

# Comparative study of different membranes as separators for rechargeable lithium-ion batteries

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**Abstract:** Membranes of polypropylene (PP), PP coated with nano- $\text{Al}_2\text{O}_3$ , PP electrospun with polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP), and trilayer laminates of polypropylene-polyethylene-polypropylene (PP/PE/PP) were comparatively studied. Their physical properties were characterized by means of thermal shrinkage test, liquid electrolyte uptake, and field emission scanning electron microscopy (FESEM). Results show that, for the different membranes as PP, PP coated with nano- $\text{Al}_2\text{O}_3$ , PP electrospun with PVdF-HFP, and PP/PE/PP, the thermal shrinkages are 14%, 6%, 12.6%, and 13.3%, while the liquid electrolyte uptakes are 110%, 150%, 217%, and 129%, respectively. In addition, the effects on the performance of lithium-ion batteries ( $\text{LiFePO}_4$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  as the cathode material) were investigated by AC impedance and galvanostatic charge/discharge test. It is found that PP coated with  $\text{Al}_2\text{O}_3$  and PP electrospun with PVdF-HFP can effectively increase the wettability between the cathode material and liquid electrolyte, and therefore reduces the charge transfer resistance, which improves the capacity retention and battery performance.

**Keywords:** lithium batteries; membranes; separators; thermal stability; electrochemical properties

## 1. Introduction

Transportation accounts for 20% of global carbon emissions via the survey of International Energy Agency (IEA), and especially, this proportion will double by 2050. It has aroused much attention for developing electric vehicles (EVs) and hybrid electric vehicles (HEVs) to solve the serious environmental pollution problems [1]. Owing to the technological maturity and long safety record, nickel-metal hydride technology is currently the dominant battery solution applied in most hybrid electric vehicles. Compared with other electrochemical power sources, a lithium-ion battery is fast developed as the long term winner because of its lightweight, higher energy, and higher power density [2-5]. The separator is a critical part that is close related to the interfacial characteristic, internal resistance, capacity, cycling performance, and safety performance of batteries.

Generally, commercial separators for lithium-ion batteries are made of polypropylene (PP), polyethylene (PE), and trilayer laminates of polypropylene-polyethylene-polypropylene (PP/PE/PP) due to their mechanical in-

tegrity and thermal shut-down under the severe abuse conditions. However, the thermal shrinkage, mechanical strength, and short circuiting due to the formation of dendrites during the charge/discharge cycling of cells are still concerned in realizing the application of lithium-ion batteries for EVs and HEVs. Recently, some researchers propose that the thermal stability and wettability of separators can be improved by coating inorganic particles on the surface of PP films [6]. In addition, to enhance the interfacial contact, the commercial microporous membranes are coated with a thin polymer layer, such as poly(ethylene oxide) (PEO) [7] and poly(vinylidene) fluoride-hexafluoropropylene (PVdF-HFP) [8-9], which becomes a gel induced by the liquid electrolyte. However, there is still lack of comparative studies on the effect of different membranes on the batteries, which is vital to develop new membranes in batteries for EVs and HEVs.

In the study, PP coated on both sides with nano-sized  $\text{Al}_2\text{O}_3$  and PP electrospun with polymer PVdF-HFP were chosen to be compared with the commercialized PP and

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PP/PE/PP membranes.

## 2. Experimental

### 2.1. Preparation

Table 1 shows the composition and thickness of different membranes used in this study. For the electrochemical studies, cathode plates were prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry, containing the active material, acetylene black, and binder poly(vinylidene fluoride) (PVdF) at a certain ratio (80:15:5 for LiFePO<sub>4</sub> and 83:10:7 for LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> by weight) on an aluminum foil. The electrode thickness was in the range of 40-50 μm after doctor blade coating and drying at 120°C for 20 min. The liquid electrolyte used for battery assembly was 1 mol/L LiPF<sub>6</sub> in ethylene carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) (1:1:1 by volume). Cells were assembled in an argon-filled glove box with different kinds of membranes as the separator and lithium foils as the counter electrode.

**Table 1. Composition and thickness values of membranes**

Membrane type	Composition	Thickness / μm
a	PP	25
b	PP coated with Al <sub>2</sub> O <sub>3</sub>	37-38
c	PP electrospun with PVdF-HFP	29-30
d	PP/PE/PP	26

### 2.2. Measurements

The membrane areas (1 cm in width and 3 cm in length) were measured before and after oven storage at different temperatures (80, 90, 100, 110, and 120°C) for 1 h and for different times (30, 60, 90, and 120 min) at 90°C to analyze the thermal shrinkage properties. The shrinkage of membranes was calculated using Eq. (1).

$$\text{Shrinkage} = \frac{A_i - A_f}{A_i} \times 100\% \quad (1)$$

where  $A_i$  and  $A_f$  are the initial and final area of mem-

branes, respectively.

The electrolyte uptake ( $A$ ) of membranes was determined by weighing method. The membranes were immersed in the liquid electrolyte (1 mol/L LiPF<sub>6</sub> in EC + DMC + DEC, 1:1:1 by volume) for 0.5 h. After being taken out, the excessive electrolyte solution at the surface was slightly absorbed by tissue, the soaked membrane was weighted, and the electrolyte solution uptake was calculated as the following equation.

$$A = \frac{W_2 - W_1}{W_1} \times 100\% \quad (2)$$

where  $W_1$  and  $W_2$  are the mass of dry and wet membranes, respectively. Each membrane was measured three times, and then, the average value was obtained.

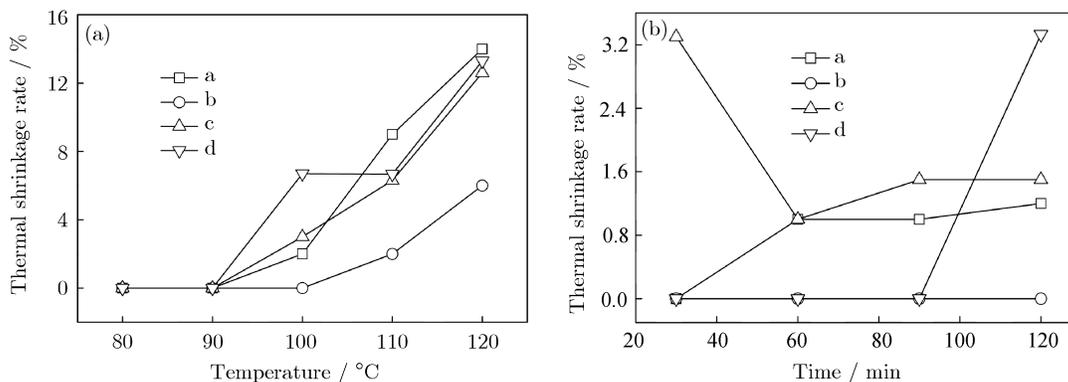
AC impedance of batteries was determined using an electrochemical work station over a frequency range of 100 kHz to 0.01 Hz with an amplitude of 5 mV. Cycling charge and discharge tests of batteries were investigated with 2032-type coin cells at room temperature at 1/5C rate for 100 cycles using a land battery test system. The voltage cut-offs were fixed between 2.5 and 4.25 V for Li/LiFePO<sub>4</sub> batteries and in the range of 3.3-4.35 V for Li/LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> batteries, respectively. Morphology of membranes was characterized by field emission scanning electron microscopy (FE-SEM) at an acceleration voltage of 5 kV.

## 3. Results and discussion

### 3.1. Thermal properties

Thermal shrinkage of membranes induced by heat generated during cell cycling contributed to the deterioration of battery performance and safety. Fig. 1 exhibits that all the membranes can keep a stable thermal property below 90°C, and shrinkage in different degrees occurs with the continued heating.

At 120°C, the thermal shrinkage rates of four kinds of membranes are 14%, 6%, 12.6%, and 13.3%, respectively, as shown in Fig. 1(a). The PP membrane coated with Al<sub>2</sub>O<sub>3</sub> has the lowest shrinkage rate compared with



**Fig. 1. Thermal properties of membranes: (a) different temperature for 1 h; (b) different times at 90°C.**

three other kinds of films. The PP electrospun with PVdF-HFP exhibits the shrinkage rate of 3.3% at the initial heating, as shown in Fig. 1(b), due to the strong shrinkage of PVdF-HFP fiber, which gradually elongates to the normal length after 1 h; after that it shows a similar shrinkage behavior with the PP film. The PP/PE/PP film keeps a good thermal stability when holding below 90°C; however, after holding at 90°C for 120 min, it exhibits the largest shrinkage of 3.3%, owing to the low melting point of polyethylene.

### 3.2. Liquid electrolyte uptake

It can be observed in Fig. 2 that the electrolyte uptakes of different membranes show the order of  $c > b > d > a$ . The PP coated with  $Al_2O_3$  and PVdF-HFP (150% and 217%, respectively) exhibit a much higher electrolyte uptake than the PP and PP/PE/PP membranes (110% and 129%, respectively). Compared with some of the porous gel polymer electrolyte membranes [10], both PP coated with  $Al_2O_3$  and PP electrospun with PVdF-HFP show a good performance of electrolyte uptake, which contributes to the reduced soakage time and the improved wettability between the cathode materials and electrolyte.

### 3.3. AC impedance spectra

The interfacial resistance of batteries assembled with

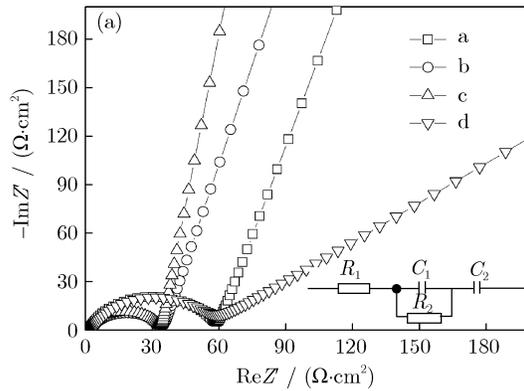


Fig. 3. AC impedance spectroscopy of batteries assembled with different membranes at room temperature: (a) Li/LiFePO<sub>4</sub>; (b) Li/LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

In Fig. 3(a), it can be seen that the  $R_{ct}$  of Li/LiFePO<sub>4</sub> batteries shows the order of  $a > d > b > c$ , which is diametrically opposite to their performances in the liquid electrolyte uptakes. Meanwhile, in Li/LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> batteries, the battery assembled with PP coated with  $Al_2O_3$  exhibits the lowest  $R_{ct}$  (shown in Fig. 3(b)). It suggests that the high liquid electrolyte uptakes of membranes facilitate the charge transfer process of fresh cells.  $Al_2O_3$  and PVdF-HFP coated on the surface of the PP film can increase the wettability between the cathode materials and liquid electrolyte, which improves the interfacial contact and reduces  $R_{ct}$ .

### 3.4. FE-SEM analysis

The surface morphology of different membranes is

shown in Fig. 4. Both the PP and PP/PE/PP membranes exhibit a uniformly interconnected submicron pore structure. In contrast to the uncoated PP membrane, close-packed  $Al_2O_3$  nanoparticles are observed on the surface of the PP substrate, as shown in Fig. 4(b). It is obvious that some large pores are formed in the coating layer of the membrane, which leads to the immersion of the electrolyte solution and the efficient uptake of the liquid electrolyte. The PP electrospun with PVdF-HFP nanofibers shows a porous structure, as seen in Fig. 4(c). PVdF-HFP nanofibers on the surface exhibit a mean diameter of 400 nm, while the average pore diameter of electrospun PVdF-HFP nanofibers is about 3 μm. The special porous structure can improve the uptake property of the electrolyte

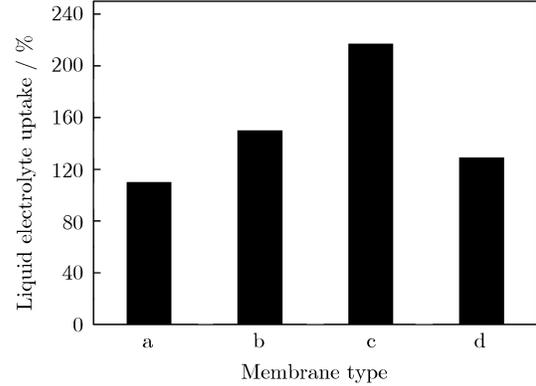
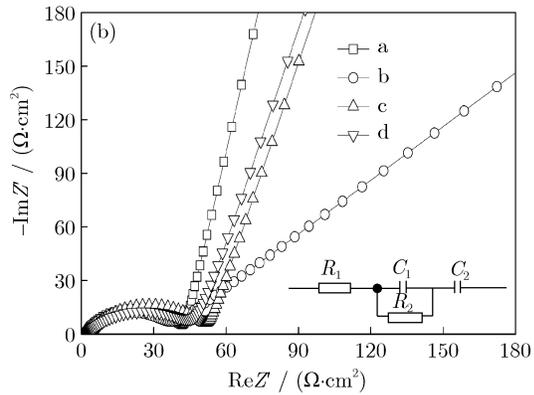


Fig. 2. Liquid electrolyte uptakes of different membranes.



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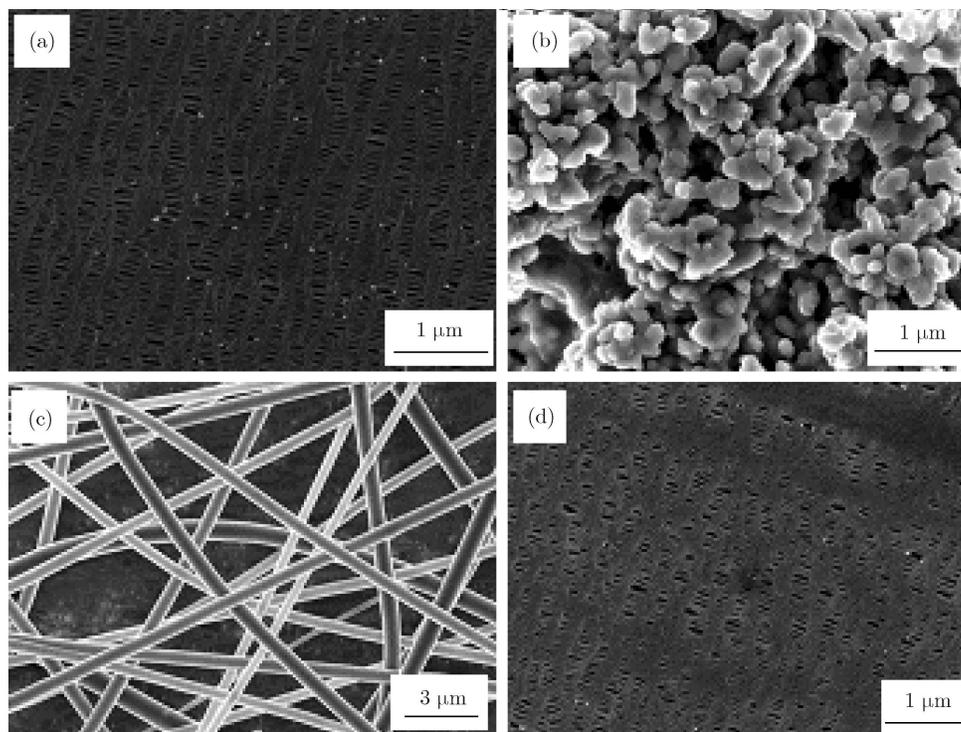


Fig. 4. FE-SEM images of different membranes.

solution and is favorable for the liquid electrolyte to form a gel electrolyte, which is in agreement with previous reports [14-15].

### 3.5. Battery performance

The performances of Li/LiFePO<sub>4</sub> and Li/LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> batteries assembled with different membranes were characterized at room temperature with the charge and discharge current of 1/5C. Their cycling properties are presented in Figs. 5 and 6.

As seen in Fig. 5, the initial discharge capacity of Li/LiFePO<sub>4</sub> batteries assembled with different membranes are found to be 148.4, 143.5, 141.6, and 142.5 mAh·g<sup>-1</sup>, respectively. The capacity of cells increases gradually dur-

ing the first nine cycles, resulting from the gradual soaking of electrolyte and cathode materials [16]. The capacity retention of cells after 100 times cycle is calculated out to be 94.26%, 96.61%, 95.51%, and 94.50%, respectively. It can be concluded that the batteries assembled with the PP film deliver the highest initial capacity, while the batteries assembled with the PP coated with Al<sub>2</sub>O<sub>3</sub> and electrospun with PVdF-HFP have the smallest polarization and the highest capacity retention.

In Fig. 6, the initial discharge capacity of batteries Li/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> assembled with different membranes are found to be 180.62, 179.32, 184.75, and 179.67 mAh·g<sup>-1</sup>, respectively. The capacity retention of batteri-

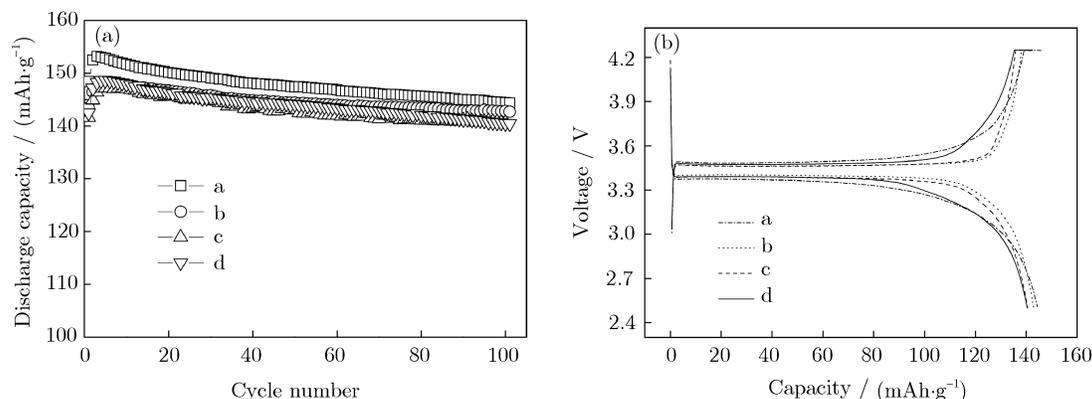
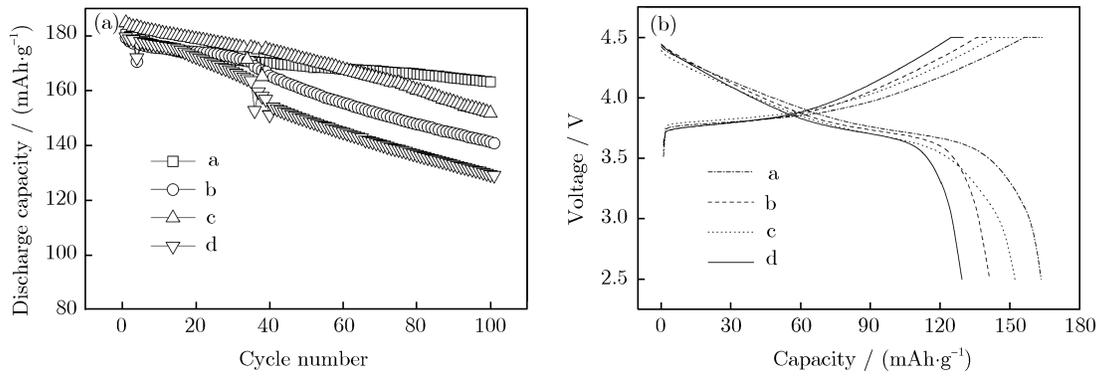


Fig. 5. Cycling performance of Li/LiFePO<sub>4</sub> batteries with different membranes at room temperature: (a) charge/discharge curves; (b) voltage-capacity curves of the 100th cycle.



**Fig. 6.** Cycling performance of  $\text{Li/LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  batteries with different separators at room temperature: (a) charge/discharge curves; (b) voltage-capacity curves of the 100th cycle.

es after the 100 times cycle is calculated out to be 90.45%, 78.76%, 82.36%, and 72.00%, respectively. The batteries assembled with the PP electrospun with PVdF-HFP deliver the highest discharge capacity within 60 cycles. Unlike the results in  $\text{Li/LiFePO}_4$  cells,  $\text{Li/LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  batteries with the PP coated with  $\text{Al}_2\text{O}_3$  and PP/PE/PP membrane show the same initial capacity as those assembled with the PP membrane.

#### 4. Conclusions

Different membranes matching with  $\text{LiFePO}_4$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  as the cathode materials were comparatively studied, including thermal stability, liquid electrolyte uptake, surface topography, and electrochemical performance. Results show that the inorganic particles surface coating and polymer electrospun can improve the interfacial property, increase the electrolyte uptake, reduce the  $R_{ct}$ , and enhance the safety issue of batteries. PP coated with  $\text{Al}_2\text{O}_3$  and electrospun with PVdF-HFP are very promising candidates for commercial separators in Li-ion batteries for EVs and HEVs.

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#### References

- [1] K. Xi, H.Y. Guan, and R.V. Kumar, Lithium sulfur batteries for electric vehicles, [in] *Fray International Symposium*, Cancun, 2011, p. 361.
- [2] B. Oh and K. Amine, Evaluation of macromonomer-based gel polymer electrolyte for high-power applications, *Solid State Ionics*, 175(2004), No. 1-4, p. 785.
- [3] D. Li, F. Lian, X.M. Hou, and K.C. Chou, Reaction mechanisms for  $0.5\text{Li}_2\text{MnO}_3\cdot 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  precursor prepared by low-heating solid state reaction, *Int. J. Miner. Metall. Mater.*, 19(2012), No. 9, p. 856.
- [4] Y.B. Chen, Y. Hu, F. Lian, and Q.G. Liu, Synthesis and characterization of spinel  $\text{Li}_{1.05}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_{4-z}\text{F}_z$  as cathode materials for lithium-ion batteries, *Int. J. Miner. Metall. Mater.*, 17(2010), No. 2, p. 220.
- [5] H. Miyashiro, S. Seki, Y. Kobayashi, Y. Ohno, Y. Mita, and A. Usami, All-solid-state lithium polymer secondary battery with  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  by mixing of  $\text{Li}_3\text{PO}_4$ , *Electrochem. Commun.*, 7(2005), No. 11, p. 1083.
- [6] J.A. Choi, S.H. Kim, and D.W. Kim, Enhancement of thermal stability and cycling performance in lithium-ion cells through the use of ceramic-coated separators, *J. Power Sources*, 195(2010), No. 18, p. 6192.
- [7] D.W. Kim, J.M. Ko, J.H. Chun, S.H. Kim, and J.K. Park, Electrochemical performances of lithium-ion cells prepared with polyethylene oxide-coated separators, *Electrochem. Commun.*, 3(2001), No. 10, p. 535.
- [8] K.J. Kim, J.H. Kim, M.S. Park, H.K. Kwon, H. Kim, and Y.J. Kim, Enhancement of electrochemical and thermal properties of polyethylene separators coated with polyvinylidene fluoride-hexafluoropropylene co-polymer for Li-ion batteries, *J. Power Sources*, 198(2012), p. 298.
- [9] B.W. Liu and X.D. Wang, Properties of doping polymer electrolyte membranes, *J. Univ. Sci. Technol. Beijing*, 28(2006), No. 12, p. 1139.
- [10] Y.H. Liao, M.M. Rao, W.S. Li, L.T. Yang, B.K. Zhu, R. Xu, and C.H. Fu, Fumed silica-doped poly (butyl methacrylate-styrene)-based gel polymer electrolyte for lithium ion battery, *J. Membr. Sci.*, 352(2010), No. 1-2, p. 95.
- [11] Z.H. Chen, L.Z. Zhang, R. West, and K. Amine, Gel electrolyte for lithium-ion batteries, *Electrochim. Acta*, 53(2008), No. 8, p. 3262.
- [12] E.S. Lee and A. Manthiram, High cathode  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-VO}_2(\text{B})$  composite cathodes with controlled irreversible capacity loss for lithium-ion batteries, *J. Electrochem. Soc.*, 158(2011), No. 1, p. A47.

- [13] E. Barsoukov and J.R. Macdonald, *Impedance Spectroscopy Theory, Experiment, and Application*, 2nd Ed., John Wiley & Sons, Hoboken, 2005, p. 444.
- [14] P. Raghavan, X.H. Zhao, J. Manuel, G.S. Chauhan, J.H. Ahn, H.S. Ryu, H.J. Ahn, K.W. Kim, and C. Nah, Electrochemical performance of electrospun poly (vinylidene fluoride-co-hexafluoropropylene)-based nanocomposite polymer electrolytes incorporating ceramic fillers and room temperature ionic liquid, *Electrochim. Acta*, 55(2010), No. 4, p. 1347.
- [15] P. Raghavan, J. Manuel, X.H. Zhao, D.S. Kim, J.H. Ahn, and C. Nah, Preparation and electrochemical characterization of gel polymer electrolyte based on electrospun polyacrylonitrile nonwoven membranes for lithium batteries, *J. Power Sources*, 196(2011), No. 16, p. 6742
- [16] S.Y. Chew, J.Z. Sun, J.Z. Wang, H.K. Liu, M. Forsyth, and D.R. MacFarlane, Lithium-polymer battery based on an ionic liquid-polymer electrolyte composite for room temperature applications, *Electrochim. Acta*, 53(2008), No. 22, p. 6460.