

Article

## Polymethylmethacrylate/Polyacrylonitrile Membranes via Centrifugal Spinning as Separator in Li-Ion Batteries

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**Abstract:** Electrospun nanofiber membranes have been extensively studied as separators in Li-ion batteries due to their large porosity, unique pore structure, and high electrolyte uptake. However, the electrospinning process has some serious drawbacks, such as low spinning rate and high production cost. The centrifugal spinning technique can be used as a fast, cost-effective and safe technique to fabricate high-performance fiber-based separators. In this work, polymethylmethacrylate (PMMA)/polyacrylonitrile (PAN) membranes with different blend ratios were produced via centrifugal spinning and characterized by using different electrochemical techniques for use as separators in Li-ion batteries. Compared with commercial microporous polyolefin membrane, centrifugally-spun PMMA/PAN membranes had larger ionic conductivity, higher electrochemical oxidation limit, and lower interfacial resistance with lithium. Centrifugally-spun PMMA/PAN membrane separators were assembled into Li/LiFePO<sub>4</sub> cells and these cells delivered high capacities and exhibited good cycling performance at room temperature. In addition, cells using centrifugally-spun PMMA/PAN membrane separators showed superior C-rate performance compared to those using microporous polypropylene (PP) membranes. It is, therefore, demonstrated that centrifugally-spun PMMA/PAN membranes are promising separator candidate for high-performance Li-ion batteries.

**Keywords:** centrifugal spinning; polymethylmethacrylate; polyacrylonitrile; nanofiber; battery; separator

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## 1. Introduction

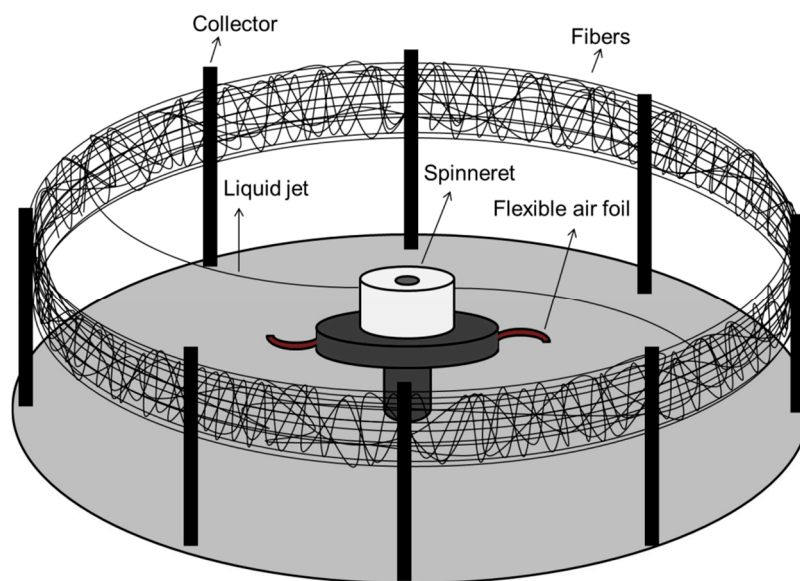
Li-ion batteries have been widely used in many electronic devices, including mobile phones, laptop computers and digital cameras, because of their high energy density, large operational voltage, long cycling life, and low self-discharge rate [1,2]. In recent years, Li-ion batteries have found new application areas such as electric/hybrid vehicles and energy storage for smart grids. To meet the requirements of these new applications, designing new battery components with improved performance is critical [3–5].

In Li-ion batteries, the separator is placed between two electrodes, the anode and the cathode. It prevents the physical contact of electrodes while serving as the electrolyte reservoir to enable ionic transport. Although the separator does not directly participate in electrode reactions, its structure and properties affect battery performance, including cycle life, safety, energy density, and power density by regulating the cell resistance and kinetics [6,7]. Microporous polyolefin membranes are widely used in Li-ion batteries since they have good chemical stability and mechanical strength. However, low porosity and poor wettability of these membranes affect the cell resistance and kinetics negatively and restrict cell performance, including energy density and rate capability [8].

Over the past 10 years, electrospun nanofiber membranes have been extensively studied as alternative separators for Li-ion batteries due to their large porosity and unique pore structure. In electrospinning technique, continuous nanosized polymer fibers are produced through the action of an external electric field imposed on a polymer solution [9–11]. Enhanced electrochemical properties such as higher C-rate capability, better cycling performance and lower cell resistance have been reported for Li-ion cells using electrospun nanofiber-based separators [12,13]. However, electrospinning process has some serious drawbacks such as low spinning rate and high production cost, which hinder the practical use of electrospun nanofiber separators in Li-ion batteries [14]. Therefore, a new technique that can produce high-performance nanofiber separators at high speed and low cost is urgently needed.

Recently, centrifugal spinning has been studied as an alternative approach to fabricate nanofibers in a large-scale and low-cost fashion [14,15]. In this technique, a high-speed rotary and perforated spinneret is used to fabricate nanofibers from polymer solutions (Figure 1). During fiber spinning, high centrifugal force is generated on the polymer solution by rotating the spinneret. When the spinneret reaches a critical rotational speed, the centrifugal force is able to overcome the surface tension of the solution and liquid jets are ejected from nozzles. Liquid jets are stretched by the centrifugal force, accompanied by solvent evaporation. The resultant solidified fibers are deposited on the rod collectors. The diameters of fibers can vary from several nanometers to micrometers and the production rate of the centrifugal spinning process could be more than 500 times faster than conventional electrospinning technique [8,14]. In an earlier study, it has been reported that the average production rate of a laboratory-scale centrifugal spinning device was around 50 g/h, which was at least two orders of magnitude higher than that of a typical laboratory-scale electrospinning process [16]. Zhang *et al.* [15] reported cost comparison for different production methods. The cost of nanofiber separators by electrospinning is high for industrial production due to the low production rate of this method. Compared with electrospun separators, nanofiber separators made by centrifugal spinning are less expensive due to the faster production and lower solvent consumption. For commercial microporous

separators, the raw materials used, such as polyethylene and polypropylene, are cheaper than the polymers used for making nanofiber separators. However, the processing of commercial microporous separators is relatively expensive because the productivity on a mass basis is inherently low. A cost estimation shows that microporous polyolefin separators, such as polypropylene Celgard membrane, account for 25%–30% of the overall cost of conventional Li-ion batteries [17]. Considering the expensive processing of commercial microporous separators and electrospun separators, centrifugally-spun nanofiber separators may have a cost advantage due to the simplicity and high speed of this technique, and have the potential to decrease the overall cost of Li-ion batteries.



**Figure 1.** Schematic of centrifugal spinning process.

In centrifugal spinning, the morphology of nanofibers is affected by solution properties, including viscosity, surface tension, molecular structure, molecular weight, solution concentration, solvent structure, additive and operational conditions such as rotating speed, spinning head diameter, nozzle diameter and nozzle-collector distance [15]. Lu *et al.* [16] investigated the effects of solution properties and operational parameters on the morphology of centrifugally-spun Polyacrylonitrile (PAN) nanofibers. It was found that increasing concentration and viscosity led to increase in fiber diameter. In addition, the average fiber diameter decreased with increasing rotational speed. Decrease in nozzle diameter led to thinner fiber and longer nozzle-collector distance caused slightly thinner fibers.

Polyacrylonitrile (PAN) has been studied as a separator material and PAN-based separators show promising properties, including high ionic conductivity, good thermal stability, high electrolyte uptake and good compatibility, with Li metal [18]. Polymethylmethacrylate (PMMA) has also been used as a separator material due to its good compatibility with Li and high affinity to liquid electrolyte [19,20]. Blending PAN and PMMA can potentially lead to new separators with enhanced microstructure, porosity and electrochemical properties that cannot be achieved by single-component polymer membranes. Different blend separators including PVDF/PMMA-*co*-PEGMA microporous separators [21], PVDF-*co*-HFP/PAN microporous membranes [22], PVDF/PMMA microporous membranes [19,23], electrospun PVDF/PAN membranes [18], and electrospun PVDF-HFP/PMMA [24] have been reported so far, and results demonstrated that blend separators have the advantages of improved electrolyte

uptake, ionic conductivity, and cycling performance. In this work, centrifugal spinning was utilized to produce PAN/PMMA blend membranes for use as high-performance separator for Li-ion batteries. The porosity, ionic conductivity, electrochemical oxidation limit and interfacial resistance of these membranes were investigated, and results showed that compared with commercial microporous polyolefin membranes, centrifugally-spun PMMA/PAN membranes had larger ionic conductivity, higher electrochemical oxidation limit, and lower interfacial resistance with lithium. Furthermore, PMMA/PAN membranes were assembled into Li/LiFePO<sub>4</sub> cells and these cells delivered high capacities and exhibited good cycling performance at room temperature. In addition, cells using PMMA/PAN membranes showed superior C-rate performance compared to those using microporous polypropylene (PP) membranes. It is, therefore, demonstrated that these centrifugally-spun PMMA/PAN membranes are promising separator candidate for high-performance Li-ion batteries.

## 2. Experimental Section

### 2.1. Materials

Polyacrylonitrile (PAN,  $M_w = 150,000$ ) was supplied from Pfaltz & Bauer Inc. (Waterbury, CT, USA). Polymethylmethacrylate (PMMA, 300,000) and *N,N*-dimethylformamide (DMF) were purchased from Sigma Aldrich (St. Louis, MO, USA). The liquid electrolyte of 1 M LiPF<sub>6</sub> in ethylene carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) (1:1:1 in volume) was supplied from MTI Corporation (Richmond, CA, USA). Celgard 2400 microporous monolayer polypropylene (PP) membrane with the thickness of 25  $\mu\text{m}$  and the porosity of 41% was used for comparison. All chemicals were used as received.

### 2.2. Separator Preparation

PMMA/PAN membranes were prepared by using centrifugal spinning. PMMA/PAN solutions with different blend ratios (100/0, 75/25 and 50/50 w/w) were prepared by dissolving PMMA and PAN into DMF with a total polymer concentration of 17 wt%. PMMA/PAN solutions with lower blend ratios of 25/75 and 0/100 were also prepared, but they did not produce free-standing nanofiber membranes probably due to their low viscosities. All solutions were stirred mechanically overnight prior to centrifugal spinning.

The centrifugal spinning system was powered by a DC motor (115 V, Grainger, Raleigh, NC, USA) and the rotational speed of the motor was controlled by a speed controller (DART CONTROLS253G-200C, Galco, Detroit, MI, USA). The spinneret had a cylindrical shape with 2 cm in height, 1.5 cm in radius, and 0.3 cm in wall thickness. Two nozzles with inner diameter of 0.4 mm were located on the sidewall of the spinneret. The distance between the nozzle tip and the rod collector was 10 cm. In this work, the spinning operations of PMMA and PMMA/PAN solutions were conducted with a rotational speed of 4000 rpm at room temperature. The thickness of the as-prepared nanofiber membranes was around 85  $\mu\text{m}$ .

### 2.3. Structure Characterization

The morphology of centrifugally-spun PMMA and PMMA/PAN membranes was studied by using a JEOL JSM-6400F field-emission scanning electron microscope (FESEM) (Bromont, QC, Canada). The fiber diameters were calculated by measuring 50 randomly-selected fibers in SEM images using Revolution 1.6 software for each sample. The porosities of the membranes were calculated by using the following equation:

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_M}{\rho_P}\right) \times 100 \quad (1)$$

where  $\rho_M$  is the apparent density of the separator, and  $\rho_P$  the density of the polymer.

### 2.4. Performance Evaluation

Liquid electrolyte uptakes were measured by soaking weighed membranes in the liquid electrolyte of 1 M LiPF<sub>6</sub> in EC + EMC (1:1 in volume) at room temperature. The electrolyte uptake (EU) was calculated by:

$$\text{EU (\%)} = \frac{w_1 - w_0}{w_0} \times 100 \quad (2)$$

where  $w_0$  and  $w_1$  are the weights of dry and wet membranes, respectively.

The ionic conductivities of liquid electrolyte-soaked membranes were measured by electrochemical impedance spectroscopy (EIS) using Reference 600 Potentiostat/Galvanostat/ZRA (GAMRY, Warminster, PA, USA). The impedance measurements were performed on liquid electrolyte-soaked membranes sandwiched between two stainless steel electrodes over a frequency range of 1 MHz to 1 Hz with AC amplitude of 10 mV at room temperature. The ionic conductivity was calculated by:

$$\sigma = \frac{d}{R_b \times S} \quad (3)$$

where  $d$  is the membrane thickness,  $S$  the cross-sectional area, and  $R_b$  the bulk resistance obtained at the high frequency intercept of the Nyquist plot on the real axis.

The electrochemical oxidation limits of liquid electrolyte-soaked membranes were determined by linear sweep voltammetry at room temperature. In these tests, electrochemical cells consisting of stainless steel working electrode and lithium metal counter electrode were used. The scan rate used was 10 mV·s<sup>−1</sup> and the potential range was 2.5 to 6.0 V.

The interfacial resistances between liquid electrolyte-soaked membranes and lithium metal were investigated by measuring the impedances of symmetrical lithium cells. The frequency range used was 1 MHz to 1 Hz.

The charge-discharge tests of Li/LiFePO<sub>4</sub> cells containing liquid electrolyte-soaked membranes were conducted by using coin-type cells. The LiFePO<sub>4</sub> cathode was prepared by blending LiFePO<sub>4</sub> powder (80 wt%), carbon black conductor (10 wt%) and PVDF binder (10 wt%). Arbin automatic battery cycler was used with a potential range of 4.2–2.5 V at a current density of 0.2 C to evaluate the cycling performance. In order to evaluate C-rate performance, different C-rates (0.2 C, 0.5 C, 1 C, 2 C, 4 C, and 8 C) were applied to the cells.

### 3. Results and Discussion

#### 3.1. Separator Morphology

The morphology of membrane separators affects the electrochemical properties of Li-ion cells by influencing the ion transport and conductivity behavior. Figure 2 shows SEM images of PMMA membrane and PMMA/PAN membranes with the blend ratios of 75/25 and 50/50. All three membranes have bead-free fibrous structure with a large number of pores. The average fiber diameters are 3.0, 1.8, and 0.7  $\mu\text{m}$ , respectively, for PMMA, PMMA/PAN (75/25), and PMMA/PAN (50/50) membranes. With the introduction of PAN into PMMA membrane, the average fiber diameter decreases. The diameters of centrifugally-spun fibers are affected by many factors, including solution properties such as viscosity, surface tension, concentration, polymer structure, polymer molecular weight and solvent structure, and operational conditions such as rotating speed, spinning head diameter, nozzle diameter and nozzle-collector distance. In this study, the PMMA/PAN blend ratio was varied while keeping the solution concentration, solvent type, and operating conditions constant. The increase in the amount of low-molecular weight PAN led to lower solution viscosity and less polymer chain entanglement during centrifugal spinning, which in turn caused reduced fiber diameter. In addition to molecular weight, microphase-separation of incompatible PMMA/PAN blends could be another reason for the significant decrease in average fiber diameter, especially for the PMMA/PAN (50/50) membrane. Similar results were also reported for electrospun PAN/PMMA nanofibers by Hong *et al.* [25], who explained the decreased average fiber diameters by using the reduced solution viscosity and phase inversion that occurred at PMMA contents of 50 and 75 wt%.

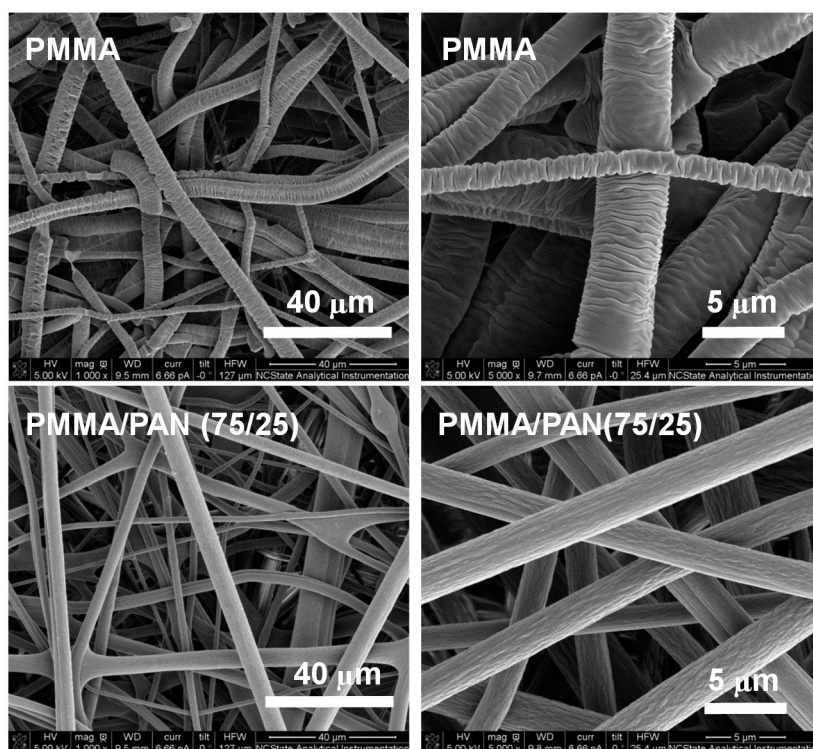
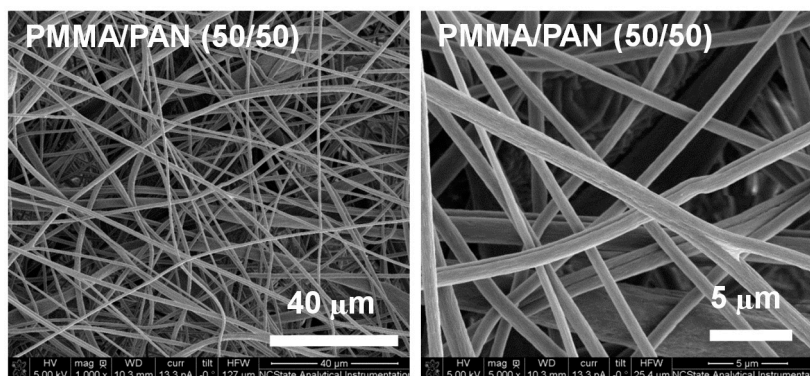


Figure 2. Cont.



**Figure 2.** SEM images of PMMA, PMMA/PAN (75/25), and PMMA/PAN (50/50) membranes.

It has been well established that high porosity is beneficial for membrane separators because it helps absorb large amount of liquid electrolyte and allows fast ion transportation between two electrodes [23]. Table 1 presents the porosities of PMMA, PMMA/PAN (75/25), and PMMA/PAN (50/50) membranes. The porosity of microporous PP membrane (41%) is also shown for comparison. Centrifugally-spun PMMA and PMMA/PAN membranes have higher porosities than PP membrane due to their fibrous structure. The porosities of PMMA, PMMA/PAN (75/25) and PMMA/PAN (50/50) membranes are 57%, 64% and 73%, respectively. PMMA/PAN membranes present higher porosities compared to PMMA membrane owing to their lower average fiber diameters. From Table 1, it is also seen that the porosity increases with increasing PAN content, which may also be ascribed to the increasing average fiber diameter.

**Table 1.** Porosities, electrolyte uptakes and ionic conductivities of PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane at room temperature.

Samples	Porosity (%)	Electrolyte Uptake (%)	Ionic Conductivity (mS/cm)
PMMA membrane	57	300	2.8
PMMA/PAN (75/25) membrane	64	330	3.0
PMMA/PAN (50/50) membrane	73	370	3.2
Microporous PP membrane	41	158	0.8

### 3.2. Liquid Electrolyte Uptake

Large liquid electrolyte uptake is essential for separators because the amount of liquid electrolyte between electrodes affect the internal ionic resistance of the cell. In order to obtain high electrochemical performance, separators should absorb large amount of liquid electrolyte. The liquid electrolyte uptake capacities of PMMA, PMMA/PAN (75/25), PMMA/PAN (50/50) and PP membranes are shown in Table 1. The liquid electrolyte uptake capacity of PMMA membrane is 300%, which is much larger than that (158%) of the microporous PP membrane. In addition, PMMA/PAN membranes show larger electrolyte uptake due to their higher porosities. The uptake capacities are 330% and 370%, respectively, for PMMA/PAN (75/25) and PMMA/PAN (50/50) membranes. The large electrolyte uptakes of PMMA and PMMA/PAN membranes are mainly caused by their large porosities. In addition, both PMMA and PAN can absorb liquid electrolyte and form gels, which also contribute

to their large liquid electrolyte uptake capacities. The absorption of liquid electrolyte and formation of gels are also beneficial for enhancing the adhesion between the separator and the electrode.

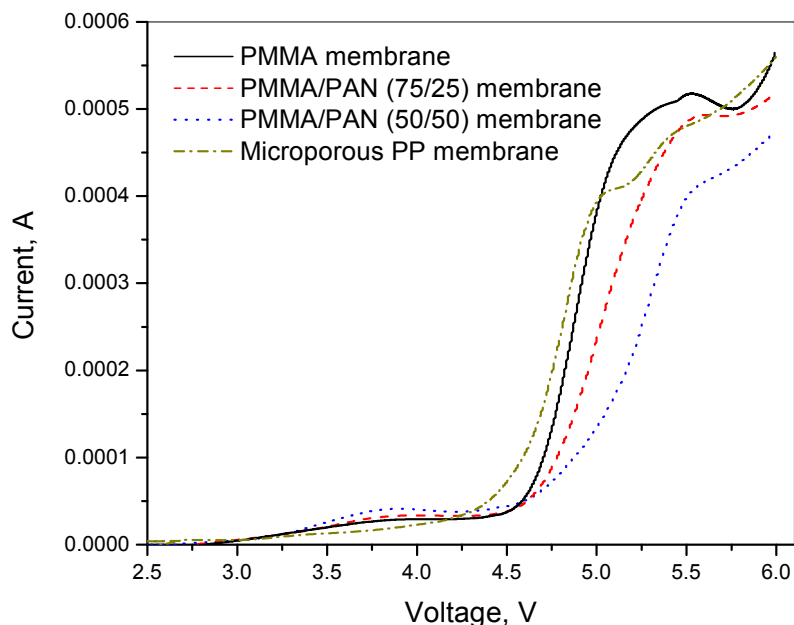
### 3.3. Ionic Conductivity

Ionic conductivities of liquid electrolyte-soaked membranes influence cell resistance, which in turn affects the cycling and C-rate performance of Li-ion batteries. Ionic conductivities of electrolyte-soaked PMMA and PMMA/PAN membranes are shown in Table 1. Ionic conductivities of electrolyte-soaked PMMA, PMMA/PAN (75/25) and PMMA/PAN (50/50) membranes are 2.8, 3.0 and 3.2 mS/cm, respectively. High ionic conductivities of electrolyte-soaked PMMA and PMMA/PAN membranes can be ascribed to highly porous structures of these membranes. In addition, with increase in PAN content, the ionic conductivity increases due to the increased membrane porosity, which allows higher electrolyte uptake.

### 3.4. Electrochemical Oxidation Limit

For practical battery applications, the electrochemical stability of the electrolyte-soaked separators must be within the operation voltage of the battery, which is typically 1.5–3.5 V vs. Li/Li<sup>+</sup>. The electrochemical oxidation limits of liquid electrolyte-soaked membranes can be evaluated by linear sweep voltammetry measurements. In these measurements, the rapid increase of the current can be observed when the electrolyte starts to decompose. Figure 3 demonstrates the electrochemical oxidation limits of PMMA, PMMA/PAN (75/25), PMMA/PAN (50/50), and microporous PP membranes. It is seen that PMMA and PMMA/PAN membranes exhibit the electrochemical oxidation limit of around 4.5 V while the electrochemical oxidation limit of the microporous PP membrane is 4.25 V. The electrochemical oxidation limit could be influenced by many factors, including electrolyte type and composition, electrode material and structure, and separator material and morphology, *etc.* [23]. When the electrolyte and electrode are fixed, the electrochemical oxidation limit could be affected by the interface between the electrolyte and the separator, which is related to the affinity between the separator and the liquid electrolyte, and the specific surface area and average fiber diameter of the separator [23,26,27]. Jung *et al.* [26] reported increased electrochemical oxidation limit for PAN fibrous separators due to the good electrolyte absorption resulted from high specific surface area and thin fiber diameter. Raghavan *et al.* [27] and Choi *et al.* [28] also reported that the electrolyte-soaked fiber membranes with large surface area had improved electrochemical oxidation limit due to the formation of a large amount of complex compounds such as associated Li<sup>+</sup>–N≡C– group, associated Li<sup>+</sup>–O=C group, and associated C≡N–Li<sup>+</sup>–O=C group. Large and fully interconnected pores, high porosity, high specific surface area, uniform morphology were also reported as reasons of increased electrochemical oxidation limits when the average fiber diameter of fibrous separators decreased [27]. In addition, the variations in physical contact caused by the different separator morphology may also play a role in changing the electrochemical oxidation limit. These explanations are in agreement with earlier studies, which reported that electrolyte-soaked PAN fibrous membranes had improved electrochemical stability due to the high affinity of these membranes to the liquid electrolyte [27,28].

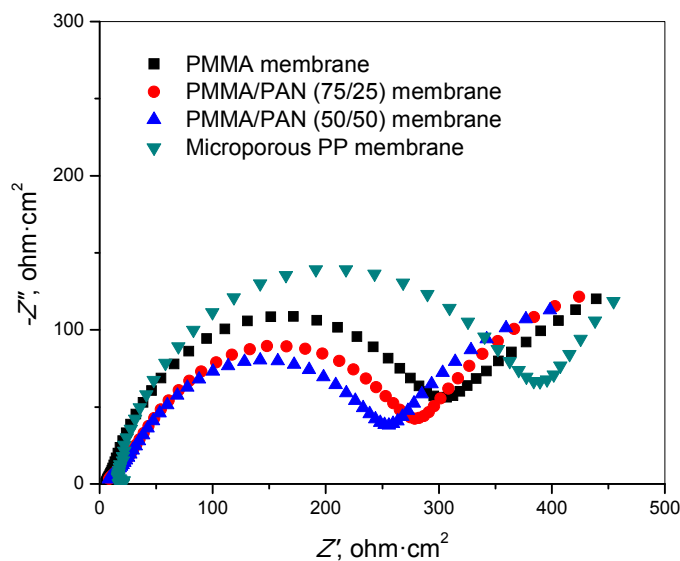




**Figure 3.** Electrochemical oxidation limits of PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane.

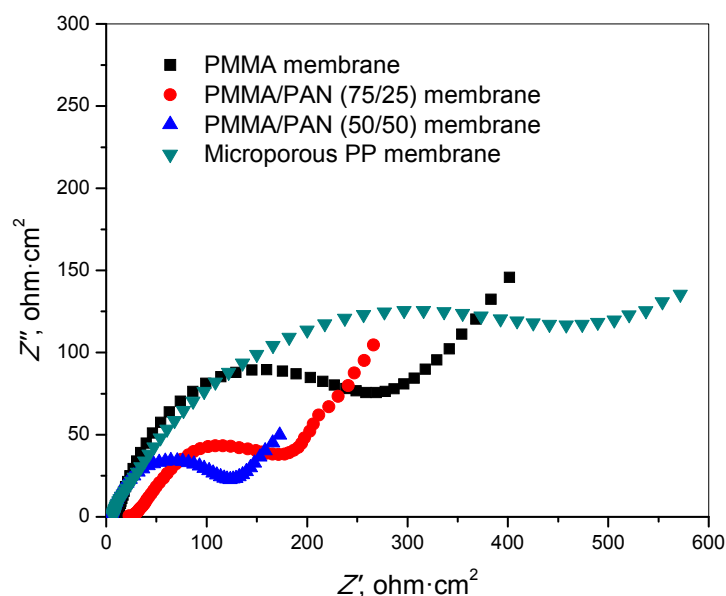
### 3.5. Interfacial Resistance

The electrochemical performance of Li-ion batteries is affected by the interfacial properties of electrolyte-soaked separators with Li metal [29]. The formation of stable solid electrolyte interface on the lithium metal helps not only conduct lithium ions freely but also prevents electrolyte decomposition [30]. The interfacial resistances between liquid electrolyte-soaked membranes and lithium metal were investigated by measuring electrochemical impedance spectra of Li/liquid electrolyte-soaked membrane/Li cells. Figure 4 shows the electrochemical impedance spectra of PMMA, PMMA/PAN and microporous PP membranes. The diameters of semi-circles at the intermediate frequency region represent the interfacial resistances of liquid electrolyte-soaked membranes with Li metal. It is seen from Figure 4 that microporous PP membrane has an interfacial resistance of  $400 \text{ ohm}\cdot\text{cm}^2$ . However, centrifugally-spun PMMA membrane exhibits a lower interfacial resistance compared to microporous PP membrane, and the presence of PAN further decreases the interfacial resistance. The interfacial resistances are  $300 \text{ ohm}\cdot\text{cm}^2$ ,  $280 \text{ ohm}\cdot\text{cm}^2$ , and  $250 \text{ ohm}\cdot\text{cm}^2$ , respectively, for PMMA membrane, PMMA/PAN (75/25) membrane, and PMMA/PAN (50/50) membrane. Smaller average fiber diameters, higher porosities and good swelling abilities of PAN and PMMA are the main reasons for lower interfacial resistances of PMMA/PAN membranes. The high ionic conductivities, resulted from the highly porous fibrous structure, and the high affinity of PAN and PMMA to the liquid electrolyte also contribute to the lower interfacial resistances [26].



**Figure 4.** Electrochemical impedance spectra of PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane.

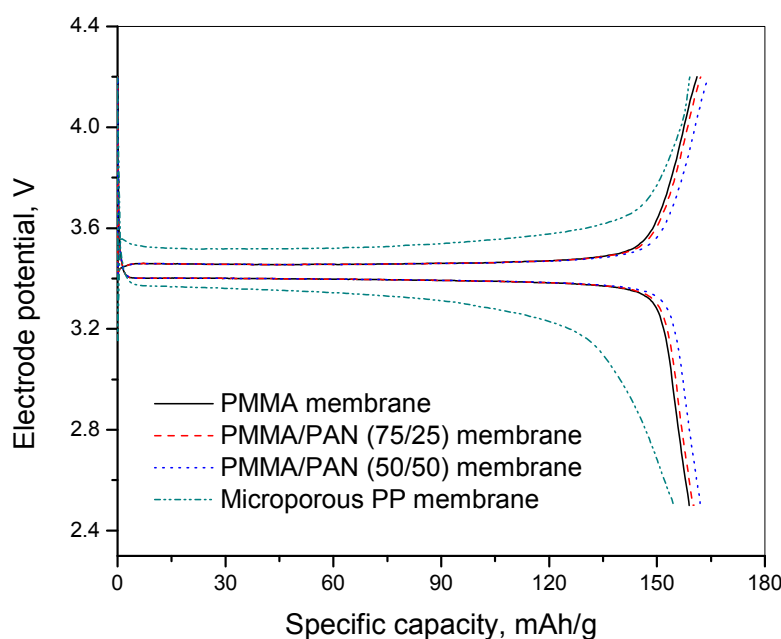
In addition to Li metal, it is also important to have good interfacial properties between liquid electrolyte-soaked membranes and other active electrode materials. Figure 5 shows the electrochemical impedance spectra of Li/LiFePO<sub>4</sub> cells containing PMMA, PMMA/PAN (75/25), PMMA/PAN (50/50), and microporous PP membranes. It is seen that the cell containing PP membrane shows the highest interfacial resistance of 460 ohm·cm<sup>2</sup> due to the low porosity, poor ionic conductivity and lack of swelling ability of the separator membrane. The interfacial resistances are 290, 195, and 125 ohm·cm<sup>2</sup>, respectively, for the cells containing PMMA, PMMA/PAN (75/25), and PMMA/PAN (50/50) membranes. The reduced interfacial resistances are beneficial for realizing excellent electrochemical properties, especially C-rate performance, of Li/LiFePO<sub>4</sub> cells, which will be discussed in the following sections.



**Figure 5.** Electrochemical impedance spectra of Li/LiFePO<sub>4</sub> cells containing PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane.

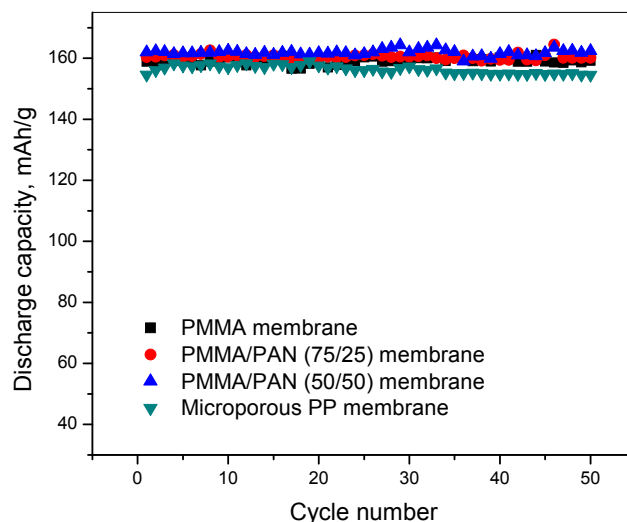
### 3.6. Charge-Discharge and Cycling Performance

In order to further examine the feasibility of using centrifugally-spun PMMA/PAN membranes as separators in rechargeable lithium-ion batteries, coin-type cells were fabricated with  $\text{LiFePO}_4$  as the cathode and Li metal as the counter electrode. The first-cycle charge-discharge curves of Li/LiFePO<sub>4</sub> cells containing PMMA, PMMA/PAN and microporous PP membranes are shown in Figure 6. Separators do not directly participate in electrode reactions. However, it is known that the separator material and structure can influence the cell performance since separators affect the ion transportation between the electrodes, which is important in regulating the cell kinetics [6,8]. As shown in Figure 6, the discharge capacity of the cell using microporous PP membrane is 154 mAh/g. The discharge capacities of cells containing PMMA, PMMA/PAN (75/25) and PMMA/PAN (50/50) membranes are 159, 160 and 162 mAh/g, respectively. In addition, the highest discharge capacity is observed when PMMA/PAN (50/50) membrane is used due to its highest ionic conductivity and lowest interfacial resistance, which are beneficial in enhancing the cell kinetics and help making the measured capacity to be closer to the theoretical value.



**Figure 6.** First-cycle charge-discharge curves of Li/LiFePO<sub>4</sub> cells containing PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane at 0.2 C.

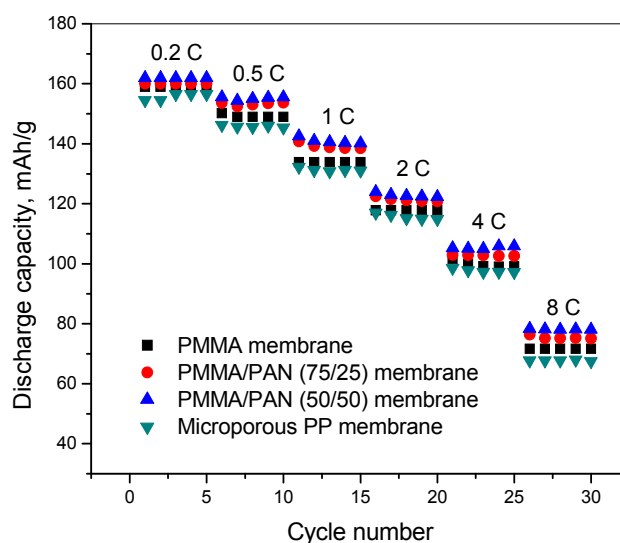
Figure 7 shows the cycling performance of Li/LiFePO<sub>4</sub> cells containing PMMA, PMMA/PAN and microporous PP membranes at 0.2 C. For all four cells, no apparent capacity loss is observed in 50 cycles at a low rate of 0.2 C.



**Figure 7.** Cycling performance of Li/LiFePO<sub>4</sub> cells containing PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane at 0.2 C.

### 3.7. C-Rate Performance

In order to evaluate the C-rate performance of LiFePO<sub>4</sub>/Li cells containing PMMA and PMMA/PAN membranes, the cells were forced to charge and discharge at high rates and the results are presented in Figure 8. The cell containing microporous PP membrane is also shown and it has a relatively low discharge capacity of around 154 mAh/g at 0.2 C, which decreases to 67 mAh/g at 8 C. The cells containing centrifugally-spun PMMA, PMMA/PAN (75/25) and PMMA/PAN (50/50) membranes have higher discharge capacities of 159, 160 and 162 mAh/g, respectively, at 0.2 C and they exhibit less capacity fading as the C-rate increases. For example, the capacities at 8 C are 71, 75 and 78 mAh/g, respectively, for the cells containing PMMA, PMMA/PAN (75/25) PMMA/PAN (50/50) membranes.



**Figure 8.** C-rate performance of Li/LiFePO<sub>4</sub> cells containing PMMA membrane, PMMA/PAN (75/25) membrane, PMMA/PAN (50/50) membrane, and microporous PP membrane.

The ionic conductivity and interfacial resistance of liquid electrolyte-soaked membrane separators affect C-rate performance [8,29,31–33]. The superior rate capabilities of the cells containing centrifugally-spun PMMA/PAN membranes could be resulted from higher ionic conductivities and better interfacial properties of these membranes after uptaking liquid electrolyte [1]. These results confirm that centrifugally-spun PMMA/PAN membranes are promising separator candidate for rechargeable Li-ion batteries.

#### 4. Conclusions

High-speed, low-cost centrifugal spinning technique was used to prepare fiber-based separator membranes for use as separators in Li-ion batteries. Porosity, ionic conductivity, electrochemical oxidation limit, interfacial resistance, cycling performance and C-rate performance were investigated and compared with a commercial microporous PP membrane. Centrifugally-spun PMMA/PAN membranes possessed higher ionic conductivity and lower interfacial resistance than microporous PP membrane. Increasing the amount of PAN in PMMA/PAN membranes promoted their ionic conductivity after uptaking liquid electrolyte. Li/LiFePO<sub>4</sub> cells containing centrifugally-spun PMMA/PAN separators showed excellent cycling and C-rate performance. Therefore, centrifugally-spun PMMA/PAN membranes are demonstrated to be promising separator candidate for high-performance Li-ion batteries.

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#### Author Contributions

Meltem Yanilmaz designed and performed the experiments and wrote the manuscript. Xiangwu Zhang directed the research and revised the manuscript.

#### Conflicts of Interest

The authors declare no conflict of interest.

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