Nano-silica-decorated Poly(m-Phenylene Isophthalamide) Separator with Enhanced Mechanical and Electrolyte Wetting Properties for Lithium-Ion Batteries

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Abstract
Heat-resistant poly(m-phenylene isophthalamide) (PMIA) has attracted considerable attention as a novel separator for application in lithium-ion batteries (LIBs); however, its mechanical strength and electrolyte wettability are not ideal. Herein, a nano-silica-decorated poly(m-phenylene isophthalamide) (PMIA@SiO2) separator was fabricated with SiO2 nanoparticles uniformly attached to the pores and pore walls of the PMIA separator. The as-prepared PMIA@SiO2 separator has good mechanical strength (a 16% improvement compared with pristine PMIA) and wettability toward the electrolyte (the contact angle decreases from 34.0° to 23.1°). The PMIA@SiO2 separator also had a high ionic conductivity (0.75 mS/cm) and low interfacial electric resistance (75 Ω). The assembled LiCoO2/PMIA@SiO2-liquid electrolyte/Li cell displays good cycle performance with a capacity retention of 88.1% after 50 cycles. Furthermore, the cycling performance and rate capacity rarely changed after high-temperature treatment. Therefore, the nano-silica-decorated PMIA separator is a potential candidate for application in LIBs with high safety.

Keywords Li-ion batteries · PMIA@SiO2 Separator · Mechanical strength · Electrolyte wetting

Introduction
Lithium-ion batteries (LIBs) are widely used in portable electronic devices and electric vehicles [1, 2]. The separator is an indispensable component of the LIB system that can impede the short circuit between positive and negative electrodes to guarantee the safety of batteries [3]. Most separators in LIBs are polyolefin owing to their good chemical stability and robust mechanical strength [4]. Nevertheless, there are limitations in their use in LIBs due to inferior thermal stability, poor wettability, and low porosity [5]. Therefore, many studies have used inorganic materials (Al2O3) [6, 7] and high heat-resistant polymers [8–10] to replace polyolefin separators. Wang et al. [11] fabricated a paper-supported inorganic composite separator with high thermal stability, and the resulting battery exhibited good cyclic and rate performances. Kang et al. [12] manufactured microporous poly(m-phenylene isophthalamide) (PMIA) with high thermal stability and excellent flame resistance properties via a conventional, non-solvent-induced phase separation method.

PMIA is a widely used high-temperature-resistant material possessing extremely high heat resistance (up to 400 °C), excellent self-extinguishment, and high chemical corrosion resistance [13–15], and has drawn considerable attention as a novel separator for application in LIBs [16, 17]. PMIA separators currently used for LIBs are typically prepared by the electrospinning method and phase inversion [4, 18, 19].

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s12209-020-00256-6) contains supplementary material, which is available to authorized users.

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The separator prepared by electrospinning has many advantages, such as a large number of interconnected holes and a high specific surface area [20, 21]. Nevertheless, the phase inversion method is more suitable given the facility of the process and scalability.

The mechanical strength and wettability of the separator toward electrolytes are essential factors in LIBs, which can influence the internal resistance and ionic conductivity, consequently affecting the safety and cycle performance of the battery. However, the as-obtained separator shows inferior performance in LIB applications because of inherent drawbacks of the PMIA separator toward the electrolyte, including low mechanical strength and poor wettability [4, 16]. To overcome the above barriers, previous studies that modified separators with nanoparticles [10, 22, 23], such as SiO₂ [24], Al₂O₃ [25], and polyhedral oligomeric silsesquioxane [4, 26], were used to improve the mechanical strength, electrolyte wettability, and corresponding cell performance. Among them, SiO₂ nanoparticles have a high concentration of hydroxyl groups on their surface, which facilitates the fast absorption of large amounts of liquid electrolytes and efficiently reduces the interfacial resistance between separators and electrodes [27, 28]. Moreover, the preparation process is mild and the particle size is adjustable. Wang et al. [29] fabricated a polyimide (PI) nanofiber separator embedded with SiO₂ nanoparticles and the separator exhibited excellent electrolyte wettability. Therefore, the performance of PMIA separators in LIBs could be enhanced by decorating with SiO₂ nanoparticles. However, nano-silica nanoparticles, which possess a high surface energy and easily aggregate into large grains, are difficult to uniformly disperse in the separator [30–32], leading to interface defects and thus a decrease in the mechanical strength. Moreover, most of the SiO₂ nanoparticles decorate the surface of the separator, while very few studies report the SiO₂ nanoparticles have decorated both the pore wall and surface to improve the mechanical strength and electrolyte wettability of a separator.

In this study, a PMIA separator with uniformly decorated SiO₂ nanoparticles (abbreviated as PMIA@SiO₂) was prepared for LIBs. Pristine PMIA was fabricated by a facile phase inversion method and then homogeneously decorated with SiO₂ nanoparticles using Tween-80 as the dispersion auxiliary. Importantly, the decorating process is binder-free. In addition, the mechanical, electrolyte wetting properties, and corresponding batteries performance of the PMIA@SiO₂ separator were compared with those of the pristine PMIA separator, and the application of the PMIA@SiO₂ separator in LIBs was evaluated.

**Experimental**

**Materials**

PMIA solution (19.5 wt%) was purchased from Yantai Tayho Advanced Materials Co., Ltd., China, and used as received. Lithium bromide (LiBr) (purity > 99%, Sigma-Aldrich (Shanghai) Trading Co., Ltd), ethyl orthosilicate (TEOS), Tween-80 (purity > 98%, Aldrich), ethanol, propanetriol, ammonium hydroxide, and N,N-dimethylacetamide (DMAc) were supplied by Tianjin Bo Hua Chemical Industry Group Co., Ltd, China. A 1.0 mol/L LiPF₆ liquid electrolyte in ethylene carbonate (EC)/dimethyl carbonate (DC)/ethyl methyl carbonate (1:1:1 mass ratio) was provided by Tianjin Jin Niu Power Supply Material Co., Ltd, China. A commercial polypropylene (PP) separator was supplied by Blaze Co., Ltd, Japan.

A LiCoO₂ cathode (loading amount: 128 g/cm²), natural graphite anode (loading amount: 120 g/m²), and lithium metal sheet materials were purchased from Hefei Kejing Material Technology Co., Ltd., China.

**Preparation of the PMIA Separator**

Figure S1 shows the schematic for the preparation of the PMIA separator. Desired amounts of pore-making agents (3 wt% deionized water, 1 wt% LiBr, 4.8 wt% glycerol, and 8.5 wt% DMAc) were slowly added to the PMIA solution (19.5 wt%), and the solution was mechanically stirred at 25 °C to obtain a uniform casting solution. This solution was cast on a release film with an 80-μm casting knife and immediately immersed in sequential coagulation baths. After solidification, the porous separator was washed with a mixture of deionized water and ethanol (7:3 volume ratio) for 12 h to remove the residual inorganic salts (such as LiBr) and solvent.
Preparation of the PMIA@SiO₂ Separator

The schematic for the preparation of the PMIA@SiO₂ separator is shown in Fig. 1. The as-prepared PMIA separator was soaked and stirred in a mixture of Tween-80 and water with mass ratio of 1:100 for 1 h. After that, it was washed with ethanol and deionized water for three times to remove unstable residues attached and then dried in a vacuum oven at 80 °C for 30 min to obtain the PMIA@Tween separator. The PMIA@Tween and PMIA separators were soaked and stirred in a mixture of ethanol, TEOS, ammonium hydroxide and water with mass ratio of 80:1:1:3 for 2 h with stirring to obtain PMIA@SiO₂ and PMIA@SiO₂-B separators, respectively. Then, all of the separators were immersed in ethanol and sonicated for 5 min to remove unstable residues attached and then dried in a vacuum oven at 80 °C for 30–1000 °C under N₂ at 10 °C/min. The ionic conductivity (δ) was computed as follows:

$$\delta = \frac{d}{R_b \times A}$$  (3)

where $R_b$, $d$ and $A$ are the bulk impedance (ohm), thickness (cm) and effective area (cm²), respectively. $R_b$ was obtained by an electrochemical work station system (Parstat 2273, USA) with the assembly of stainless steel (SS)/separator-liquid electrolyte/SS. Interfacial resistance ($R_{int}$) was obtained by Parstat 2273 with the assembly of the lithium/separatorelectronol/tweezer in alternating current (AC) impedance mode. The cycling performances and rate ability were tested with a LiCoO₂ cathode and lithium tablet anode, respectively. Assembled coin batteries were cycled on a cell testing system (Land CT2001A, China) under 2.5 and 4.2 V at room temperature and various discharge rates from 0.2 to 2.0 °C to test the rate capability. The cycling tests of the LIBs were galvanostatic and conducted at a discharge rate of 0.2 °C.

Characterization

The Fourier transform infrared (FTIR) (Equinox 55, Bruker, Germany) spectra of the separators were recorded using the attenuated total reflectance (ATR) model with a resolution of 4 cm⁻¹. The surface and cross-sectional morphologies of the relevant separators were characterized using field-emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan) equipped with an energy-dispersive spectrometer. The surface chemical composition of the separators was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab, USA) with Al Kα excitation radiation ($hν = 1486.6$ eV). The contact angle of the separator was measured through contact angle analysis (DSA255, Kruss, Germany). The size and morphology of the silica nanoparticles were observed by transmission electron microscopy (TEM). The SiO₂ nanoparticles were dispersed in ethanol and dried on a carbon-coated copper grid. The mechanical properties of the separators (10 mm × 50 mm) were tested using XD-121A (Shanghai Xinrena Instrument Co., Ltd, China) at a stretching speed of 1 mm/min. The percentage of uptake was calculated by soaking the separators into a liquid electrolyte (1 mol/L LiPF₆ in EC:DC:DMC = 1:1:1 mass ratio) using Eq. (1):

$$U(\%) = \frac{m_i - m_0}{m_0} \times 100\%$$  (1)

where $m_0$ and $m_i$ are the mass of the dry separators and separators soaked in the electrolyte solution, respectively. The porosity ($P$) of the separators in percentage was measured by weighing and then calculated using Eq. (2):

$$P(\%) = \frac{m_s - m_d}{\rho \times V} \times 100\%$$  (2)

where $m_s$ and $m_d$ are the mass of the separators after and before impregnation with 1-butanol, respectively, and $\rho$ and $V$ are the density of 1-butanol and the volume of the separators, respectively. The thermal shrinkage of the separators was mitigated without Tween-80 as the auxiliary, as shown in Fig. 2c, d and Fig. S7. Alternatively, SiO₂ nanoparticles homogeneously attached to the pore and surface of the porous separators when Tween-80 was used (Fig. 2e, f) and the SiO₂ nanoparticle size was approximately 35 nm (Fig. S2). Tween-80

Results and Discussion

Morphology

Figure 2 shows the SEM images of the pristine PMIA and PMIA@SiO₂ separators. As shown in Fig. 2a, b, the pristine PMIA separator shows typically well-proportioned and a highly interconnected sponge-like cross-sectional structure that facilitates the rapid migration of lithium ions [33]. Additionally, the interconnected and tortuous pore structure can effectively prevent the penetration of lithium dendrites, which is favorable for avoiding an internal short circuit and mitigating self-discharge. After the decoration of SiO₂ nanoparticles on the separator, the SiO₂ nanoparticles agglomerated without Tween-80 as the auxiliary, as shown in Fig. 2c, d and Fig. S7. Alternatively, SiO₂ nanoparticles homogeneously attached to the pore and surface of the porous separators when Tween-80 was used (Fig. 2e, f) and the SiO₂ nanoparticle size was approximately 35 nm (Fig. S2). Tween-80
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has good wettability for polar PMIA, which may cause Tween-80 to be uniformly adsorbed on the PMIA separator. Therefore, the large number of hydroxyl functional groups of Tween-80 assists in the uniform decoration of silica on the PMIA separator via the hydrogen bonding interaction [30]. Alternatively, Tween-80 has a long main chain and bulk side units that can generate strong steric repulsion to prevent agglomeration. Elemental mapping images (Fig. S3) show the distribution of oxygen and silicon in the PMIA@SiO₂ separator, which further proves the uniform decoration of silica nanoparticles on the PMIA separator.

**Chemical Composition**

XPS and FTIR (Fig. 3) were conducted to determine the composition of the PMIA@SiO₂ products. Figure 3a represents the XPS of the PMIA and PMIA@SiO₂ separators. The binding energies recorded at 104.49, 154.86, 284.63, 400.81, and 531.34 eV can be assigned to Si 2p, Si 2s, C 1s, N 1s, and O 1s, respectively, confirming the successful decoration of SiO₂ on the PMIA separator. Furthermore, Fig. 3b, d shows the specific O1s spectra of PMIA and PMIA@SiO₂. In Fig. 3d, the spectra deconstruct into three peaks that are centered at 532.3, 531.1, and 531.4 eV, corresponding to the C–O (carboxyl end groups of PMIA), C=O (amide groups), and Si–O, respectively [34–36]. The FTIR spectra of the PMIA and PMIA@SiO₂ separators are shown in Fig. 3c. Compared with the pristine PMIA separator, the new absorption peak at 1105 cm⁻¹ of the PMIA@SiO₂ separator is assigned to the internal asymmetric stretching vibration of Si–O–Si [37], unambiguously ensuring the successful decoration of SiO₂ nanoparticles on the PMIA separator.

**Mechanical Properties**

The mechanical properties of battery separators are primary factors contributing to the device safety of LIBs. The mechanical properties of the PMIA and PMIA@SiO₂ separators are shown in Fig. 4. The decoration of SiO₂ nanoparticles remarkably increased the elongation at break and tensile
strength. Specifically, the tensile strain increased by 30% and the maximum mechanical strength improved by 16% compared with pristine PMIA, thus suggesting the robustness of the PMIA@SiO2 separator in LIBs. According to the crazing effect, the main reason for the enhancement of mechanical strength is that the external force under attack is mainly applied to attach the SiO2 nanoparticles rather than the polymer chain [38]. The excellent strength of the PMIA@SiO2 separator can remarkably repress the crack-induced short circuit and restrain the penetration injury of lithium dendrites during the repeated charge–discharge process.

Thermal Stability

Thermal shrinkage of separators is an important property associated with battery electrochemical properties and safety characteristics. A superior heat-resistant separator can hinder an internal electrical short circuit and thus improve safety, especially when the batteries are used at elevated temperatures or subjected to high charge–discharge rates. Figure 5a shows the heat shrinkage testing results of PP, pure PMIA, and PMIA@SiO2 separators. The PP separator showed an obvious shrinkage after treatment at 160 °C for 1 h, whereas the surface of the PMIA and PMIA@SiO2 separators exerts negligible shrinkage even at 240 °C, proving that PMIA and PMIA@SiO2 possess a high thermal stability. Figure 5b shows the thermal stability of the separator under nitrogen atmosphere. In the TGA curve, the first mass loss spans from room temperature to 100 °C, which can be ascribed to the release of H2O adsorbed by the separator. The second mass loss at around 175 °C is caused by solvent evaporation (such as DMAc). In the third stage around 400 °C, all separators show a distinct mass loss, which might be due to the breakdown of the polymer backbone [39]. From 240 to 400 °C, the mass loss rates of the PMIA and PMIA@SiO2 separators are 3.31% and 0.47%, respectively. The difference in mass loss may be due to the SiO2 nanoparticles that hinder the migration of the PMIA chains, which increases the energy to trigger decomposition [24]. When the temperature increased from 400 to 1000 °C, the curve declined gently until a steady stage was reached, implying complete decomposition of the organic species and solvent in the separators and only the inorganic species (SiO2 and coke powder) remained. Therefore, the difference between the residuals of PMIA and PMIA@SiO2 at 1000 °C is the content of SiO2, which is 4.24%. The above results confirm that the PMIA@SiO2 separator has outstanding

Fig. 3 XPS spectra of a full-range scan of the PMIA and PMIA@SiO2 separators: a survey spectrum, O1s peak of b PMIA, and d PMIA@SiO2. e FTIR spectra of the PMIA and PMIA@SiO2 separators

Fig. 4 Stress–strain curves of PMIA and PMIA@SiO2
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Thermal stability, which can effectively prevent short circuits induced by the dimensional reduction of separators.

**Wettability and Liquid Electrolyte Uptake**

The wettability of separators in the electrolyte solution was evaluated, and the results are shown in Fig. 6. The pristine PMIA separator shows an electrolyte contact angle of 34.0°, indicating weak affinity for liquid electrolytes. After the decoration of SiO₂ nanoparticles, the affinity between the PMIA@SiO₂ separators and electrolyte increases, as evidenced by the contact angle (23.1°) of the PMIA@SiO₂ separator, which can accelerate electrolyte diffusion [40].

The electrolyte uptake and porosity data of the separators are summarized in Table 1. The liquid electrolyte uptake of the PMIA@SiO₂ separator increases from 149 to 208% compared with that of the pristine PMIA separator for the following reasons. The addition of SiO₂ can increase the surface roughness of the PMIA@SiO₂ separator, which improves the absorption of the electrolyte. Alternatively, SiO₂ nanoparticles with high surface areas increase the liquid electrolytes absorption of separator [41]. The pore size distribution of the PMIA and PMIA@SiO₂ separators was obtained by mercury intrusion porosimetry (Fig. S4). The majority of the pore sizes was between 0.8 and 1.0 μm, which benefits to preventing the penetration of lithium dendrites and electrode component particles [42].

**Electrochemical Properties**

The ionic conductivity of the separator is a key parameter determining the electrochemical performance of LIBs, which is mainly affected by two factors: (1) the high liquid electrolyte uptake, which increases the ionophores of the separator and (2) the interconnected porous structure of the separator, which facilitates lithium-ion migration. As shown in the electrochemical impedance spectroscopy (EIS) spectra in Fig. 7a, the bulk resistances ($R_b$) of the PMIA and PMIA@SiO₂ separators are 2.7 and 1.9 Ω, respectively. The calculated ionic conductivity follows the sequence of PMIA@SiO₂ separator (0.75 mS/cm) > PMIA separator (0.52 mS/cm). Given its high porosity and electrolyte uptake, the PMIA@SiO₂ separator could absorb more electrolytes, which help the fluent flow of Li ions through the pore channels in the PMIA@SiO₂ separator.

Interfacial resistance is another key parameter determining the electrochemical performance of LIBs. The interfacial resistance of the lithium/separator-liquid electrolyte/lithium coin cells is shown in Fig. 7c. The average initial interface resistance of LIBs assembled with the PMIA@SiO₂ separator is 75 Ω, which is lower than that of the LIBs assembled with the pristine PMIA separator (100 Ω). It shows that the PMIA@SiO₂ separator allows easy passage of the charge carriers. One reason is that the PMIA@SiO₂ separator exhibits electrolyte wettability and enhances electrolyte uptake (Table 1). Another reason is that the Si–O units exposed to the PMIA@SiO₂ separator can act as Lewis acid sites to capture electrolyte anions, thus inhibiting the oxidative decomposition of lithium salt anions, which can
The $I-V$ curves of the separators are shown in Fig. S5. The current of the PMIA and PMIA@SiO$_2$ separators abruptly increased at approximately 4.9 V versus Li$^+/\text{Li}$, owing to the electrochemical decomposition of electrolyte (LiPF$_6$) at this potential, and also implying that 4.9 V is the electrochemical window of cells. However, a working potential between 1.8 and 3.5 V is actually used for LIBs [44, 45], indicating that the PMIA and PMIA@SiO$_2$ separators have a good potential for application in LIBs.

Coin cells were constructed using a LiCoO$_2$ cathode, Li metal anode, and various separators to investigate the application of the PMIA@SiO$_2$ separator in LIBs. Figure 7c shows the charge–discharge measurements at different current densities (0.2–2 °C) of coin cells with different separators. The coin cells with the PMIA@SiO$_2$ separator have a higher discharge capacity than the pristine PMIA separator, which is ascribed to the low interfacial resistance between the electrodes and PMIA@SiO$_2$ separator as well as the high ionic conductivity. Figure 7d shows the cycling stability of the coin cells with the pristine PMIA and PMIA@SiO$_2$ separators through the galvanostatic charge–discharge test after 50 cycles at 0.2 C. The cell with the PMIA@SiO$_2$ separator shows the highest discharge capacity of 142.1 mAh/g (Fig. S6) after 50 cycles with a capacity retention of 88.1%. This result clearly indicates that the LIBs with the PMIA@SiO$_2$ separator have better cycle stability than the pristine PMIA separator, which can be attributed to the higher ionic conductivity and lower interfacial resistance for the former than the latter. The PMIA and PMIA@SiO$_2$ separators were annealed at 240 °C prior to assembly to verify the stability of batteries assembled with these separators. The LiCoO$_2$/Li cell using the separator with high-temperature treatment (240 °C) shows better performance than the separator with treatment less than 80 °C, which may be attributed to the removing of trace amounts of moisture and residual solvent in the separator that has been heat treated at high temperature [46]. Therefore, the PMIA@SiO$_2$ composite separator is a potential candidate for LIBs with a high-safety requirement.

**Conclusion**

In summary, a nano-silica-decorated PMIA separator with good mechanical strength (improved by 16% compared with pristine PMIA) and wettability toward the electrolyte was successfully prepared. The decorating process is binder-free, and SiO$_2$ nanoparticles uniformly decorated the surfaces and internal pore walls of the porous separators, which were helpful to improve the mechanical strength and wettability of the separator. The as-prepared PMIA@SiO$_2$ separator showed high ionic conductivity (0.75 mS/cm) as well as low interfacial impedance, which were crucial for improving the cycling stability of LIBs. Furthermore, the LIBs assembled with the PMIA@SiO$_2$ separator exerted a capacity retention of 88.1% after 50 cycles. In addition, the PMIA@SiO$_2$ separator retains good performance in LIBs even after a high-temperature treatment. Therefore, the nano-silica-decorated PMIA separator is a potential candidate for application in LIBs.
Acknowledgements This study was supported by National Science and Technology Major Project (No. 2016ZX02025-004-006) and Science and Technology Project of China National Offshore Oil Corporation (No. CNOOC-KJ 135 ZDXM 35 TJY 009-2017).

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