Preparation and properties of a kind of thermal stable porous membranes based on OPBI as Lithium ion battery membrane

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Abstract:

A series of porous poly[2,2'-(p-oxydipheylene)-5,5'-bibenzimidazole] (OPBI) membranes with high porosity were prepared by a new kind of phase inversion process named blend phase inversion process. The polyethylene glycols (PEGs) were used as pore forming substances. The porous OPBI membranes showed excellent thermal stability, nearly no thermal shrinkage after being heated at 220℃ for 1h, high electrolyte uptakes and high ionic conductivity. The highest ionic conductivity of the membranes was about 1.30 mS/cm which is much higher than the commercial separator Celgard2400 (0.7mS/cm). The battery performances also were studied. The excellent discharge specific capacity of the cell with porous OPBI membrane made it possible to be used for electric vehicles.

Keywords: Lithium ion Battery separator, Phase inversion, Polybenzimidazole, Poly ethylene oxide, Blend.

Introduction:

Recent years secondary lithium ion batteries (LIBs) have raised widely attention because of their unique cycle properties and high energy densities. Separator is the key element of the LIBs. It avoids direct contact of cathode and anode and lets the Li ion pass through the membrane to provide conductivity.[1] Microporous polyolefin separators have been used in commercial LIBs over the last few decades. [2,3]There have many advantages, such as good mechanical strengths, reasonable chemical stability and sufficient electrochemical stability at an acceptable cost. However their low thermal stability can result in direct contact of the cathode and the anode, inducing extensive current flow, overheating, and possible safety hazards. [4,5]In this study, polybenzimidazole (PBI) was a kind of engineering plastics with excellent chemical and solvent resistance, electrochemical stability, mechanical strength, thermal stability and fire resistance was studied as the separator of LIBs. The porous OPBI membrane with high porosity were prepared by a new kind of phase inversion process named blend phase inversion process using polyethylene glycols (PEGs) as pore forming substances. The obtained porous OPBI showed excellent thermal stability, high electrolyte uptakes, high ionic conductivity and good battery performances also were studied. The excellent discharge specific capacity of the cell with porous OPBI membrane made it possible to be used for electric vehicles. .

Experimental:

Poly[2,2'-(p-oxydipheylene)-5,5'-bibenzimidazole] (OPBI) was prepared from 3,3'-Diaminobenzidine (DAB) and 4,4'-Dicarboxydiphenyl ether (DCDPE) as the following procedure according to a literature way.[6] OPBI and PEG were dissolved in DMSO to get the solution. The obtained solution was cast onto a glass substrate and dried in an air oven at 80℃ for 8 h to form a film. In this work, membrane used typically was about 10*10cm, 20-30μm thickness. The obtained blend membrane was soaked in deionized water at 60℃ for 48 hours to remove the PEG, then the membrane was dried in vacuum oven at 100℃ for 10 hours, finally the dried porous OPBI membrane was obtained. A series of properties of porous OPBI membrane were tested.

Results and discussion:

To obtain the porous membrane used in the Lithium ion battery, in the porous membrane, the pore size should be more than several hundred nm. In the blend membrane, the OPBI will be a continuous phase and the same as the PEG. When the PEG were removed by the deionized water, the porous are formed in the blend membrane. All the porous formed before can be reserved after dry the obtained wet porous membranes. With the PEG content increasing in the blend membrane, the porosity the porous OPBI membrane will increase, which was better for li ion pass and higher Li ion conductivity. In this study, the weight ratio of OPBI/PEG was studied from 1/1 to 1/5. The porous OPBI membrane with the 1/5 weight ratio of OPBI/PEG has highest porosity and sufficient mechanical strength. So the weight ratio of OPBI and PEG is fixed at 1:5.

In Figure 1, the SEM images showed there were continuous pores and continuous OPBI phase in the membrane. With the increasing of the molecular weight of PEG, the size of the pores of the porous OPBI membrane decreased and the porosity increased (Table1). All the membranes were homogeneous and transparent before being immersed blend membranes in the water, which indicated that there is a bicontinuous structure in the OPBI/PEG blend membrane. Because the chain length of different molecular weight PEG is different, the shorter chain length of the lower molecular weight PEG can move and aggregate more easily. The gathered PEG will form the pore after being removed by water. The formed pore size became bigger than that formed by higher molecular weight PEG with longer chain length.

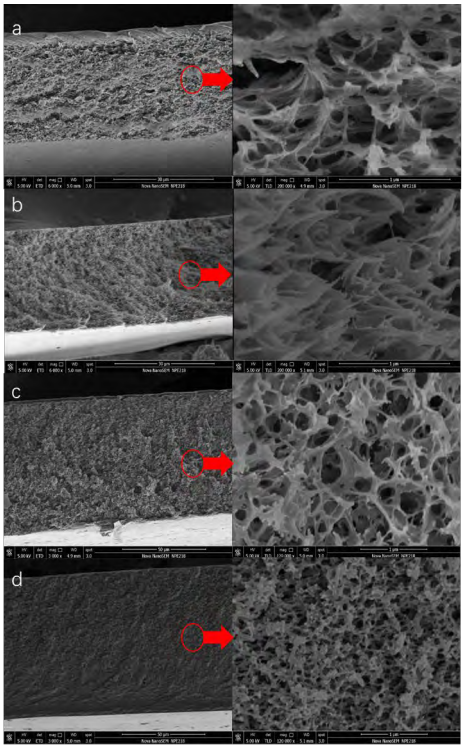

Figure 1. The cross section SEM images of the porous OPBI membranes, OPBI/PEG=1/5
(a, b, c, d represented the porous OPBI membrane with PEG 350,550,1000,10000.)

All the porous OPBI membrane showed excellent thermal stability. The Tg is higher than 220 °C, the decomposition temperature is higher than 500 °C. The thermal shrinkage of all these membranes were measured by keeping them in a hot oven at temperatures ranging from 100 to 200℃ for 1h. The porous OPBI membrane with OPBI/PEG=1/5 and the PEG10000 as the pore forming substance is named as m-4. Photographs of thermal shrinkage of the m-4 and Celgard2400 were shown in the Figure 2. The Celgard2400 exhibited significant shrinkage in the machine direction at 150℃. At 200℃, the Celgard2400 lose its shape because of the melting of the crystalline region. While as shown in Figure 2, the m-4 exhibited almost no shrinkage at 150℃. The shrinkage of m-4 at diameter is about 5.26% (1mm) at 200℃, indicated that the m-4 has better thermal stability than the Celgard2400.

Table 1. Tensile strength, elongation at break, porosity, electrolyte uptake and ionic conductivity of the porous OPBI membrane and Celgard2400.

Materials	Tensile strength/Mpa	Elongation at break/%	Porosity(%)	Electrolyte Uptake(%)	Ionic Conductivity (mS/cm)
OPBI	120	10.0	0	3.3	—
m-1	31	11.9	43	125.2	0.03
m-2	20	16.0	62	144.8	0.11
m-3	12	12.2	68	247.8	0.17
m-4	10	9.5	71	292.1	1.30
Celgard2400	128(MD)[1] 16(TD)[2]	76.7(MD) 39.3 (TD)	40	36.8	0.71

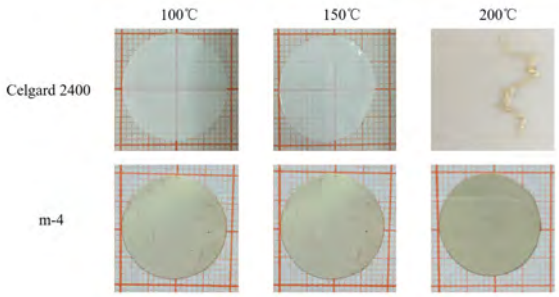

Figure 7. Thermal shrinkage of m-4 and Celgard2400 at 100,150 and 200℃ for 1 hour

The initial charge-discharge course was cycled in the range of 2.3V to 4.2V at electric charge at 0.1C. All the curves showed stable charge-discharge platforms. As shown in the Figure 3. The initial charge capacity of the cell contains m-4 was about 170mAh/g and the initial discharge capacity of that is about 160mAh/g, coulombic efficiency for the first cycle was about 0.9412. The initial charge capacity of the cell contains Celgard2400 was about 160mAh/g and the initial discharge capacity of that is about 150mAh/g, coulombic efficiency for the first cycle was about 0.9375.

Figure 4. Shows the cycle performance of the coin cell with m-4 and Celgard2400. The Y-axis shows the discharge specific capacity of the nth cycle. The operation temperature was 25℃. As shown in Figure 4, the Li/LiFePO4 cell with the m-4 and Celgard2400 showed stable capability in the tested 50 cycles at 25℃. The discharge specific capacity of m-4 (150 mAh/g) is 20 mAh/g higher than that of Celgard2400 (130mAh/g) at end of the 50 cycles. The higher discharge specific capacity retention of the m-4 is likely due to the higher inter-electrode (electrolyte + separator) ionic conduction by using the new separator.

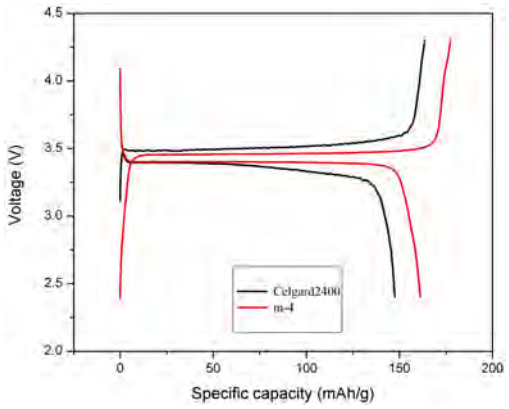

Figure 8. The initial charge-discharge capacity of the coin cells with m-4 and Celgard2400 (0.1C, 25℃)

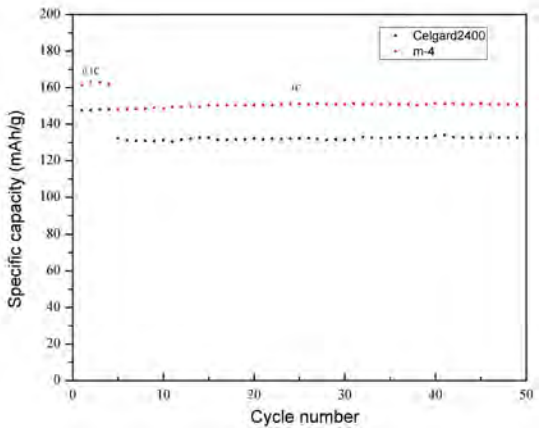

Figure 9. Cycle performances of the coin cell with m-4 and Celgard2400

Figure 5.shows the C-rate capacity of cells containing the m-4 and Celgard2400. The rate was from 0.1C to 1C, 2C, 3C, 4C, 5C and finally back to 1C. The C-rate capacity of cells containing m-4 and Celgard2400 decreased with the increasing of the rate. The cell containing m-4 exhibited higher capacity than that of Celgard2400 at each rate. The cell with m-4 showed good discharge capacity, 130 mAh/g, 110 mAh/g, 90 mAh/g, 60 mAh/g and 40 mAh/g at 1C, 2C, 3C, 4C and 5C rate, respectively. And finally at cycle 54-63 the C-rate was back to 1C rate, the discharge capacity was still about 130mAh/g, which was same as the cycle 4-13 at 1C rate. But for the commercial Celgard2400, the initial specific capacity at discharge was about 140mAh/g (0.1C), and it turn to 120 mAh/g, 100 mAh/g, 80 mAh/g, 50 mAh/g and 0mAh/g at 1C, 2C, 3C, 4C, and 5C. And finally the capacity is back to 120mAh/g at 1C. At higher charge rate (4C and 5C), m-4 exhibited significant higher discharge specific capacity compare to the Celgard2400. The discharge specific capacity of the cell containing porous OPBI membrane still maintain 50 mAh/g at 5C which is equal to that of the cell with Celgard2400 at 4C. While the capacity of the cell with Celgard2400 at 5C was drop to nearly 0mAh/g. The excellent discharge specific capacity of the cell with porous OPBI membrane made it possible to be used for electric vehicles.

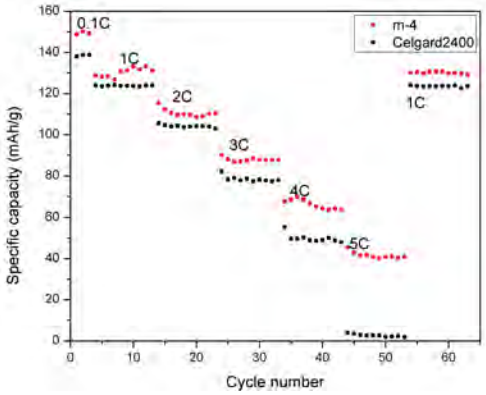

Figure 10. C-Rate performance of the Li/LiFePO4 coin cell with m-4 and Celgard2400.
(Li/LiFePO4 coin cell, cycle1-3: 0.1C, cycle 4-13: 1C, cycle 14-23: 2C, cycle 24-33: 3C, cycle 34-43: 4C, cycle 44-53: 5C, cycle 54-63: 1C)

Conclusion

The processing way is easier and more environmental compare to normal stretching process. The porous OPBI membranes prepared by this new method to prepare as LIBs separator showed excellent

thermal stability. The porous OPBI membranes can endure high temperatures over 200 ℃, while Celagard2400 was completely melted. It can satisfy the LIBs use especially at high temperature. The optimized porous OPBI membrane showed higher porosity, higher liquid electrolyte uptake and better ionic conductivity than Celgard2400 membrane. The results of the rate capacity exhibited that the porous OPBI membrane is possible substitutes for the current porous polyolefin separators in LIBs. The discharge specific capacity of the cell containing porous OPBI membrane still maintain 50 mAh/g at 5C which is equal to that of the cell with Celgard2400 at 4C. The excellent discharge specific capacity of the cell with porous OPBI membrane made it possible to be used for electric vehicles.

References

[1] J.K. Park, et, al. Princinple and Applications of Lithium Secondary Batteries. John Wiley& Sons, Ltd. (2012), PP 1-6.

[2] Y.M. Lee, J.-W. Kim, N.-S. Choi, J.A. Lee, W.-H. Seol, J.-K. Park. J. Power Sources 139 (2005) 235–241.

[3] G. Venugopal, J. Moore, J. Howard, S. Pendalwar. J. Power Sources 77 (1999) 34–41.

[4] Y. Lee, M.-H. Ryou, M. Seo, J.W. Choi, Y.M. Lee. Electrochim. Acta 113 (2013) 433–438.

[5] I. Uchida, H. Ishikawa, M. Mohamedi, M. Umeda. J. Power Sources 119–121 (2003) 821–825.

[6] Ueda M, Sato M, Mochizuki A. Macromolecules 18 (1985) 2723-6.