



# Single-ion Polyelectrolyte/ Mesoporous Hollow-Silica Spheres, Composite Electrolyte Membranes for Lithium-ion Batteries



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## ABSTRACT

A single lithium-ion polyelectrolyte composite membrane was designed and prepared. It consisted of lithiated Nafion<sup>®</sup>, propylene carbonate (PC) and mesoporous hollow silica spheres (MHSi). SEM and TEM analysis illustrated that the MHSi disperse uniformly in the membrane. The thermal stability of the composite membrane was tested using TGA which showed that the decomposition temperature is as high as 400 °C. The maximum PC absorbability was 127% and caused a 23.1% volume change. The transference number of the membrane was 0.94, which is very close to unity. The MHSi and PC in the membrane synergistically contributed to the lithium-ion conductivity of  $2.29 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C. In addition, Li/LiFePO<sub>4</sub> half-cells employing the subject prepared membrane without addition of any other lithium salt demonstrated acceptable performance. This new type of polymer membrane may find acceptable application in high energy lithium-ion batteries in the near future.

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## 1. Introduction

Lithium-ion batteries (LIBs) [1–4] are one of the most popular and important battery technologies available today. To further proliferate the technology, systems must be able to deliver high energy density as well as high power density. Recently, gel polymer electrolytes (GPEs) [5–7] have received considerable attention for use in Li-ion batteries, because they are flexible, compact structures require a minimum of liquid electrolyte, which precludes electrolyte leakage. These novel electrolytes have been widely used in the commercial LIBs. GPEs are composed of a polymer matrix (e.g. polyethylene oxide, polyvinylidene fluoride and polymethylmethacrylate) which is swollen by an amorphous plasticizer, such as propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC), in which electrolyte salts (e.g. LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, etc.) are dissolved [8–13].

To date, the most conventional GPEs are dual-ion conductors similar to a liquid solution, in which both cations and anions are mobile. Thus, the Li<sup>+</sup> transference numbers in those GPEs are usually low, about 0.3–0.5 [14,15]. Low Li<sup>+</sup> transference number causes power loss in LIBs. Since the electrodes of LIBs exchange only Li<sup>+</sup> with the electrolyte, a salt concentration gradient will be established during operation which results in poor electrochemical

performance [16]. The solution to the problem of concentration polarization in LIBs is to design single lithium-ion conducting polymers that contain fixed, immobile anions [17–20]. Two methods are traditionally applied to immobilize the anions. One is to locate suitable polymers which contain sites that may preferentially interact with the anions [18]. The other approach is to covalently link anionic functional groups to the polymer chains to obtain a true single-ion conductor. Initially, a type kind of single-ion conductor was prepared by lithiating a cation-exchange polymer, e.g. the commercial available Nafion<sup>®</sup> ester (Dupont). However, the room temperature conductivity of lithiated Nafion<sup>®</sup> membranes without incorporation of an organic solvent is very poor (about  $10^{-6} \text{ S cm}^{-1}$ ) [17].

Various approaches have been tried to improve the poor ion conductivity of lithiated Nafion<sup>®</sup>. For example, Navarrini et al. synthesized a perfluorinated sulfonic ionomer containing a short lithiated side chain. The membrane was manufactured using the melt-press process. The lithium ion conductivity of this new polymer, swollen with PC, was  $6 \times 10^{-4} \text{ S cm}^{-1}$  [21]. Zhijun Cai reported using a perfluorinated sulfonic acid ion exchange a polymer with an ion exchange capacity higher than Nafion<sup>®</sup> in place of the commercial Nafion<sup>®</sup> membrane. Due to this higher ion exchange capacity, the density of Li<sup>+</sup> in the polymer matrix was increased, which resulted in an improved Li<sup>+</sup> conductivity of  $4.6 \times 10^{-4} \text{ S cm}^{-1}$  [19].

The ionic conductivity of the polymer can be improved by raising the concentration of the ions or by increasing the ionic

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mobility. The plasticizer in the gel electrolyte helps to dissociate the ionic couple, freeing the ions to move more easily in through the matrix. However, a large quantity of plasticizer in the polymer can deteriorate the film's mechanical properties. To properly function as a separator, GPEs require specific strength and dimensional parameters. It has been commonly recognized that the mechanical properties of GPEs can be enhanced greatly by addition of inorganic fillers, which results in an organic-inorganic composite gel polymer electrolyte (CGPEs) [20,22]. The commonly used fillers for this purpose are normally inexpensive, easy to obtain inorganic oxides, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> etc. The inorganic nano-filler dispersed uniformly in the gel electrolyte polymers can improve the mechanical strength of membrane, as well as the lithium ion conductivity and the stability of the interface between electrode and electrolyte [23–26].

In this reported work, a novel single-ion conducting CGPE was designed to meet the requirements of advanced lithium ion batteries. The host polymer was prepared from a commercial available Nafion<sup>®</sup> solution by tape-casting which offered excellent chemical and thermal stability. Mesoporous hollow silica spheres were uniformly dispersed into the polymer, to absorb additional plasticizer without dramatically reducing the mechanical strength of the final product. Following lithiation of the film, a single ion conductor was obtained which was then soaked in PC. The mechanical and electrochemical properties of the final product were investigated. Finally, Li/CGPE/LiFePO<sub>4</sub> cells employing the optimized membrane were assembled and the performance of these test cells was determined.

## 2. Experimental

### 2.1. Methods of Characterization

Thermal stability of the membrane was tested using a Perkin-Elmer Pyris 1 thermal gravimetric analyzer (TGA). Before TGA testing, all the samples were dried at 80 °C under vacuum for 12 hours. The heating rate was of the TGA analysis 10 K min<sup>-1</sup>. The tests were conducted under N<sub>2</sub>.

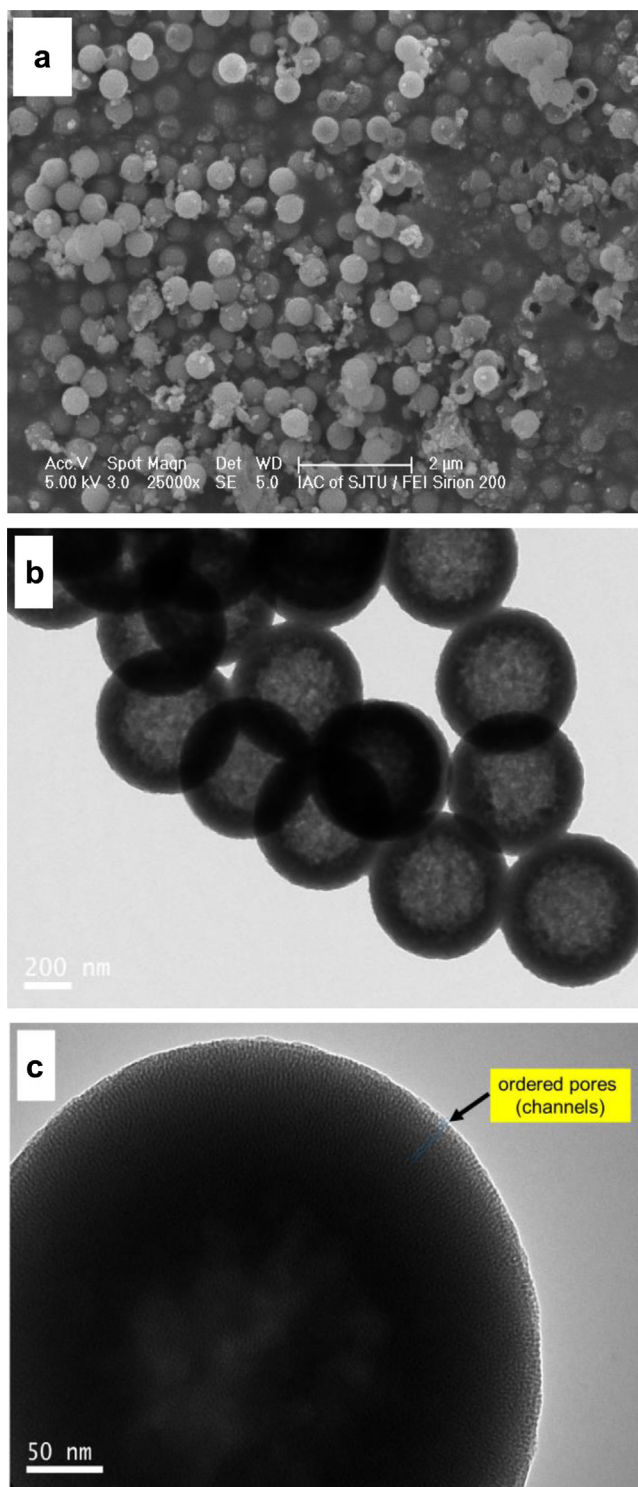
The morphology of the membranes was observed using a scanning electron microscope (SEM) (Sirion 200, FEI). The samples were coated with Au before SEM analysis.

Solvent absorbability is an important property of a gel-type polymer electrolyte membrane. In this work, propylene carbonate (PC) was used as a Li-ion solvent. Solvent absorbability  $\eta$  was calculated by:

$$\eta = \frac{W_t - W_o}{W_o} \times 100\% \quad (1)$$

Where  $W_o$  is the dry weight of the membrane without PC,  $W_t$  is the wet weight of the membrane after absorbing of PC.

The ionic conductivity of the membrane was measured using electrochemical impedance spectroscopy employing a two-electrode geometry using an SI-1260 impedance/gain-phase analyzer over the frequency range of 10<sup>-1</sup>-10<sup>6</sup> Hz (SI-1260, Solartron) at temperatures between 25 and 100 °C. For the conductivity measurements, the CGPE membrane was placed between two stainless steel (SS) electrodes to form a SS/CGPE/SS sandwich structure. Conductivities,  $\sigma$  of the samples were calculated using



**Fig. 1.** (a) SEM image of MHSi, (b) TEM image of MHSi, and (c) High magnification TEM image of MHSi.

the following equation:

$$\sigma = L/AR \quad (2)$$

where R is the measured resistance from the semi-circle response on the real axis of the complex impedance plot (Cole-Cole plot), L represents the thickness of the film, and A is the area of the membrane.

The lithium-ion transference number ( $t_{Li^+}$ ) of an ion conductor indicates the ratio of Li-ion conductivity in relation to the total

**Table 1**  
Content of MHSi in the membrane samples.

Samples	CGPE-0	CGPE-4	CGPE-6	CGPE-8	CGPE-10
Content of MHSi /wt%	0	4	6	8	10

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