

A simple approach for preparation of porous polybenzimidazole membranes as a promising separator for lithium ion batteries

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Abstract:

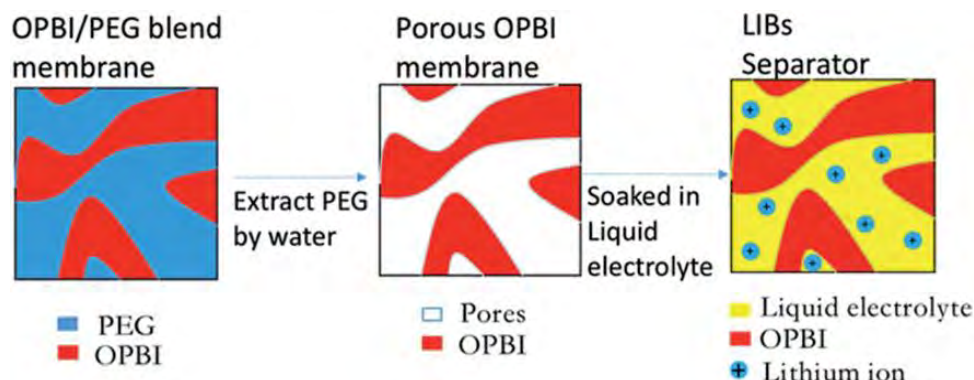
A simple and controllable approach has been developed for the preparation of a series of poly(2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole) (OPBI) porous membranes with controlled porosity and pore size. The micropores were formed by simply extracting poly(ethylene glycol) (PEG) from the dry OPBI/PEG blend membranes with water. The porous membrane, M-4, prepared from PEG10000 ($M_w = 10\ 000$) at a weight ratio of OPBI/PEG10000 = 1 : 5 exhibited a high porosity (71%), a high ionic conductivity ($1.3\ \text{mS cm}^{-1}$ at room temperature), and reasonably high tensile strength (10 MPa). Furthermore, M-4 showed only ~5% thermal shrinkage after heating at 200 °C for 1 h and good fire-retardant properties which were much better than those of the commercial separator Celgard 2400. The charge–discharge cycle test and C-rate performance test results revealed that M-4 was a promising candidate as a separator for lithium ion batteries.

Keywords: Polybenzimidazole, Lithium-ion battery

1. INTRODUCTION

Recently lithium ion batteries (LIBs) have attracted much attention because of their vital applications in applications such as electrical vehicles and various electronic devices.^{1,2} Separator is one of the key components of a LIB. It has three functions: (1) to avoid direct contact of the positive electrode and the negative electrode, (2) to hold the liquid electrolyte in its micropores for lithium ion transport, (3) to prevent electronic conduction (electronic insulator).³ At present, the most commonly used separators in LIBs are porous polyolefin membranes made using a dry or wet stretch process. These porous polyolefin membranes have fairly high mechanical strength in the machine direction but high resistance to liquid electrolyte and electrode materials.^{4,5} Furthermore, because both processes involve a stretching step to initiate or facilitate the formation of a penetrating porous structure, polyolefin porous membranes have a strong shrinkage tendency especially at elevated temperatures.^{6,7} This may cause an internal short circuit, even the risk of explosion.⁸⁻¹⁰ Furthermore, polyolefins such as poly(ethylene) and poly(propylene) are highly flammable and this can lead to potential safety problems of the LIBs.

In this study, a simple and controllable approach for the preparation of a series of poly(2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole) (OPBI) porous membranes by simply extracting poly(ethylene glycol) (PEG) from dry OPBI/PEG blend membranes with water (as shown in Scheme 1) is reported. Because PEG is almost nontoxic and the removal of PEG is much easier than the removal of common organic solvents such as DMAc and NMP from their aqueous solution mixtures, the present pore forming technique is expected to be more environmentally friendly. The effects of PEG molecular weight and OPBI/PEG weight ratio on pore formation and porosity, and the properties of the prepared OPBI porous membranes were investigated.



Scheme 1 Preparation process of the porous OPBI membrane for use in the LIB separator

2. EXPERIMENTAL

OPBI and PEG were dissolved in DMSO to form a homogeneous solution. The polymer solution was cast onto a glass substrate and dried in an air oven at 80 °C for 8 h. The thickness of the blend membrane was controlled to about 20–30 μm. The resulting blend membrane was soaked in deionized water at 60 °C for 48 h to remove the PEG component followed by drying in a vacuum oven at 100 °C for 10 h to yield the dry porous OPBI membrane.

3. RESULTS AND DISCUSSION

To investigate the effect of PEG molecular weight on the pore size and porosity of membranes, a series of PEGs with different Mw (350, 550, 1000, 10 000) were used for the preparation of porous membranes and the weight ratio of OPBI to PEG was controlled at 1 : 5. The prepared porous membranes were denoted by M-1, M-2, M-3 and M-4 for PEG350, PEG550, PEG1000 and PEG10000, respectively. The cross-sectional scanning electron microscopy (SEM) images of these OPBI porous membranes were studied and are shown in Fig. 1. The images show that sponge like micropores exist in these membranes.

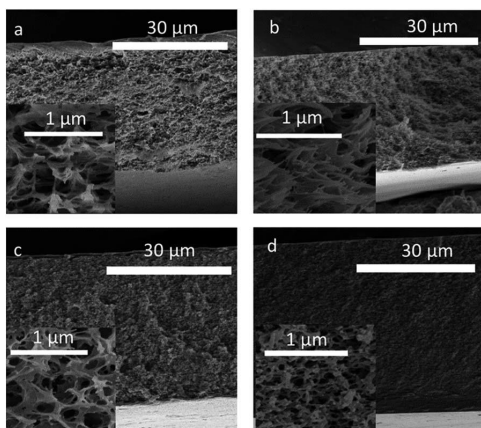


Figure 1 Cross-sectional SEM images of the OPBI porous membranes: (a) M-1, (b) M-2, (c) M-3, (d) M-4.

Fig. 2 shows the cycle performance of the Li/LiFePO₄ coin cells with M-4 and Celgard 2400 at 25 °C. The initial four cycles were measured at 0.1C, whereas the following 80 cycles were performed at 1C. Both cells showed little capability decay, which was an indication of the good stability of the membranes. The specific discharge capacity of the M-4-based battery (150 mA h g⁻¹) was significantly higher than that of Celgard 2400 (130 mA h g⁻¹) at 1C. This is likely to be, as mentioned previously, attributed to the lower internal resistance. It should be noted that the stable charge/discharge specific capacity and coulombic efficiency are comparable or higher than those of many other polymer separators with Li/LiFePO₄ cells

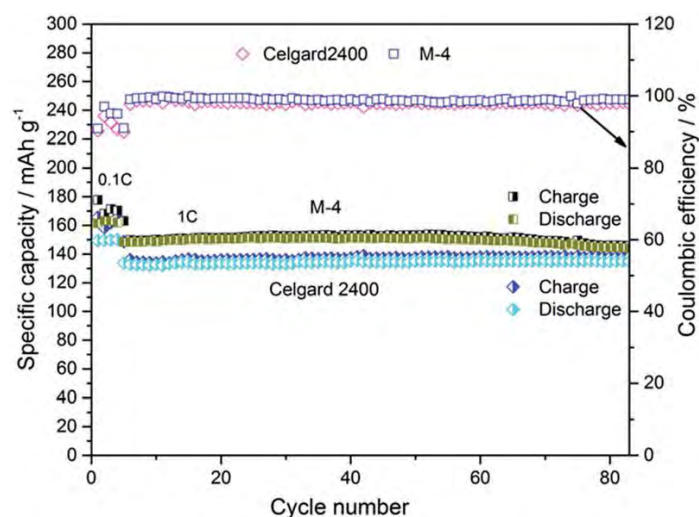


Figure 2 Cycle performances of the coin cells assembled with M-4 (27mm) and Celgard 2400 (25 mm) (initial four cycles: 0.1C, the other 80cycles: 1C, 25 °C).

4.CONCLUSIONS

A new, simple and controllable approach was developed for the preparation of a series of OPBI microporous membranes by simply extracting PEG from dry OPBI/PEG blend membranes with water. The membrane being proved to be porous membrane and it shown a good battery performance than commercial separator Celgard2400.

References

- [1] J. M. Tarascon and M. Armand, *Nature*, 2001, 414, 359–367.
- [2] V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energy Environ. Sci.*, 2011, 4, 3243–3262.
- [3] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu and X. W. Zhang, *Energy Environ. Sci.*, 2014, 7, 3857–3886.
- [4] C. T. Love, *J. Power Sources*, 2011, 196, 2905–2912.
- [5] M. H. Ryou, Y. M. Lee, J. K. Park and J. W. Choi, *Adv. Mater.*, 2011, 23, 3066–3070.
- [6] X. S. Huang, *J. Solid State Electrochem.*, 2011, 15, 649–662.
- [7] J. J. Zhang, Z. H. Liu, Q. S. Kong, C. J. Zhang, S. P. Pang, L. P. Yue, X. J. Wang, J. H. Yao and G. L. Cui, *ACS Appl. Mater. Interfaces*, 2013, 5, 128–134.
- [8] Z. Chen, P. C. Hsu, J. Lopez, Y. Z. Li, J. W. F. To, N. Liu, C. Wang, S. C. Andrews, J. Liu, Y. Cui and Z. N. Bao, *Nat. Energy*, 2016, 1, 15009.
- [9] D. P. Finegan, M. Scheel, J. B. Robinson, B. Tjaden, I. Hunt, T. J. Mason, J. Millichamp, M. Di Michiel, G. J. Offer, G. Hinds, D. J. Brett and P. R. Shearing, *Nat. Commun.*, 2015, 6, 6924.
- [10] M. T. F. Rodrigues, K. Kalaga, H. Gullapalli, G. Babu, A. L. M. Reddy and P. M. Ajayan, *Adv. Energy Mater.*, 2016, 6, 1600218.3