

Application of PVDF composite for lithium-ion battery separator

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Abstract. In this study a composite observed in PVDF composite as lithium ion battery separator. Observation of performance cell battery with cyclic voltametry and charge discharge capacity. Surface morphology PVDF separator and commercial separator observed with Scanning electron microscopy (SEM). Cyclic Voltamerty test (CV) and Charge Discharge (CD) showed a capacity value on the coin cell. Coin cell is composed of material LiFePO_4 cathode, anode material of lithium metal and varies as graphite, liquid electrolyte varied use LiBOB and LiPF_6 . While the PVDF as compared to the commercial separator. Coin cell commercial separator has a better high capacity value when compared with Coin cell with the PVDF separator. Life cycle coin cell with the commercial separator material is still longer than coin cell separator with PVDF Copolymer. Development of PVDF as separator remains to be done in order to improve the performance of the battery exceeds the usage of commercial material.

1. Introduction

In recent years, many challenges have been made in battery technology. Specific electrochemical systems still continues improvement, nevertheless there is still no one separator that can be considered “ideal” for all battery chemistries. Separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes. Separators play a key role in all batteries to keep the positive and negative electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell. The capability of conducting ions by either intrinsic ionic conductor or by soaking electrolyte to minimize any processes that adversely affect the electrochemical energy efficiency of the batteries[1].

A separator could be an ionic resistor because lithium ions pass through a separator during charge discharge processes. Electrochemical performance of the lithium-ion battery is closely related to structure of separator, i.e., thickness, porosity, and permeability[2]. Generally, a thin membrane separator can minimize the ionic resistance, enabling high-specific battery power. However, too great of a small membrane thickness can reduce the mechanical strength of the membrane and increase the risk of inner battery electrical shorting. In practice, most separators for liquid electrolyte batteries in use today are 20 to 30 μm thick[3]. The purpose of this paper is to describe the various types of separators based on their applications in batteries and their chemical, mechanical and electrochemical properties, with particular emphasis on separators for lithium-ion batteries. PVDF composite has



potential candidate for advanced lithium ion battery separator application, because PVDF copolymer has excellence in thermal stability, chemical resistance and mechanical property[4].

2. Experimental

In this study, performance PVDF as separator compared with commercial separator applied in half cells.

2.1. Material Preparation

2.1.1. Preparation of PVDF Separator. PVDF were dissolved in N-N DMAc at 60°C and continuously stirring for several hours. Entrapped air in polymer solution was removed before using for electrospinning process. Polymer solution was attached to electrospinning machine with applied voltage is 18 kV and flow rate 0.004 ml/h[4]. Measurement thickness of PVDF separator is 15 μm and commercial separator 25 μm . Commercial separator available in Li-ion battery are made out of polyolefins like polyethylene and polypropylene. These materials have been found to be compatible with the cell chemistry and can be cycled for several hundred cycles without significant degradation in chemical or physical properties.

2.1.2. Preparation of half cells. Cathode lithium iron phosphate (LiFePO_4) being a safe and low cost material that can offer a relatively high theoretical capacity of 170 mAh/g, it is attracting much attention for applications in lithium batteries. LiFePO_4 has good thermal stability and as table charge/discharge property at ~ 3.4 V, which provides safety margin in terms of electrolytic decomposition ion for many of the organic electrolytes used in batteries. In spite of the several advantages of this material, earlier studies have demonstrated its incapability in achieving high material utilization at lower temperatures and /or higher current densities. The rate capability limitation of LiFePO_4 results from the low electronic conductivity of the material ($\sim 10^{-9}$ S/cm)[5]. The LiFePO_4 cathode appears to be exceptionally stable to long-term cycling[6]. The advantage we use graphite anode to this experiment is low cost, relatively high reversible capacity of 370 mAh g^{-1} , high coulombic efficiency in proper electrolytes[7]. LiPF_6 based electrolytes have favourable high conductivity and electrochemical stability, they suffer from a lower than average thermal stability[8]. LiBOB-containing electrolyte has been shown to possess a wide electrochemical stability window on the Pt electrodes, a critical question remaining unanswered is whether it is stable on practical lithium-ion battery electrodes[9]. The LiFePO_4 /Graphite half cells were assembled coin cell in the argon-filled glove box using PVDF and commercial celgard 2400 as separator and an appropriate amount of electrolyte LiPF_6 and LiBOB.

2.2. Characterization

The morphology of the PVDF separator and commercial separator was characterized by using a scanning electron microscope (SEM) operate at 10-15 kV.

2.3. Electrochemical Evaluation

Electrochemical impedance spectroscopy (EIS) were measured using Hioki LCR. Electrochemical measurements cyclic voltammetry (CV) and Charge discharge (CD) were measured in coin-type cells using WBCS3000. CV is a common technique for studying the properties of an electrochemical system—a cyclic linear potential sweep is imposed onto the electrode and the resulting current is recorded[10]. The cell were initially cycled 3 times between 2 V and 3.7 V at constant current of 0.1 C at room temperature.

3. Results and Discussion

Morphology

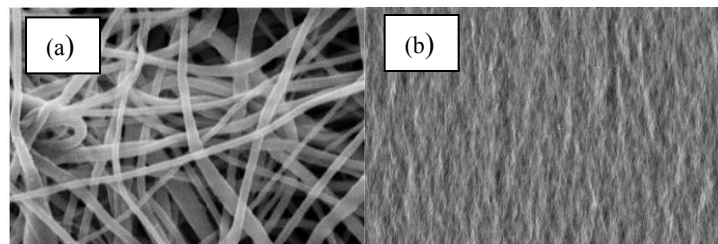


Figure 1. Morphology (10 kv x500) of the (a) PVDF separator (b) commercial separator observed by using SEM

Figure 1(a) shows representative morphology of PVDF separator by using SEM. The surface morphology of copolymer separator was smooth without bead. SEM pictures of commercial membrane separator 1(b) shown image that the pores are uniformly distributed. Base on the previous research, the separator with small membrane thickness has better advantage than separator which has big membrane thickness because it can increase the power specific power. Commercial separator has a good mechanical strength so it can decreasing the risk of inner battery electrical shorting. From the SEM data can be conclude that the commercial separator has a better morphology than PVDF separator.

Impedance Analysis

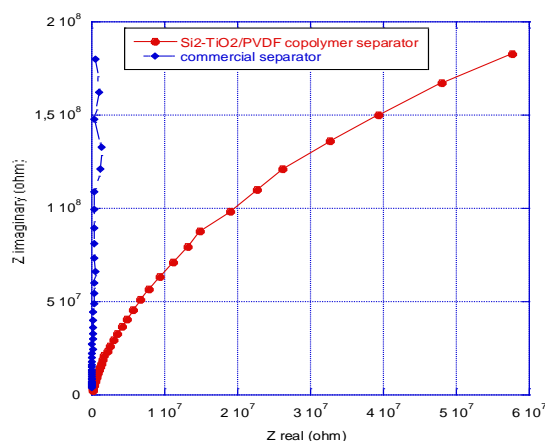


Figure 2. Spectrum EIS of PVDF separator and commercial separator

The function of separator in battery system are to prevent electrodes short circuits and contributing for ionization process between anode and cathode. Electron cannot flow through the separator but it's different of ion that can flow there. One of separator quality pre requirement is its electrical resistance value. A better separator has a small resistance value, because separator resistance affected of internal resistance of the battery so it will be effected of battery performance. Base on EIS spectra analysis performed by the equivalent circuits that simulate the real state of the circuit components for predicting impedance electrode. The commercial separator nyquist graph shows the vertical straight line and PVDF separator nyquist graph shows a half of semicircle. Intersection with x-axis at small frequency value indicate the magnitude of impedance.

Figure 2 shows that impedance component of commercial separator blue line just consist of capacitor and impedance component of PVDF separator red line consist of resistor and capacitor. It's mean that no reduction energy occurred at the battery if the separator used for battery. It's different if the PVDF separator used as battery separator that affecting the battery performance is not good. Impedance value of PVDF separator at low frequency was too large than commercial separator because the different

thickness, composition, and morphology between PVDF and commercial separator. The conclusion that the commercial separator has a better impedance value than PVDF separator.

Cyclic Voltammetry Analysis

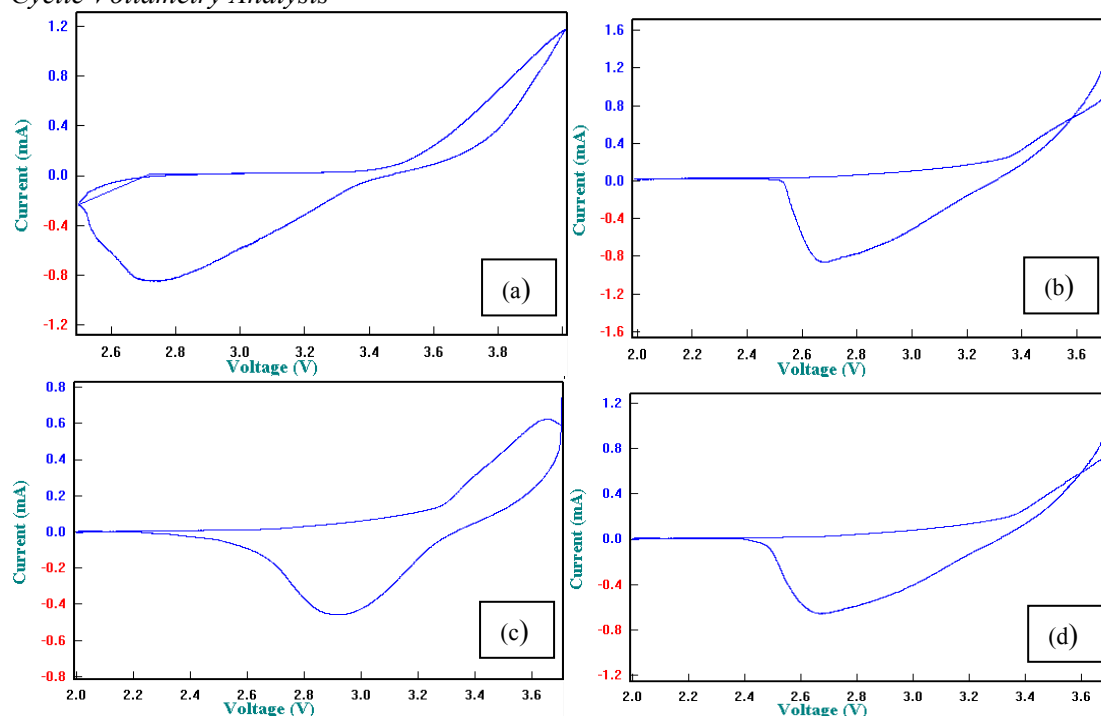


Figure 3. General graph cyclic voltammetry (a) Separator commercial with electrolyte LiPF_6 (b) Separator PVDF with electrolyte LiPF_6 (c) Separator commercial with electrolyte LiBOB (d) Separator PVDF with electrolyte LiBOB .

Figure 3 shows the cyclic voltammetry characteristics four coin cells. An increasing number of inorganic chemists have been using cyclic voltammetry to evaluate the effects of ligands on the oxidation/reduction potential of the central metal ion in complexes and multinuclear clusters. The current response is plotted as a function of the applied potential. The current depends on two steps in the overall process, the movement of electroactive material to the surface and the electron transfer reaction. Reversible electrochemist mean that the reaction is fast enough to maintain the concentration of the oxidized and reduced forms in equilibrium with each other at the electrode surface. [11]

Figure 3(a) and 3 (c) has the same type that are have the complete redox peak and there are different with figure 3(b) and 3 (d). Figure 3(a) shows that charge peak at 3,8 V and discharge peak at 2,65 V and figure 3(c) shows the charge peak at 3,6 V and discharge peak at 2,85 V. figure 3(b) and 3(d) just has the discharge peak. It was caused the cell which using the commercial separator has better redox process there than the PVDF separator.

Charge/ Discharge Analysis

The capacity retention of the LiFePO_4 / Graphite Li-ion cell using separator PVDF with the LiBOB – based electrolyte, was significantly better than for similar separator in coin cells that used the LiPF_6 – based electrolyte. This is because the Fe^{2+} ions are still dissolving, migrating to the negative electrode, and being reduced at the electrode surface to cause an impedance increase (similar to what occurs in LiPF_6 -based electrolytes, but at a reduced rate).

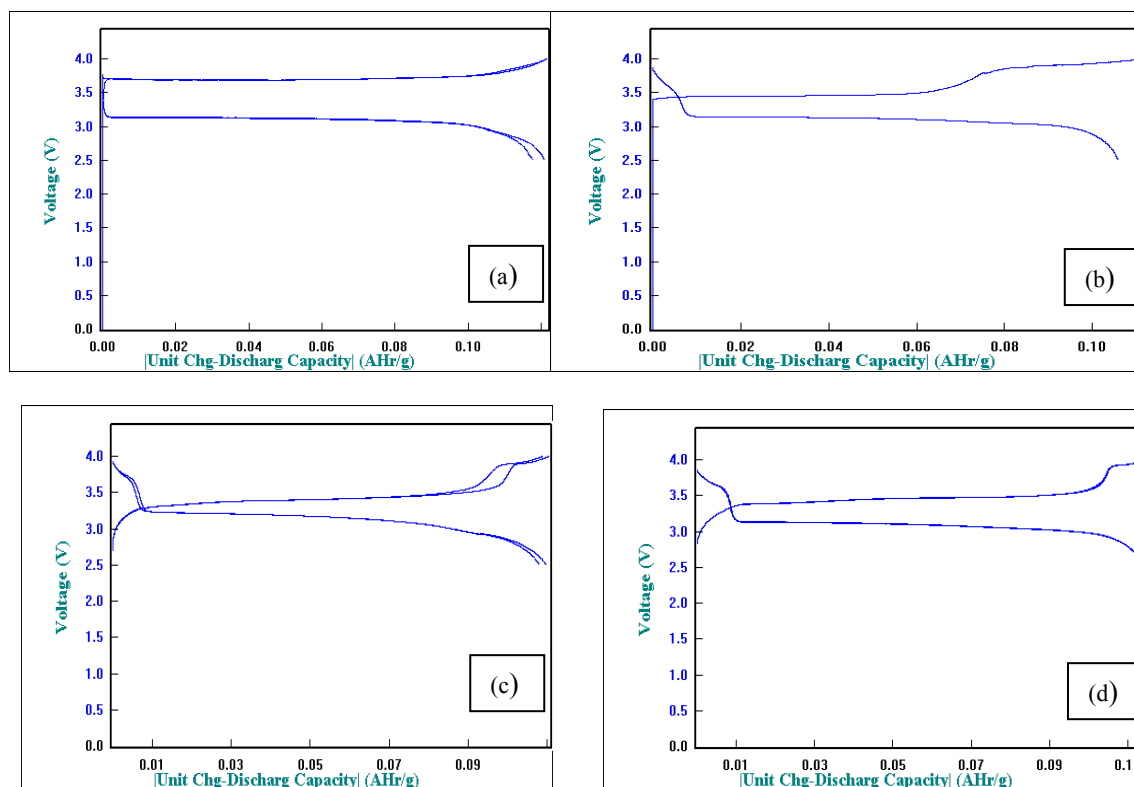


Figure 4. Charge discharge capacity (a) Separator commercial with electrolyte LiPF_6 (b) Separator PVDF with electrolyte LiPF_6 (c) Separator commercial with electrolyte LiBOB (d) Separator PVDF with electrolyte LiBOB

Table 1. Data report capacity

Half coin cell battery	Data report Capacity
Separator commercial with electrolyte LiPF_6	120.39 e-3 (Ahr/gr)
Separator PVDF with electrolyte LiPF_6	105.50 e-3 (Ahr/gr)
Separator commercial with electrolyte LiBOB	100.85 e-3 (Ahr/gr)
Separator PVDF with electrolyte LiBOB	113.81 e-3 (Ahr/gr)

Figure 4 shows the charge discharge of four cell sample. Sample which using commercial separator and LiPF_6 has the best charge discharge figure. That figure shows the standard figure of lithium ion battery charge discharge figure that are contained with the flat zone of charge and discharge voltage. These flat graph zone indicate the open circuit voltage of battery. Different with sample which used PVDF as separator. Figure 4(b) and 4(d) shows the different type if compared with standard lithium ion battery graph. The best battery with commercial separator and LiPF_6 as electrolyte has the biggest capacity and the battery with PVDF as separator and LiBOB as electrolyte has the smallest capacity value. It mean that the redox process and ionization process was occur at commercial separator and LiPF_6 electrolyte.

The ideal battery separator would be infinitesimally thin, offer no resistance to ionic transport in electrolytes, provide infinite resistance to electronic conductivity for isolation of electrodes, be highly tortuous to prevent dendritic growths and be inert to chemical reactions. There has been a continued demand for thinner battery separators to increase battery power and capacity. This has been especially true for lithium-ion batteries used in portable electronics. However, it is very important to ensure the continued safety of batteries, and this is where the role of the separator is greatest. Thus, it is essential to optimize all the components of battery to improve the performance while maintaining the safety of

these cells. Separator manufacturers should work along with the battery manufacturers to create the next generation of batteries with increased reliability and performance, but always keeping safety.

4. Conclusion

The commercial separator has a better impedance value than PVDF separator. LiFePO₄/ Graphite Li-ion cell using separator PVDF with the LiBOB –based electrolyte, was significantly shows capacity better than for similar separator in coin cells that used the LiPF₆ –based electrolyte. PVDF separator that has been made thinner than the commercial separator shows increase battery capacity.

References

- [1] P. Arora, Z. J. Zhang, S. Lakes, and N. Carolina, “Battery Separators,” 2004.
- [2] T. H. Cho, T. Sakai, S. Tanase, K. Kimura, Y. Kondo, and T. Tarao, “Electrochemical Performances of Polyacrylonitrile Nanofiber-Based Nonwoven Separator for Lithium-Ion Battery,” pp. 159–162, 2007.
- [3] X. Huang, “Separator technologies for lithium-ion batteries,” pp. 649–662, 2011.
- [4] M. Nasir, Juliardi, and P. Bambang, “Available online at www.sciencedirect.com,” vol. 16, pp. 184–189, 2015.
- [5] J. Kim, G. Cheruvally, and J. Ahn, “Electrochemical properties of LiFePO₄ / C synthesized by mechanical activation using sucrose as carbon source,” pp. 799–805, 2008.
- [6] K. Striebel, J. Shim, A. Sierra, H. Yang, X. Song, R. Kostecki, and K. McCarthy, “The development of low cost LiFePO₄ -based high power lithium-ion batteries,” vol. 146, pp. 33–38, 2005.
- [7] M. Yoshio, H. Wang, K. Fukuda, and T. Umeno, “Improvement of natural graphite as a lithium-ion battery anode material , from raw flake to carbon-coated sphere {,” pp. 1754–1758, 2004.
- [8] T. For, T. H. E. Degree, O. F. Doctor, I. N. Philosophy, and J. Scheers, *Department of Applied Physics*. 2011.
- [9] K. Xu, S. Zhang, T. R. Jow, W. Xu, C. A. Angell, E. S. Lett, and P. A-a, “LiBOB as Salt for Lithium-Ion Batteries : A Possible Solution for High Temperature Operation service LiBOB as Salt for Lithium-Ion Batteries A Possible Solution for High Temperature Operation,” vol. 5, no. 1, pp. 2–6, 2002.
- [10] D. Y. W. Yu, C. Fietzek, W. Weydanz, K. Donoue, T. Inoue, H. Kurokawa, and S. Fujitani, “Study of LiFePO₄ by Cyclic Voltammetry,” pp. 253–257, 2007.
- [11] G. A. Mabboil, “An Introduction to Cyclic Voltammetry I ,,,,,” vol. 60, no. 9, pp. 697–702, 1983.