



# A gel polymer electrolyte based on Polyacrylonitrile/organic montmorillonite membrane exhibiting dense structure for lithium ion battery

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## ABSTRACT

Polyacrylonitrile (PAN)/organic montmorillonite (OMMT) membranes served as a host which is swelled using a liquid electrolyte of 1.0 M LiPF<sub>6</sub> in carbonate solvent for gel polymer electrolyte have been fabricated by non-solvent induced phase separation (NIPS) method. The OMMT fillers have affected the morphology, thermal stability, electrolyte uptake, ionic conductivity and electrochemical properties of PAN/OMMT membranes in different ways. The PAN/OMMT membrane exhibits high liquid uptake (375.5%), superior dimensional stability under 150 °C for 15 min and superior electrochemical stability up to 4.62 V. Moreover, the gel polymer electrolyte based on PAN/OMMT membrane not only possesses lower polarization and interfacial resistance, but also effectively suppresses the formation of Li dendrites as reflected in the surface morphology of lithium anode after cycling test. The application of natural montmorillonite has been demonstrated by a coin cell using Li metal as counter electrode at 1 C, resulting in the high capacity of 141 mAh g<sup>-1</sup> after 100 cycles and high capacity retention of 95.9%. The possibility of PAN/OMMT membrane applied for the sustainable safety lithium ion battery can be realized.

## 1. Introduction

In a broad sense, the battery separator was defined as the separation between the positive and negative electrode to prevent the internal short circuit of the battery, and provide a channel for lithium ion transporting [1]. The separator directly affects the interface structure [2], internal resistance [3,4], battery capacity [3,5–11], cycle characteristics [12] and safety performance. Microporous polyolefin separator due to the advantages of good chemical stability and high mechanical strength has obtained the most commonly-used separator in Li-ion batteries. However, the low porosity, poor thermal stability and poor wettability with the carbonate electrolyte motivate researchers to reconsider the best candidate for lithium-ion battery [6,13]. These weaknesses can affect the internal resistance of the cell, cycle performance, causing the liquid leakage and especially the safety. Generally, the electrolyte is mainly divided into three types including liquid electrolyte, gel polymer electrolyte [14] and solid polymer electrolyte [7,15], wherein the liquid electrolyte is the most widely used one for its good and stable electrochemical performance. In 1972, solid polymer electrolyte based on polyoxyethylene and metal salt composite was proposed by Fenton [16]. Poly(ethylene oxide) (PEO) is a well-known

polymer matrix for solid polymer electrolyte (SPE) since the highly flexible EO (ethylene oxide) segments in amorphous phase could provide channels for lithium ion transport [17]. However, these solid electrolytes deliver a low room temperature ionic conductivity (10<sup>-8</sup>–10<sup>-7</sup> S cm<sup>-1</sup> only) which is not qualified for practical application. Cui et al. reported that a high ionic conductivity (2.5 × 10<sup>-5</sup> S cm<sup>-1</sup>) multilayer system by packing polyethylene glycol (PEG)-α-cyclodextrin (α-CD) complex and poly(acrylic acid) (PAA) via hydrogen-bonding is designed and investigated [18].

To eliminate the drawbacks between liquid electrolytes and solid polymer electrolytes, gel polymer electrolytes (GPEs) have been proposed for rechargeable lithium batteries. The GPEs used in Lithium ion batteries (LIBs) contain various functional polymer segments, which include poly(methyl methacrylate) (PMMA) [19,20], poly(acrylonitrile) (PAN) [3,6,9,21–24], poly(vinylidene fluoride) (PVDF) [25,26], poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) [27,28] and poly(vinyl alcohol) (PVA) [23]. These plasticized polymer electrolytes possess a room temperature ionic conductivity of 10<sup>-3</sup> S cm<sup>-1</sup>, a good affinity with electrodes and effective encapsulation of organic solvents. Among them, PAN was chosen in this paper because of its excellent processability, flame resistance and high uptake of the electrolyte

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solution which may result in swelling or gelation of polymer rather than dissolution [29]. More recently, Won-Kyung Shin [14] reported a cross-linked PAN membrane which was prepared and applied to lithium-ion polymer cells as a safer and more reliable electrolyte, resulting in a high ionic conductivity and favorable interfacial characteristics of composite gel polymer electrolyte. Inorganic/organic fillers, such as SiO<sub>2</sub> [25], TiO<sub>2</sub> [30], Al<sub>2</sub>O<sub>3</sub> [6,31] and HDPE [28], were introduced into polymers to enhance the thermal stability and the poor mechanical strength which is an inherent defect after swelling in organic solvents. Among inorganic fillers, montmorillonite (MMT) is a well-known layered silicate, in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets with individual layers [21]. The MMT presents a cationic exchange capacity due to the substitution of Mg<sup>2+</sup> for Al<sup>3+</sup> induces a negative charge. The thermal stability and flame retardancy of polyurethane resin can be significantly improved by functionalized MMTs with intumescent flame retardant [32]. Besides, Sliman has reported that incorporating Na-MMT into PAN composite nanofibers induces an increase in their thermal stability and mechanical strength [21]. Hence, the hydrophobic MMT [33–36], good affinity in polymer and enhanced thermal stability and ionic conductivity in PAN based polymer electrolyte, was prepared by ion exchange with hexadecyl trimethyl ammonium bromide (HTAB) [33].

In this paper, PAN/organic montmorillonite (OMMT) composite membranes were prepared by non-solvent induced phase separation (NIPS) [37] method. The prepared PAN/OMMT membranes have been applied into half-cells (LiCoO<sub>2</sub> vs Li) and cycle performances (charge/discharge = 1C/1C), ionic conductivity, interfacial stability and dimensional stability under extreme temperature were evaluated by employing this membrane. Especially, the impact of dense structure with OMMT fillers enhanced on decreasing the risk of short circuits and restraining the growth of lithium dendrite were investigated.

## 2. Experimental

### 2.1. Preparation of PAN/OMMT membrane

The preparation of organic MMT was based on cationic exchange capacity, 2 g commercially available MMT powder (LAPONITE S482, Daiquan Tech. Co. Ltd., specific area: 240 m<sup>2</sup> g<sup>-1</sup>) was dispersed in deionized water (40 ml) under 50 °C for an hour, and 0.8 g hexadecyl trimethyl ammonium bromide (HTAB, [C<sub>16</sub>H<sub>19</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> Br<sup>-</sup>, Aladdin, ≥ 99.0%) was dissolved in boiling deionized water (10 ml) until completely dissolved, then HTAB solution was gradually added to MMT solution with vigorous stirring. The cationic exchange lasted for 6 h, and then the mixture solution was washed with deionized water several times until Br<sup>-</sup> was completely removed (tested by AgNO<sub>3</sub>). Finally, the precipitation (OMMT) was put in a vacuum drying oven for 24 h at 90 °C and grinded for further use.

The prepared OMMT, 13 wt% polyacrylonitrile (PAN, Sigma-Aldrich, M<sub>w</sub> = 150,000 g mol<sup>-1</sup>) and 2 wt% polyvinyl pyrrolidone (PVP, Aladdin, M<sub>w</sub> = 58,000 g mol<sup>-1</sup>) were dissolved in N, N-Dimethylacetamide (DMAc, Aladdin, ≥ 99.0%). The weight ratios of OMMT/PAN (wt%/wt%) in the composite membranes under investigation were 0:100, 5:95, 10:90, 15:85 and 20:80, respectively. The mixture was stirred in oil bath for 24 h at 70 °C, and then placed the solution in the shade for 24 h to eliminate the tiny bubbles after stirring. The resulting polymer solution was casted on glass plate by using a doctor blade, the wet membrane was left in air for 15 s at room temperature and then immersed into mixing coagulation bath [28] (DMAc/deionized water = 3/20, V/V) for 60 s before immersing into deionized water to obtain the polymer membrane. The resulting membranes (thickness: 50–70 μm) were further immersed in deionized water to remove residual DMAc and dried in vacuum oven at 70 °C for 5 h and well stored before use. The PAN membranes without OMMT were also investigated for comparison.

### 2.2. Electrode preparation and cell assembly

A cathode slurry comprising 80 wt% LiCoO<sub>2</sub> (Hunan Shanshan Battery Materials Co. Ltd. China), 10 wt% PVDF (Aladdin, M<sub>w</sub> = 150,000 g mol<sup>-1</sup>), 10 wt% carbon black (Super P, Timcal) and N-methyl-1-pyrrolidone (NMP, Aldrich) were casted on aluminum foil by using a doctor blade and dried at 60 °C for 12 h. A lithium metal was used as counter electrode in this study. Half-cells (CR2025-type coin cell) were assembled by sandwiching the prepared membranes between LiCoO<sub>2</sub> cathode (mass loading ranging from 1.88 to 2 mg cm<sup>-2</sup>) and lithium metal within an argon filled glove box (Universal 2440/750) with a low moisture level (< 1 ppm). The liquid electrolyte was 1.0 M LiPF<sub>6</sub>-ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, v/v/v) (Duoduo Reagent Co. Ltd. China).

### 2.3. Measurements

The electrolyte uptake (ω, wt%) was investigated by immersing the membranes in liquid electrolyte for 2 h at 25 °C. The weighted membranes, both weighted before and after soaked in liquid electrolyte, were cut into disk with diameter of 40 mm. The electrolyte uptake value was calculated as Eq. (1):

$$\omega (\%) = \frac{W - W_0}{W_0} \times 100\% \quad (1)$$

where W and W<sub>0</sub> are the weight of membranes before and after soaked in liquid electrolyte, respectively.

The ionic conductivity (σ, S cm<sup>-1</sup>) was evaluated by AC impedance spectroscopy in a frequency ranging from 10<sup>-2</sup> Hz to 10<sup>6</sup> Hz with 5 mV of AC amplitude at 25 °C. The membranes (electrolyte soaked) were sandwiched between two stainless steels (SS, diameter = 16.2 mm) which were assembled in CR2025-type coin cells. The cell assembly was also done in the glove box with argon gas of low water content. The ionic conductivity was calculated as the Eq. (2):

$$\sigma = \frac{l}{R_b \times A} \quad (2)$$

where R<sub>b</sub> is the bulk resistance of the electrolyte and the intercept of the Z'-axis of the straight line, l and A are the thickness and area of the membranes disk, respectively.

The activation energy (E<sub>a</sub>) was calculated by Arrhenius equation (Eq. (3)):

$$\sigma = \delta_0 \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where σ is the ionic conductivity, δ<sub>0</sub> is the pre-exponential factor, E<sub>a</sub> is the activation energy, R is the gas constant and T is absolute temperature.

The surface morphologies of the pristine PAN, PAN/OMMT membrane and the lithium metals after cycled at 1 C-rate for 300 cycles were examined using a scanning electron microscope (SEM, JSM5600L, Japan).

Thermogravimetric Analysis (TGA) of the membranes was carried out by 704 F1 Phoenix. The samples were tested in an argon atmosphere at a heating rate of 5 °C min<sup>-1</sup>.

For the Fourier Transform Infrared Spectroscopy (FTIR) measurements, the spectra (400–4000 cm<sup>-1</sup>, resolution 2 cm<sup>-1</sup>) of the MMT, OMMT, PAN and PAN/OMMT samples were collected with a BIO-RAD FTS 6000 SPECTROMETER.

The half cells were assembled in an argon filled glove box and sealed in 2025-type coin cells. Galvanostatic charge/discharge cycling was performed at voltage range of 3.0–4.3 V in a Neware Battery Test System (Shenzhen Neware New Energy Tech. Co. Ltd).

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