengde Jinjian Testing Instrument Co., Ltd, China).

Electrochemical Measurement

The ionic conductivity of the separators was measured using an electrochemical workstation (ZAHNER Zennium, Germany) over a frequency range between 1 Hz to 10^5 Hz. Lithium cells (2032-type coin) were assembled in an argon filled glove box. Separator was sandwiched between LiCoO_2 cathode and lithium-metal anode, and then activated by the liquid electrolyte (1M LiPF_6 in DEC/EC (1 : 1, vol/vol)). Cells were charged up to 4.2 V and discharged to 2.75 V. C-rate capability of cells was evaluated by charging the cell at various current densities from 0.1C to 2C and discharging at the same current density with each charging. Cycle performance of cells was measured by a constant charge/discharge current density (0.5C/0.5C). All cells were conducted by using Land Battery Test System (Wuhan Land Electronic Co. Ltd, China).

RESULTS AND DISCUSSION

Characterization of Coated Layers

The surface and cross-section morphologies of composite separators are shown in Figure 1. The surface images show that a SiO_2 /PVDF-HFP layer is successfully formed on pristine separator surface. The coated layer has highly porous structure, and SiO_2 particles are packed more closely as more SiO_2 is added. The cross-section images show that the thickness of the coated layer increases slightly when SiO_2 content is less than 2.5% (from 0.3 μm to 0.8 μm) but increases significantly when above 2.5% (1.7–3 μm).

Effect of SiO_2 Content on Gurley Value

To quantitatively analyze the porous structure of the separators, we examine the air permeability by measuring the Gurley value of the separator. The separator is sandwiched between the spacers, and the Gurley value is defined as the time (s) required for a specific amount of air (100 cc) passing through a specific area (1 square inch) of the separator under a specific pressure (1.22 kPa). Figure 2 shows that as the content of SiO_2 increases, the Gurley values of composite separators tend to increase, that is, the air permeability decreases. When the content of SiO_2 increases in the suspension liquid, the thickness of separator increases and SiO_2 particles are packed more close, which lead to longer path for air transport through the composite separators. An interesting observation is that the Gurley values of coated separators appear to be lower than that of pristine separator. This confirms that coated layers have porous structure which has little effect on air permeability and the composite separators are more facile to air transport which may be because of intrinsic capillarity. The separator has porous structure, and its internal cavities can be seen as capillaries. The pristine separator is nonpolar and it has low air absorption, which leads to high surface tension. According to Young-Laplace equation (eq. 1), ΔP is proportional to γ and the pristine separator has high additional pressure. Before air is transported through the separator, the additional pressure must be first removed which may occupy additional time. As for the composite separators, their surface polarity is modified by the coated layers

and they have better air absorption because of the introduction of SiO_2 . The low ΔP leads to lower Gurley values than that of pristine separator.

$$\Delta P = 2\gamma/r \quad (1)$$

where ΔP is additional pressure, γ is surface tension, and r is surface curvature radius.

Effect of SiO_2 Content on Thermal Shrinkage

During cell cycling especially under high power output conditions such as for electric vehicles, the heat generated may result in thermal shrinkage of separators and lead to internal short circuit. Due to the existence of heat-resistant SiO_2 particles, the coated layers are expected to prevent the separator from thermal shrinkage. Figure 3 shows that all coated separators have a reduced thermal shrinkage than pristine separator, which verifies that the introduction of ceramic coated layers is effective in suppressing thermal shrinkage of separators. The more SiO_2 is added, the stronger is the suppression. Compared to pristine separator (60%), thermal shrinkage of composite separator is 40% at 2% SiO_2 content and only 10% at 3.5% SiO_2 content, which shows excellent thermal stability.

Effect of SiO_2 Content on Electrolyte Uptake

Apart from thermal stability, electrolyte uptake is another important issue for separator. The liquid electrolyte uptake of separators is investigated as a function of SiO_2 content, as shown in Figure 4. Compared to pristine separator, composite separators have higher electrolyte uptake because of the introduction of hydrophilic SiO_2 particles in coated layers which can improve the wettability of separators and the liquid electrolyte uptake increases significantly as SiO_2 content increases. For pristine separator, the electrolyte uptake was only proportional to its porosity. But for coated separators, liquid electrolyte was not only trapped in the coated substrate but also retained inside the porous network of the coated layers.⁸ When more SiO_2 is added, more porous structure is formed, contributing to higher electrolyte uptake. Moreover, after the composite separator is immersed in liquid electrolyte, the coated layers do not peel off from the surface and there are no SiO_2 particles leaching from the layers, which demonstrate that the coated layers can be stable in liquid electrolyte.

Effect of SiO_2 Content on Maximum Load and Tensile Strength

During battery assembly, the separator must be mechanically strong to withstand the tension of the winding operation, especially in machine direction (MD). Figure 5 shows the maximum load [Figure 5(a)] and tensile strength [Figure 5(b)] in MD of the various separators. Compared to pristine separator, composite separators have higher maximum load, as shown in Figure 5(a). When SiO_2 content is 1.67%, the maximum load of composite separator is only 10.7 N, a little higher than pristine separator (10.6 N). As more SiO_2 is added, the maximum load increases significantly, and it is increased by $\sim 10\%$ at 2.5% content (11.6 N) and $\sim 15\%$ at 3.5% content (12.1 N), respectively. It is believed that the porous network formed by SiO_2 and PVDF-HFP in coated layers can restrict the motion of separator.²² As more SiO_2 is added, SiO_2 particles are packed more

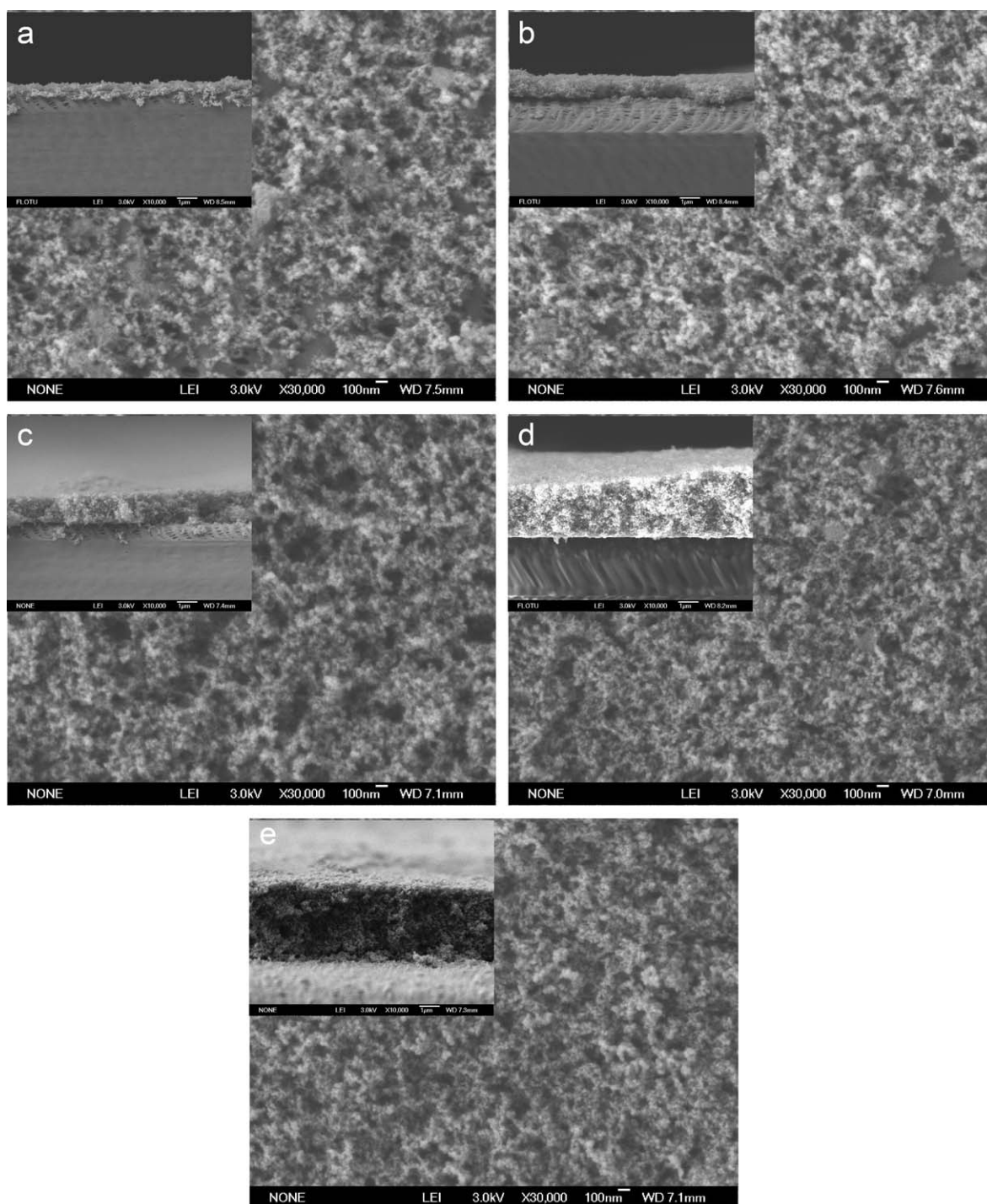


Figure 1. SEM surface and cross-section photographs of composite separators: (a) 1.67%, (b) 2%, (c) 2.5%, (d) 3%, and (e) 3.5%, wt.

closely (as shown in Figure 1) and the restriction of the layers becomes stronger. Figure 5(b) shows that tensile strength of composite separator increases slightly ($<2.5\%$) but decreases significantly ($>2.5\%$) as SiO_2 content increases. Tensile strength is proportional to the maximum load but inversely proportional to the thickness of the separator. When SiO_2 content is less than 2.5%, the maximum load increases significantly and the

thickness of composite separator increases slightly, so tensile strength increases slightly. Tensile strength of composite separators is nearly the same as that of pristine separator, which demonstrates that the layers are tightly coated on the surface and tensile strength of composite separators does not decrease significantly when the thickness of the layer is thinner. When SiO_2 content is more than 2.5%, the maximum load increases but

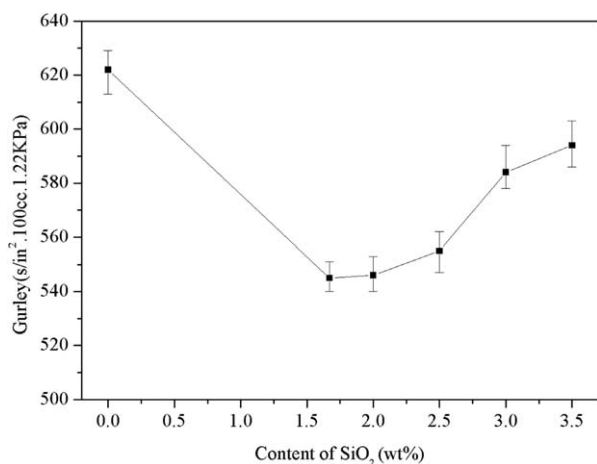


Figure 2. Changes of Gurley value as a function of SiO₂ content.

the thickness of composite separator increases more significantly, so tensile strength decreases significantly.

Effect of SiO₂ Content on Puncture Force

In order to resist the protrusion of the Li dendrites formed during cell cycling, the separator must have high puncture strength, which is defined as the maximum load required for a given needle to puncture a given separator,³ as shown in Figure 6. Compared to pristine separator, composite separators have higher puncture force because of the introduction of SiO₂ coated layers, which can resist the protrusion of separator. As more SiO₂ is added, the puncture force increases owing to the increased thickness and more close packed SiO₂.

Effect of SiO₂ Content on Ionic Conductivity

In order to investigate the effect of SiO₂ content on the electrochemical performance of cells, ionic conductivity of the separators is measured by AC impedance analysis,²³ as shown in Figure 7. Compared to pristine separator, composite separators show higher ionic conductivity, owing to the porous structure of the layers which has little effect on ionic conduction and the higher electrolyte uptake which may be facile to the diffusion of lithium-ion. An

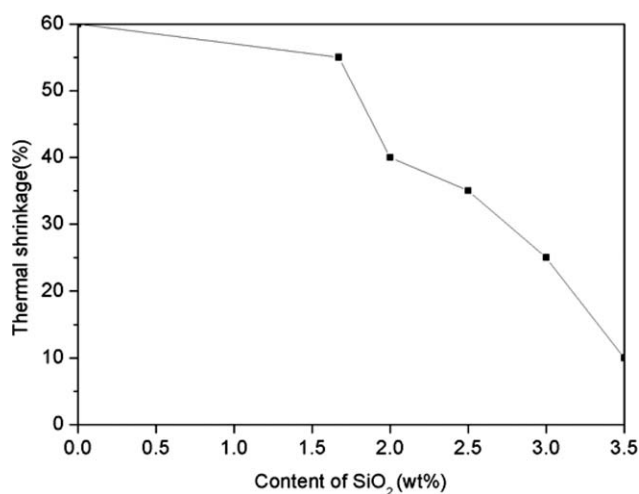


Figure 3. Thermal shrinkage of separators at 170°C as a function of SiO₂ content.

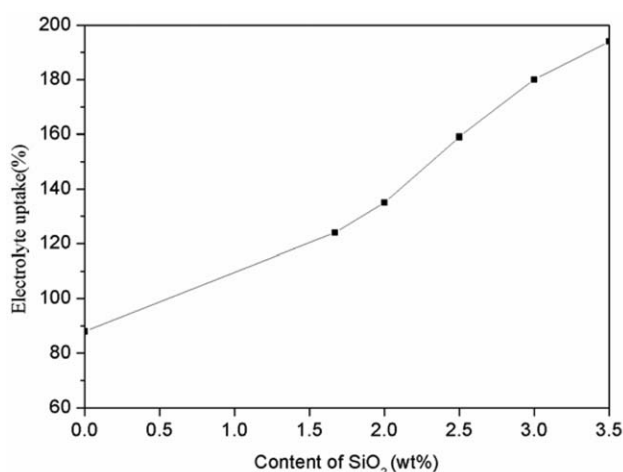


Figure 4. Electrolyte uptake of separators with various SiO₂ content.

interesting finding is that the ionic conductivity increases as SiO₂ content increases (less than 2.5%) but decreases with higher SiO₂ content. When SiO₂ content is less than 2.5%, the thickness of the coated layers is thinner, which does not hinder the ionic conductivity. As SiO₂ content increases, electrolyte uptake increases and the

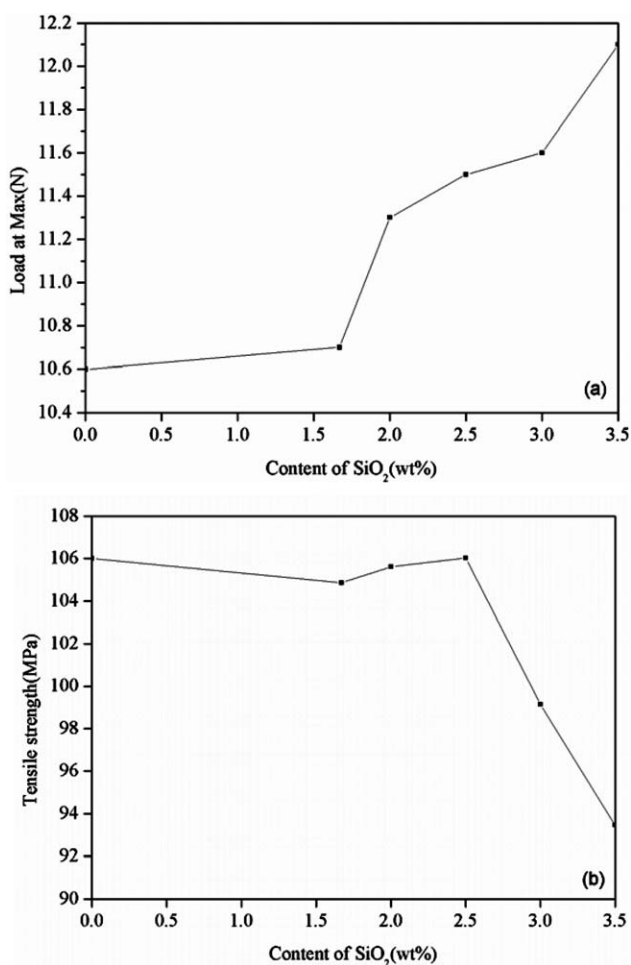


Figure 5. Changes of load (max) and tensile strength as a function of SiO₂ content.

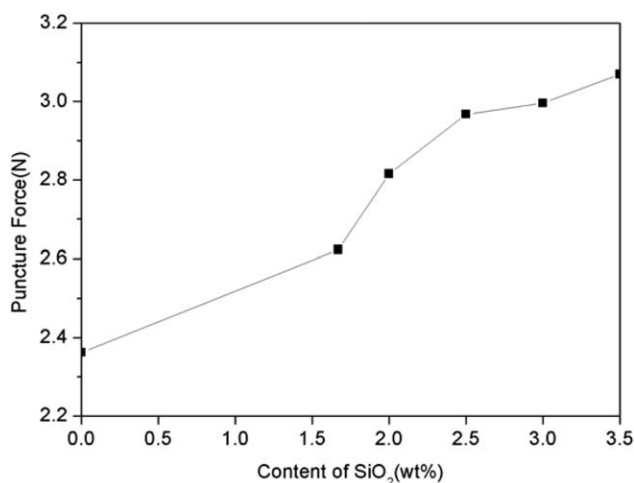


Figure 6. Changes of puncture force as a function of SiO₂ content.

composite separators are more facile to ionic conduction, so the ionic conductivity increases. When SiO₂ content is more than 2.5%, electrolyte uptake increases slightly but the thickness of the composite separators increases significantly, which lead to longer path for ionic conduction and lower ionic conductivity.

Effect of SiO₂ Content on C-Rate Capability

Higher ionic conductivity may be beneficial in improving C-rate capabilities, and this can be confirmed by examining C-rate capabilities of various separators, as shown in Figure 8. Compared to pristine separator, composite separators show better discharging capacity in all C-rates, and the difference in discharging capacities becomes more noticeable at higher C-rates, where the influence of ion transportation on the ohmic polarization²⁴ is more important. The discharging capacity of composite separators increases as SiO₂ increases up to 2.5% but decreases with higher SiO₂ content. When SiO₂ content is less than 2.5%, thin coated layers have no effect on ionic conduction. As ionic conductivity increases, composite separators show better discharging capacity. However, when SiO₂ content is

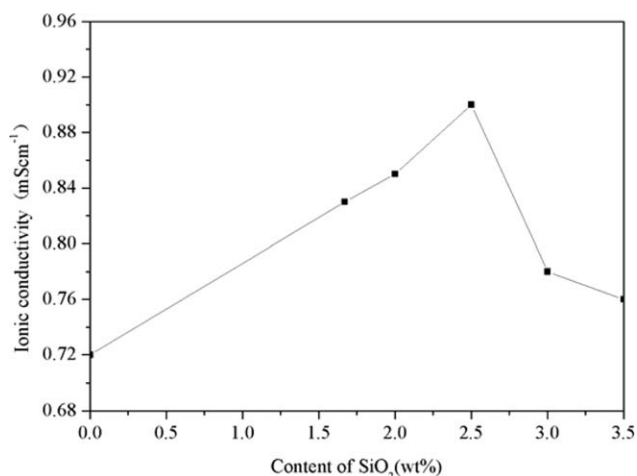


Figure 7. Ionic conductivity of separators as a function of SiO₂ content.

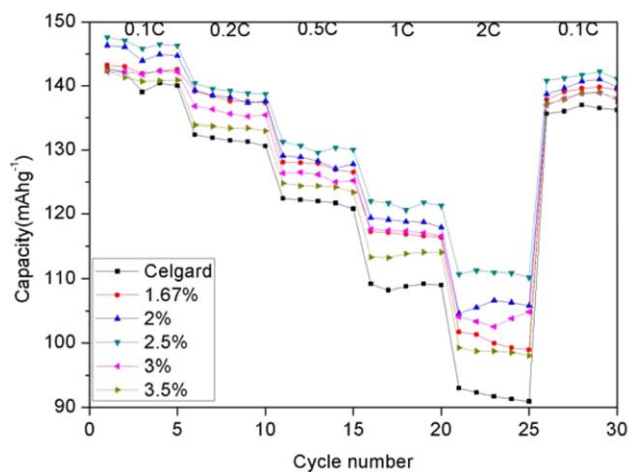


Figure 8. Comparison of C-rate capabilities at various SiO₂ content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more than 2.5%, although electrolyte uptake increases, ionic conductivity decreases, and the discharging capacity decreases.

Effect of SiO₂ Content on Cyclability

Cyclability, i.e. discharge capacity as a function of cycle number, of various separators is shown in Figure 9. Composite separators show excellent discharging capacity up to 100 cycles, which are higher than that of pristine separator. Hydrophilic SiO₂ in coated layers of composite separators has better ability to retain liquid electrolyte than hydrophobic PP separator, and it helps to prevent the leakage of liquid electrolyte during cycling which improves cyclability.¹⁶ The cyclability of composite separators increases as SiO₂ increases up to 2.5% but decreases with above 2.5% SiO₂. Ionic conduction is the reason, which is similar to C-rate capabilities. An intriguing finding is that the discharge capacity of 2.5% SiO₂ decreases slightly with cycling when compared to other separators, which may due to little increase in internal resistance during cycling because of its thin thickness and higher liquid electrolyte retention.²⁵

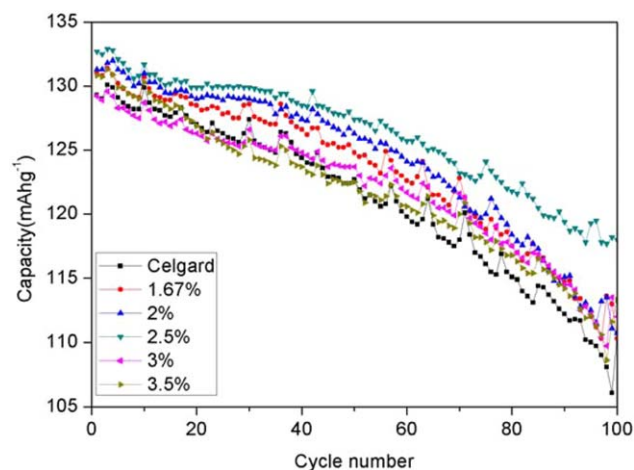


Figure 9. Comparison of cycle performance at various SiO₂ content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

A composite separator is successfully developed by introducing SiO₂/PVDF-HFP layers onto both sides of pristine PP separators. The coated layers show a highly porous structure and the thickness of the coated layer increases as more SiO₂ is added. Composite separators show better properties than that of pristine separator, and thermal shrinkage decreases but Gurley value, electrolyte uptake, mechanical properties increase as SiO₂ content increases. When its content is 2.5%, the composite separator has the best discharge C-rate capability and cyclability.

ACKNOWLEDGMENTS

This work is supported by the Tsinghua University Initiative Scientific Research Program (Grant No. 2012THZ08129).

REFERENCES

1. Ryou, M. H.; Lee, Y. M.; Park, J. K.; Choi, J. W. *Adv. Mater.* **2011**, *23*, 3066.
2. Arora, P.; Zhang, Z. *Chem. Rev.* **2004**, *104*, 4419.
3. Zhang, S. S. *J. Power Sources* **2007**, *164*, 351.
4. Park, J. H.; Cho, J. H.; Park, W.; Ryoo, D.; Yoon, S. J.; Kim, J. H.; Jeong, Y. U.; Lee, S. Y. *J. Power Sources* **2010**, *195*, 8306.
5. Jeong, H. S.; Hong, S. C.; Lee, S. Y. *J. Membr. Sci.* **2010**, *364*, 177.
6. Jeong, H. S.; Lee, S. Y. *J. Power Sources* **2011**, *196*, 6716.
7. Kim, M.; Han, G. Y.; Yoon, K. J.; Park, J. H. *J. Power Sources* **2010**, *195*, 8302.
8. Fu, D.; Luan, B.; Argue, S.; Bureau, M. N.; Davidson, I. J. *J. Power Sources* **2012**, *206*, 325.
9. Huang, X. S.; Hitt, J. J. *J. Membr. Sci.* **2013**, *425–426*, 163.
10. Zhang, S. S.; Xu, K.; Jow, T. R. *J. Solid State Electrochem.* **2003**, *7*, 492.
11. Zhang, S. S.; Xu, K.; Jow, T. R. *J. Power Sources* **2005**, *140*, 361.
12. Jeong, H. S.; Kim, J. H.; Lee, S. Y. *J. Mater. Chem.* **2010**, *20*, 9180.
13. Lee, Y. M.; Kim, J. W.; Choi, N. S.; Lee, J. A.; Seol, W. H.; Park, J. K. *J. Power Sources* **2005**, *139*, 235.
14. Sohn, J. Y.; Im, J. S.; Shin, J.; Nho, Y. C. *J. Solid State Electrochem.* **2012**, *16*, 551.
15. Kim, K. J.; Kim, J. H.; Park, M. S.; Kwon, H. K.; Kim, H.; Kim, Y. J. *J. Power Sources* **2012**, *198*, 298.
16. Choi, J. A.; Kim, S. H.; Kim, D. W. *J. Power Sources* **2010**, *195*, 6192.
17. Wachtler, M.; Ostrovskii, D.; Jacobsson, P.; Scrosati, B. *Electrochim. Acta* **2004**, *50*, 357.
18. Kim, K. M.; Park, N. G.; Ryu, K. S.; Chang, S. H. *Electrochim. Acta* **2006**, *51*, 5636.
19. Li, Z. H.; Su, G. Y.; Gao, D. S.; Wang, X. Y.; Li, X. P. *Electrochim. Acta* **2004**, *49*, 4633.
20. Takemura, D.; Aihara, S.; Hamano, K.; Kise, M.; Nishimura, T.; Urushibata, H.; Yoshiyasu, H. *J. Power Sources* **2005**, *146*, 779.
21. Huang, X. S. *J. Solid State Electrochem.* **2011**, *15*, 649.
22. Zhang, Y. Q.; Zhang, G. D.; Du, T. D.; Zhang, L. Z. *Electrochim. Acta* **2010**, *55*, 5793.
23. Liu, X. J.; Kusawake, H.; Kuwajima, S. *J. Power Sources* **2001**, *97–98*, 661.
24. Jeong, H. S.; Kim, D. W.; Jeong, Y. U.; Lee, S. Y. *J. Power Sources* **2010**, *195*, 6116.
25. Kim, D. W.; Oh, B.; Park, J. H.; Sun, Y. K. *Solid State Ionics* **2000**, *138*, 41.