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Research Article

Analysis of the Separator Thickness and Porosity on the Performance of Lithium-Ion Batteries

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In this paper, investigation on the effect of separator thickness and porosity on the performance of Lithium Iron Phosphate batteries are analyzed. In recent years there have been intensive efforts to improve the performance of the lithium-ion batteries. Separators are important component of lithium-ion batteries since they isolate the electrodes and prevent electrical short-circuits. Separators are also used as an electrolyte reservoir which is used as a medium for ions transfer during charge and discharge. Electrochemical performance of the batteries is highly dependent on the material, structure, and separators used. This paper compares the effects of material properties and the porosity of the separator on the performance of lithium-ion batteries. Four different separators, polypropylene (PP) monolayer and polypropylene/polyethylene/polypropylene (PP/PE/PP) trilayer, with the thickness of 20 μm and 25 μm and porosities of 41%, 45%, 48%, and 50% were used for testing. It was found that PP separator with porosity of 41% and PP/PE/PP separator of 45% porosity perform better compared to other separators.

1. Introduction

Rechargeable LIBs are widely used in many types of electronic devices because of their high energy density and good electrochemical performance. The development in energy-storage devices with high energy and power densities has progressed at an unprecedented high speed over the last decade [1]. Li-ion battery is one of the most promising solutions for these storage systems because of its outstanding electrochemical performance and high capacity. Lithium iron phosphate ($LiFePO_4$ or LFP), one of the very popular commercial cathode materials for Li battery, exhibits several advantageous features such as low cost, good environmental compatibility, relatively large capacity, and intrinsic stability [2].

Lithium-ion battery consists of three important functional components: cathode, anode, and electrolyte. During charging and discharging, the lithium ions move from one electrode to another through the electrolyte. Similar to the battery materials, separators play a vital role in the cell operation [3]. The essential function of the separator is to separate the two electrodes and to prevent internal short circuit and stability towards thermal runaway [4].

Separators are not involved directly in cell reactions, but the physical properties plays an important role in determining the performance of the battery including energy density, power density, and safety [5]. Research on the influence of separator thickness and porosity on the performance appears less in publications when compared to other factors. Separators modified with carbon, effectiveness of the glass fiber separator are reported regularly in the battery operation. Separators used in rechargeable batteries are typically in the range of 20-30 μm [6]. Celgard 2400 is one of the widely used separators. Research on the fabrication process focuses on the reduction of weight and on the stable performance of the battery. Most batteries use the commercial separators based on microporous monolayer and trilayer polyolefins [3, 7, 8]. Separators used in this analysis are Celgard-2400, PP2075, H2013, and H2512.

Separators must be chemically stable in contact with electrolyte and electrode materials used. They should not undergo degradation during the process of charging and discharging [6]. It should also be thermally stable during elevated temperature during normal battery operation. The wettability of the electrolyte is also an important property for a battery separator because electrolyte adsorption and stability of the separator are required for ion transport [4]. Adsorption of electrolyte is important to achieve low internal resistance and high ionic conductivity [9].

Porosity is also an important characteristic of a separator [10, 11]. Pore sizes should be small enough to block the penetration of active components of the electrode materials and conductive additives. Porosity of a separator has to be uniformly distributed to inhibit dendritic lithium and prevent the penetration of active particles through the separators [6]. Typically, submicron pore size of less than 1 μm is required for separators [10]. Porosity of the separators must be appropriate to retain electrolyte so that it provides sufficient ionic conductivity. If the porosity is too high it has an adverse impact on the cell performance because of low mechanical strength and high internal resistance [12].

Separators must be thermally stable; it should not shrink or curl when the temperature rises [6]. Typical, multilayer design of the separators provides shutdown features in which one-layer melts to close the pores near thermal runaway temperatures and other layers provide oxidation resistance and mechanical strength. Most separators facilitate ion transport only when they are filled with electrolyte. Electrolyte retention is also a critical factor for long-term performance [4, 6, 11].

2. Experimental

$LiFePO_4$ (LFP) material was mixed by wet method. The effects of separator thickness and porosity on the performance of the cell are analyzed in terms of charge-discharge processes, surface morphology, and AC impedance analysis.

LFP powder, carbon (conductive carbon (3%) + super P (3%)), and PVDF are mixed in the ratio of 84:6:10 percentage ratio by mass. PVDF and NMP were first mixed for 3 hours in the ball milling machine at 150 RPM. Later conductive carbon, super P, and NMP were added and mixed for another 3 hours at 180 RPM.

Finally, LFP powder was added and mixed for 5 hours in the machine at 200 RPM. The slurry was coated on carbon coated aluminum sheets using the doctor blade method of the same thickness and then dried in a standard convection oven overnight. After that, they were cut in half and compressed using a calendering machine. The electrode density was calculated with the mass of the active material and thickness of the active material on the sheet. Finally, the LFP electrodes were divided into calendared and uncalendered samples.

The electrode sheets were punched and kept in a vacuum oven overnight. Later, they were used to assemble half cells with $LiFePO_4$ as cathode, electrolyte from BASF, 1 M $LiPF_6$. EC: EMC 1:2, and lithium metal as negative electrode. Initial charge-discharge testing using single layer of separators was not stable for cycling because of short circuit issues. So, the separators were doubled for all the samples to provide stability and to obtain consistent comparison. The doubling of the separator will have minimal impact on the performance of the cell and hence it is ignored.

Separators of different thicknesses such as 40 μm with 45% and 48% porosities and 50 μm with 41% and 50% porosities were used. JEOL JSM-7410F machine was used for SEM analysis. Surface morphology of the separators, uncalendered and calendered electrodes, was analyzed using SEM. Neware BTS was used to charge and discharge the battery using constant current constant voltage (CC-CV) routine between 2.0 and 4.0 V. Potentiostatic Electrochemical Impedance Spectroscopy analysis was done using Gamry Instruments. EIS was performed using an AC voltage of 10 mV and frequency ranging from 1 MHz to 0.01 Hz.

3. Results and Discussion

3.1. Surface Morphology. Morphology of the separators was characterized using scanning electron microscopy (SEM) at 5 KV. Figure 1 shows the surface of the separators at the same magnification. Porosity and thickness of the separators provided by the company are discussed in the Table 1. Separators are not conductive; therefore, it was coated with gold particles for 1 minute in a sputter coater before observing the images. As it can be seen in Figure 1 that the pores of the separators are uniformly distributed.

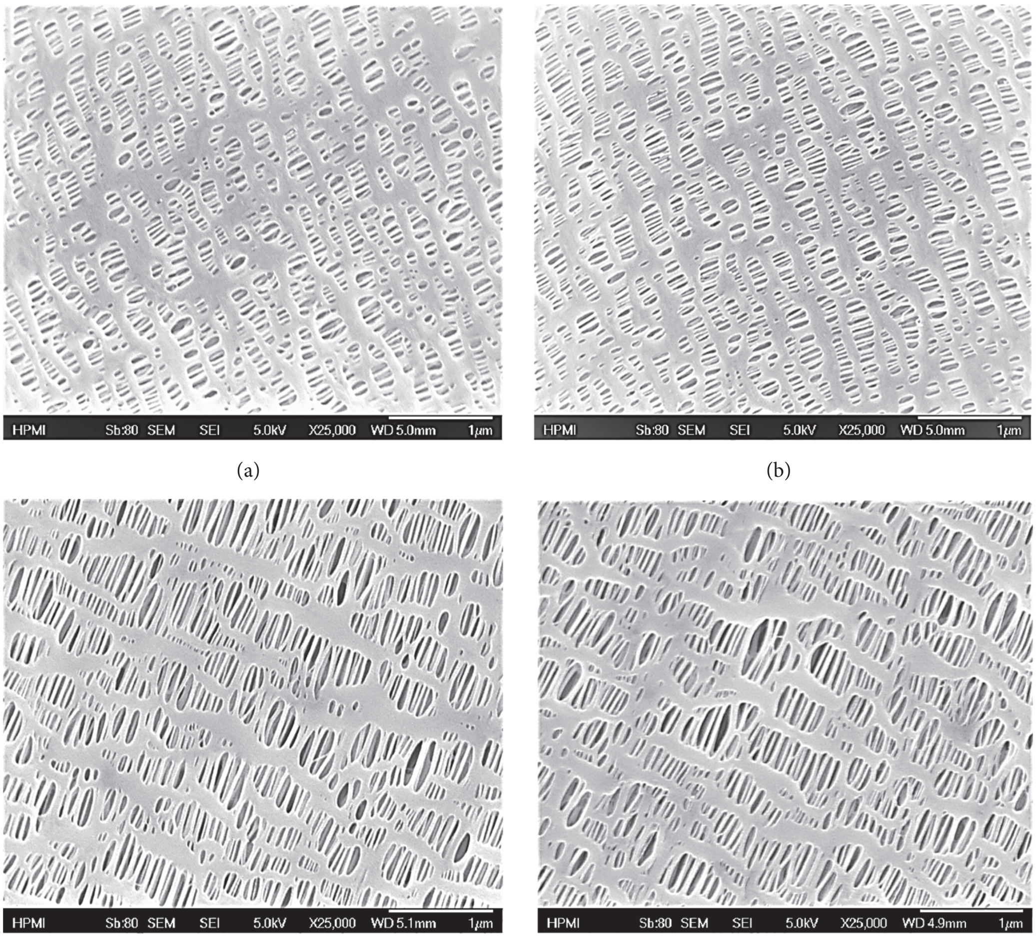
According to the manufacturer the shrinkage of all the separators is 0%; this indicates that the separators do not shrink at 85°C in an oven for one hour. The simplest microporous membrane is monolayer membrane. It can be made from different polymer materials. Polyolefins have been widely used for manufacturing separators because of their excellent mechanical strength and chemical stability. Membrane morphology does not have a significant impact on battery performance at low C-rate. Typically, separators with high porosity and less thickness are required. However, observing the results in terms of the performance of each cell with the same operating conditions, active material weight, and electrode density provides an insight into the optimum porosity and thickness needed for better battery performance.

Glass fiber separators are one of the commonly used separators. However, they are thicker and heavier when compared to Polyolefin based separators [11]. Size and thickness of the separators are important to reduce the overall weight of the batteries without compromising the performance.

Separators (a) and (b) are microporous trilayer separators and (c) and (d) are microporous monolayer separators. These separators have smooth surface when compared to glass fiber separators.

Figure 2 shows the surface of the LFP electrode uncalendered and calendered at the same magnification. For the purpose of this experiment, electrode samples from the same sheet were used.

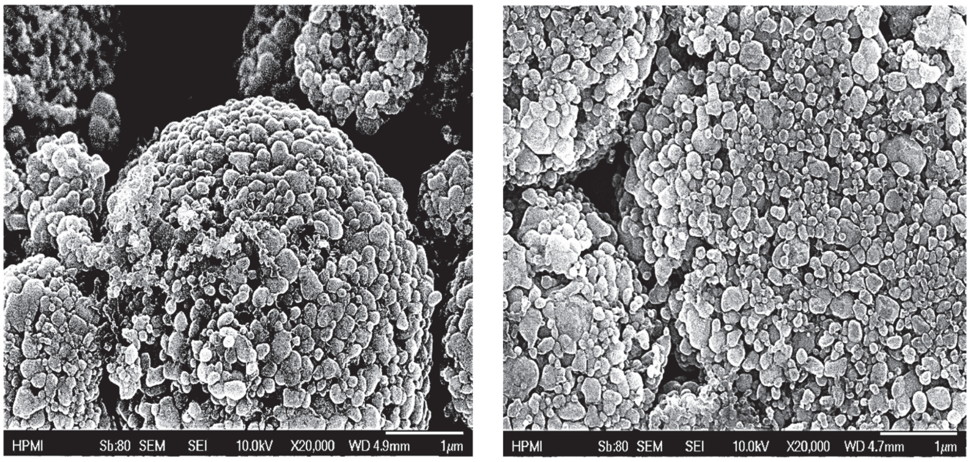
As seen in the SEM images, the density of the calendered electrode is higher. The average densities of the uncalendered samples were calculated to be 0.8 g/cm^3 and average densities of the calendered samples were 1.2 g/cm^3.



(a) (b)

(c) (d)

Figure 1: SEM images of the Celgard commercial separators trilayers (a) H2013 (porosity 45%) and (b) H2512 (porosity 50%); monolayers (c) 2400 (porosity 41%) and (d) PP2075 (porosity 48%).



(a) (b)

Figure 2: SEM Images of LFP electrode: (a) uncalendered electrode; (b) calendered electrode.

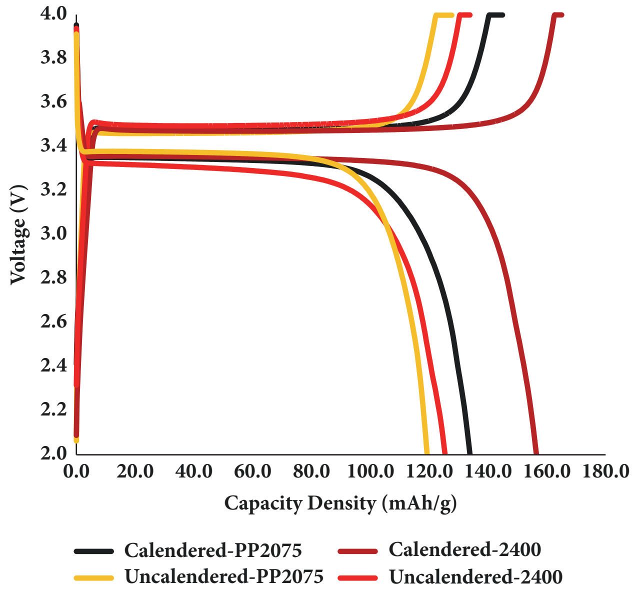


Figure 3: Charge and discharge performance of LFP batteries assembled with monolayer separators PP2075 and 2400.

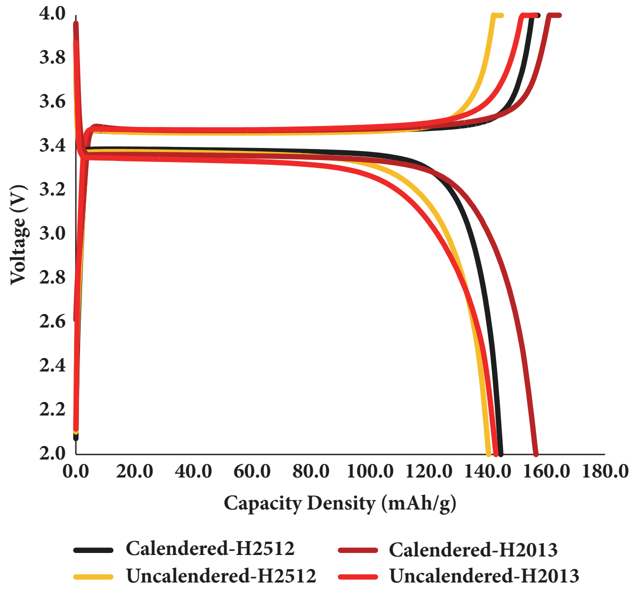


Figure 4: Charge and discharge performance of LFP batteries assembled with trilayer separators H2512 and H2013.

3.2. C-Rate Test. We tested the effects of the separator thickness and porosity on the performance of LFP batteries. Cells were assembled in the CR2032 coin cell cases using metallic lithium as anode and LFP as cathode.

In order to analyze the results, electrodes with the same thicknesses (with a difference of around ±2 μm) and weight were chosen. Also, the cells were fabricated with both calendered and uncalendered electrode for effective comparison on the influence of separator thickness and porosity. All the cells were tested at 1 C. Separators were classified based on the type of material used by the manufacturer. Calendering is an important process which increases the density of the electrode and reduces the internal resistance of the battery.

Figure 3 shows the charge and discharge performance of the cell with monolayer separators 2400 and PP2075 for both calendered and uncalendered samples. It is to be noted that the legend in the graphs are written in the format of sample type-type of separator used.

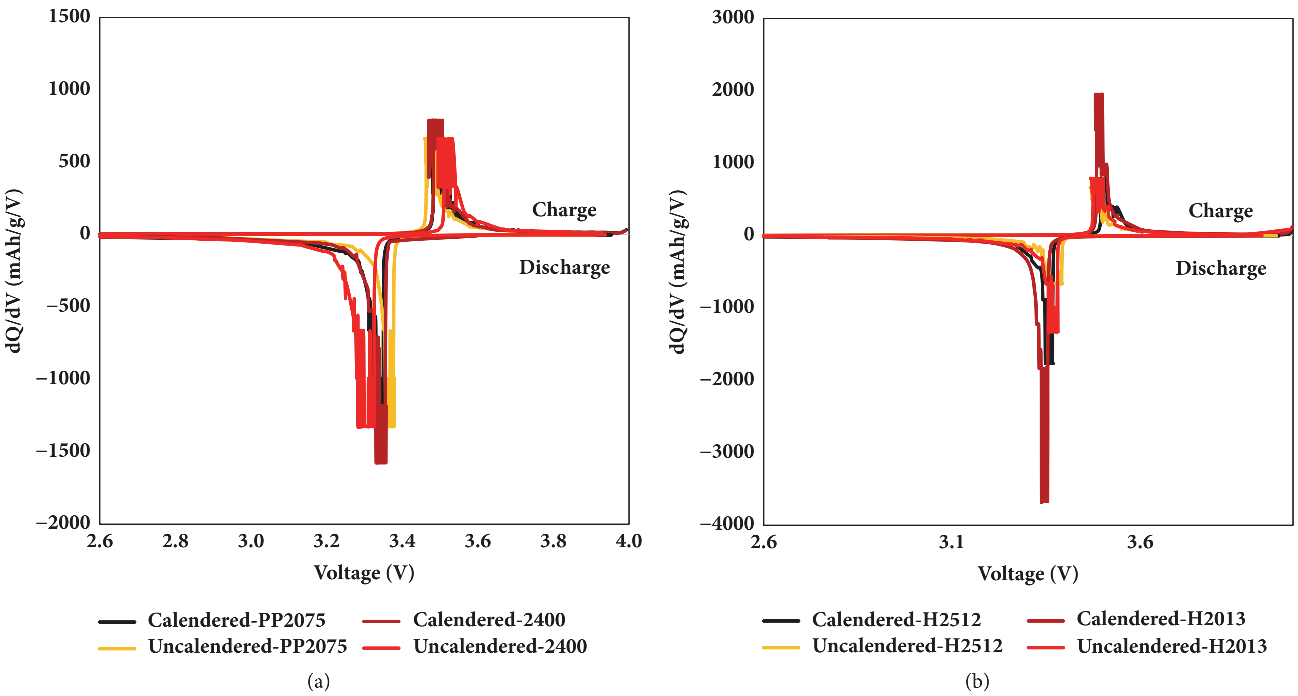
Figure 4 shows the charge and discharge performance of trilayer PP/PE/PP separator under the similar operating conditions on both calendered and uncalendered electrode samples.

As it can be seen in Figures 3 and 4, the discharge performance of calendered samples is better than uncalendered samples. Also, by observing the plot in Figure 3 it can be seen that Celgard 2400 separator performs better when compared to the Celgard PP2075 separator. It can be explained based on porosity and thickness of the separators used. When comparing the monolayer separators, optimum porosity and thickness are 41% and 50 μm, respectively. The variations in thickness of the separators influence the performance of the battery in high C-rate applications because of high internal impedance. For our experiment it can be assumed that the thickness plays a minimum role in performance because of low C-rate used for the testing. Similarly, as seen in Figure 4, the discharge performance of the calendered sample using the Celgard H2013 separator produces better performance when compared to the Celgard H2512 separator. We can attribute the higher charge and discharge capacity of the cells made using Celgard 2400 (monolayer) and Celgard H2013 (trilayer) compared to cells made using PP2075 (monolayer) and H2512 (trilayer) to the porous structure of the separator [13]. The porosity will impact the ionic charge compensation rate between the positive and negative electrodes soaked in electrolyte solution and therefore will impact the overall impedance of the cell. This is observed from the impedance results provided in Figures 6 and 7.

Figure 5 shows the dQ/dV curve for both charge and discharge of both monolayer and trilayer separators. Peaks for the charge and discharge using various separators are observed between the voltage range of 3.3 V–3.6 V. Also, the charge peaks for calendered electrodes using the separators had higher differential capacity when compared to the uncalendered electrodes. This is consistent with the results that are observed for all the samples using monolayer and trilayer separators. Tables 1(a) and 1(b) provide the comparison of the separators used for testing and the specific capacities that were observed at 1C discharge.

3.3. Electrochemical Impedance Spectroscopy (EIS). Figures 6 and 7 show the comparison of the impedance spectroscopy results of separators of both uncalendered and calendered electrodes for monolayer and trilayer groups.

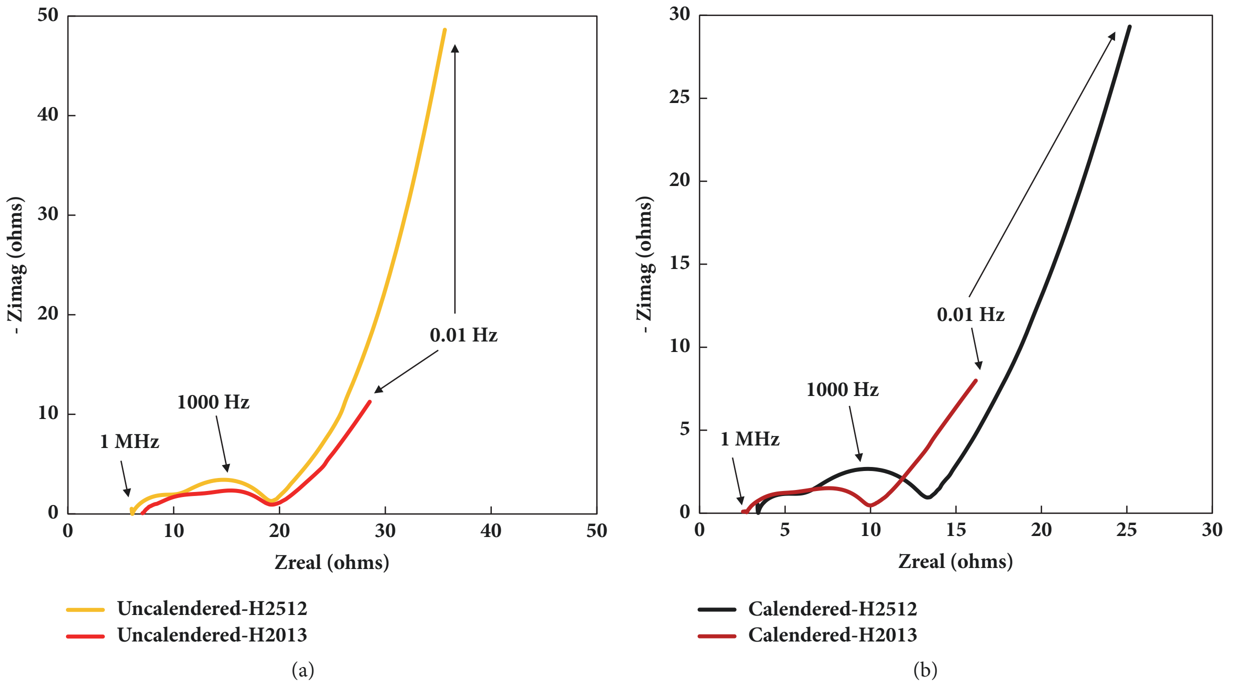
It can be observed from the EIS results that the ohmic resistance is lower for the cells that used the 2400 and H2013 separators when compared to PP2075 and H2512 separators, respectively. The diffusion impedance was also lower for the cells that used the 2400 and H2013 separators when compared with the same type of material-based separators of PP2075 and H2512, respectively. Thus, the results from the



(a)

(b)

Figure 5: dQ/dV versus voltage curve of both charge and discharge data of (a) monolayer separators and (b) trilayer separators.



(a)

(b)

Figure 6: Measured EIS data for calendered and uncalendered electrodes for trilayer separators: (a) uncalendered electrodes using H2512 and H2013 separators; (b) calendered electrodes using H2512 and H2013 separators.

impedances support the charge-discharge performances of the cells that were observed in Figures 3 and 4. The better performing cells were observed with the separators of lower porosity in the monolayer and trilayer groups.

We attributed this behavior to the loss of cyclable lithium during the initial stages of charge transfer and decomposition of the electrolyte which forms the solid electrolyte interphase (SEI). Also, there is a possibility of the decomposition products of electrolyte blocking the pores of the separators [4]. This loss of lithium and formation of interphase layer affects the charge transfer kinetics and also the diffusion process [14].

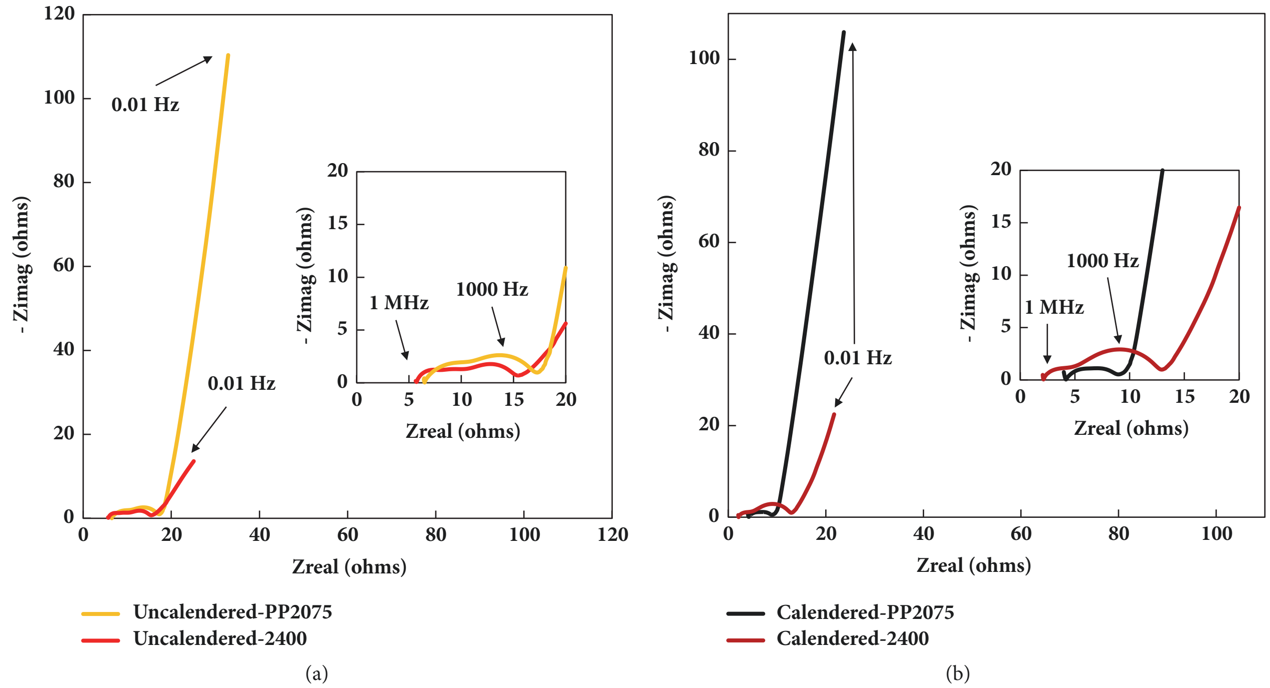


Figure 7: Measured EIS data for calendered and uncalendered electrodes for monolayer separators: (a) uncalendered electrodes using 2400 and PP2075 separators; (b) calendered electrodes using 2400 and PP2075 separators.

Table 1: Comparison of the separators based on thickness, porosity, and specific capacity.

(a) Monolayer separator properties and discharge results comparison

Separator	Thickness	Porosity	Specific Capacity Uncalendered Electrode (mAh/g)	Specific Capacity Calendered Electrode (mAh/g)
2400 (PP) [Monolayer]	50 μm	41%	125.4	156.3
PP2075 (PP) [Monolayer]	40 μm	48%	119.1	133.5

(b) Trilayer Separator properties and discharge results comparison

Separator	Thickness	Porosity	Specific Capacity Uncalendered Electrode (mAh/g)	Specific Capacity Calendered Electrode (mAh/g)
H2013 (PP/PE/PP) [Trilayer]	40 μm	45%	141.9	156.1
H2512 (PP/PE/PP) [Trilayer]	50 μm	50%	140.2	144.3

4. Conclusion

Lithium iron phosphate material is used for fabricating coin cells which is used in this testing. Calendered and uncalendered electrodes were characterized to study the difference between the influence of porosity and thickness of the separator on the performance of the cell. C-rate test, SEM analysis, and impedance spectroscopy experiments were performed to study the effects of the separators porosity and thickness. As observed from the results, porosity of the separator clearly plays an important role in the cell operation. Cells fabricated with higher porosity separators yields lower performance. This can be attributed to the initial loss of lithium and decomposition of electrolyte which forms interphase layer. This affects charge transfer kinetics and diffusion process in the cell. Since the separators are made from different material, it cannot be compared under the same conditions of the cell. It was concluded that the trilayer separator of porosity 45% and monolayer separator of 41% porosity perform better when compared to other separators with higher porosity.

Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

[1] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, "Li-ion battery materials: present and future," *Materials Today*, vol. 18, no. 5, pp. 252–264, 2015.

[2] C. Leong, Y. Gan, G. Gan et al., "Ultra fast charging system on lithium ion battery," in *Proceedings of the 2010 IEEE Conference on Sustainable Utilization and Development in Engineering and Technology (STUDENT)*, pp. 37–39, Kuala Lumpur, Malaysia, November 2010.

[3] S. Choudhury, M. Azizi, I. Raguzin et al., "Effect of fibrous separators on the performance of lithium-sulfur batteries," *Physical Chemistry Chemical Physics*, vol. 19, no. 18, pp. 11239–11248, 2017.

[4] D. V. Carvalho, N. Loeffler, G.-T. Kim, and S. Passerini, "High temperature stable separator for lithium batteries based on SiO2 and hydroxypropyl guar gum," *Membranes*, vol. 5, no. 4, pp. 632–645, 2015.

[5] Y. Wang, S. Zhu, D. Sun, and Y. Jin, "Preparation and evaluation of a separator with an asymmetric structure for lithium-ion batteries," *RSC Advances*, vol. 6, no. 107, pp. 105461–105468, 2016.

[6] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, and X. Zhang, "A review of recent developments in membrane separators for rechargeable lithium-ion batteries," *Energy & Environmental Science*, vol. 7, no. 12, pp. 3857–3886, 2014.

[7] P. Arora and Z. Zhang, "Battery separators," *Chemical Reviews*, vol. 104, no. 10, pp. 4419–4462, 2004.

[8] L. Zolin, M. Destro, D. Chaussy, N. Penazzi, C. Gerbaldi, and D. Beneventi, "Aqueous processing of paper separators by filtration dewatering: towards Li-ion paper batteries," *Journal of Materials Chemistry A*, vol. 3, no. 28, pp. 14894–14901, 2015.

[9] L. J. Fu, H. Liu, C. Li et al., "Surface modifications of electrode materials for lithium ion batteries," *Solid State Sciences*, vol. 8, no. 2, pp. 113–128, 2006.

[10] R. S. Baldwin, W. R. Bennett, E. K. Wong, M. R. Lewton, and M. K. Harris, "Battery Separator Characterization and Evaluation Procedures for NASA's Advanced Lithium-Ion Batteries," *Program*, 2010.

[11] C. J. Weber, S. Geiger, S. Falusi, and M. Roth, "Material review of Li ion battery separators," in *Proceedings of the 1st International Freiberg Conference on Electrochemical Storage Materials: Review on Electrochemical Storage Materials and Technology, ESTORM 2013*, pp. 66–81, deu, June 2013.

[12] W. L. Wang, E. M. Jin, and H.-B. Gu, "Electrochemical performance of lithium iron phosphate by adding graphite nanofiber for lithium ion batteries," *Transactions on Electrical and Electronic Materials*, vol. 13, no. 3, pp. 121–124, 2012.

[13] D. Djian, F. Alloin, S. Martinet, H. Lignier, and J. Y. Sanchez, "Lithium-ion batteries with high charge rate capacity: Influence of the porous separator," *Journal of Power Sources*, vol. 172, no. 1, pp. 416–421, 2007.

[14] T. R. Jow, S. A. Delp, J. L. Allen, J. Jones, and M. C. Smart, " Factors Limiting Li ," *Journal of The Electrochemical Society*, vol. 165, no. 2, pp. A361–A367, 2018.