



Nanocomposite electrolytes for lithium batteries with reduced flammability

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ABSTRACT

We report a family of flame-retardant electrolytes for lithium batteries based on ionic nanocomposites. The nanocomposites are synthesized in one pot by dispersing SiO₂ nanoparticles charge-balanced by both Li ions and mono-amino-terminated polyether (PEO-*b*-PPO-NH₃⁺) in an oligomeric PEO matrix. The Li⁺ and PEO-*b*-PPO-NH₃⁺ ions lead to enhanced Li⁺ transference number and compatibility with the PEO matrix, respectively. The nanocomposite electrolyte containing 40% mass fraction of silica shows a notable electrochemical stability window of more than 6 V in contact with Lithium and high Li⁺ transference number over 0.5. Rheology measurements demonstrate the tunability of the system from liquid to gel-like as the silica mass fraction percentage increases from 0 to 40% while the conductivity remains almost constant. Thermal gravimetric and microscale combustion calorimeter measurements of the nanocomposites show decreased rate of mass loss and heat release rate compared to neat electrolyte. Finally, the fire retardancy of the nanocomposites measured by directly observing the formation and sustainability of flame, when exposed to direct fire, make them promising candidates in the ever-growing quest for safe lithium batteries.

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1. Introduction

Interest in lithium batteries has been growing in the last decade due to their significance in various portable electronic devices and electric vehicles [1, 2]. In addition to the other components, the role of the electrolyte has also become critical for ensuring good battery performance. The electrolyte needs to meet a series of requirements including high ionic conductivity, high transference number of lithium ions, chemical and thermal stability, high mechanical strength and ease of processing to create high-performance batteries [3,4]. Recently, increased attention has been given to the flammability resistance of electrolytes in order to avoid any potential fire hazard in various types of accidents [5,6].

Polyethylene oxide, (PEO) is one of the most widely researched and most attractive polymer electrolytes for several classes of advanced lithium batteries [7–9]. PEO displays excellent solvation

and complexing ability towards alkali metal ions such as lithium. In recent years, substantial interest has been devoted to developing solvent-free electrolytes using neat moderate/low molar mass PEGs (poly ethylene glycol), for highly conductive gels [10–12]. However, mechanical properties, long-term stability, and low ignition temperature remain an issue.

A common strategy to improve the mechanical and electrochemical properties of polymer electrolytes is the incorporation of inorganic particles [1,10,13,14]. In several systems, the inorganic particles enhance the segmental motion of the host polymer acting as solid plasticizers thus increasing ion conduction while improving at the same time the mechanical properties of the electrolyte. However, particle dispersion in the polymer matrix is a challenging task that has prevented nanocomposites from reaching their true potential. To that end, our group has introduced *ionic* nanocomposite systems consisting of a polymeric canopy bound to a well-defined nanoparticle core by ionic interactions [15,16]. Due to the ionic interactions present, the perennial dispersion challenges associated with conventional nanocomposites void of

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specific interactions are minimized while the dynamic nature of the ionic bonds provides opportunities for adaptive/multi-responsive properties.

The incorporation of inorganic particles in several polymers can also improve thermal resistance and flame retardancy [17,18]. Kashiwagi [19] et al., for example, studied the flame retardancy of various types of silica/polyethylene oxide hybrids. They found that addition of silica leads to the formation of strong char/silica surface layers acting as thermal insulation and barrier protecting the PEO against the migration of thermal degradation products to the surface.

Building on the ionic motif Schaefer [20] et al., Liu [14] et al. and Lee [21] et al. reported a series of single-ion electrolytes based on lithium-exchanged sulfonated silica nanoparticles. In both cases, surface modification of the silica nanoparticles with sulfonated silane to endow the particles with ionic groups was required. Our group reported an alternative approach to synthesize ionic nanocomposites by exploiting the acid/base properties of bare SiO₂ particles. By reacting directly, the inherently acidic hydroxyl groups of silica nanoparticles with an end-functionalized amine-PEG (PEG-NH₂) leads to nanocomposites with an excellent dispersion of the nanoparticles.

In this paper, we integrate the need of good dispersion with high ionic conductivity/high transference number to demonstrate a new family of nanocomposite electrolytes. The nanocomposites are synthesized in one pot by dispersing SiO₂ nanoparticles charge-balanced by both Li ions and PEO-*b*-PPO-NH₃⁺ in an oligomeric PEO matrix (Fig. 1). The Li⁺ ions on the silica provide enhanced ionic conductivity and higher transference number while the short PEO-*b*-PPO-NH₃⁺ chains enhance the compatibility with the PEO matrix. In addition to the enhanced electrochemical and thermal stability, the nanocomposite electrolytes containing 40% by mass of silica show remarkable resistance to open-flame ignition.

2. Experimental¹

Materials. Silica nanoparticles (LUDOX HS30 colloidal silica, 30% mass fraction suspension in H₂O, 16–18 nm diameter), lithium hydroxide monohydrate (≥98.0%), Dowex HCR-W2 ion-exchange resin, bis(trifluoromethane)sulfonimide lithium salt (99.95% trace metals basis) and poly(ethylene glycol) methyl ether (average Mn 550) were obtained from Aldrich Chemical Company. Jeffamine[®] M-2070 polyether amine, composed of block of polypropylene oxide and polyethylene oxide oligomers (PPO-*b*-PEO-NH₂) was received from Huntsman Corporation (The Woodlands, TX). All materials were used as supplied.

Synthesis of Electrolytes. HS30 silica suspension is first diluted to 3 wt % and passed three times through a column of proton-exchanged Dowex resin to produce silica with fully protonated surface hydroxyls, (HS30)-OH. Then a stoichiometric amount of LiOH and PPO-*b*-PEO-NH₂ (in 50/50 M ratio) to fully neutralize the acid sites was added while specific amounts of PEG matrix (550 mol/g) was added in the end to create the various mass silica fractions (0, 10, 20, 25, 30 and 40%) in one pot synthesis. The amount of PPO-*b*-PEO-NH₂/LiOH was determined by first titrating a known volume of 3 wt % (HS30)-OH solution with a 1 mmol/L NaOH

solution and monitoring the pH. The suspension was stirred vigorously for about 6 h before it was frozen with liquid nitrogen and then placed in a lyophilizer to remove the water. Then, the sample was dried at 45 °C in vacuum for 48 h and placed in a glove box. Finally, bis(trifluoromethane)sulfonimide lithium salt added to the electrolytes to keep EO/Li = 50 ratio taking account the immobilized Li-ions on the silica particles surfaces especially in the case of the nanocomposite electrolytes. The final ionic electrolytes denoted hereafter as IE_X%, where X is the silica mass fraction.

Characterization. TGA and DSC measurements were obtained on a TA Instruments model Q5000 and TA Instruments model Q2000, respectively under air flow. The amount of crystalline PEO (% wt) was calculated using the following equation [22]:

$$K = \frac{\Delta H_c}{(1 - a) \cdot \Delta H_0}$$

where ΔH_c is the apparent heat of fusion per gram of the sample, a is the concentration of silica nanoparticles in wt %, and ΔH_0 is the thermodynamic heat of fusion per gram of 100% crystalline PEO [23].

Dielectric measurements were performed on a Novacontrol model N40 dielectric broadband spectrometer. The ionic conductivity was measured by AC impedance spectroscopy in the frequency range from 100 KHz to 1 Hz at temperatures between -10 °C and 80 °C [24]. For electron microscopy, the samples were diluted to 1% by mass in deionized water, and then a 5 μ L drop was placed on a copper grid and allowed to rest for a minute before most of the water was blotted away. The grid was dried completely in the air. Bright-field TEM was carried out on an FEI Tecnai T12 microscope operating at 120 kV. Rheological measurements were conducted on an Anton Paar MCR-501 rheometer equipped with a 25 mm diameter cone and plate geometry (measuring system CP25-1). Electrochemical properties were measured using a Swagelok assembly by sandwiching the electrolyte between stainless steel cells and lithium metal as a counter electrode at 25 °C on Solartron Electrochemical Impedance Spectrometer. Polypropylene (PP) separator or donut shaped Teflon ring was used to prevent any short circuit of a symmetrical coin cell battery. Transference numbers were determined at room temperature according to the polarization method proposed by Bruce and Scrosati [25,26] using a Solartron Potentiostat (with a step of 3 mV) and a Solartron Frequency Response Analyzer. The test was repeated three times and the reported value is the average with a standard deviation of ± 0.1 . The electrochemical window was measured by linear scan sweep voltammetry at a scan rate of 1 mV/s also performed at room temperature.

The flammability of the electrolytes was evaluated first by observing the formation of flame when exposed to direct fire, as described in the literature [27,28]. More specifically, we use a naphtha-type lighter with a ≈ 1 cm flame size. In the case of liquid-like electrolytes in which the use of a separator membrane is necessary, we bring the flame to a distance of 1 cm–2 cm from the sample while for the free-standing, gel-like sample, the flame comes in direct contact with the sample. Microscale combustibility experiments were carried out in a Govmark MCC-1 microscale combustion calorimeter. The specimens were first kept at 100 °C for 5 min to remove adsorbed moisture and then heated up to 600 °C at a heating rate of 1 °C/s, in a stream of nitrogen flowing at 80 cm³/min. The pyrolysis volatiles released from the thermal degradation of the sample into the nitrogen gas stream were mixed with a 20 cm³/min stream of pure oxygen prior to entering a 900 °C combustion furnace. Three samples weighing about 5 mg were tested for each system. The amount of residue is calculated by weighing the sample before and after testing.

¹ Part of this work was carried out by the National Institute of Standards and Technology (NIST), an agency of the US government and by statute is not subject to copyright in USA. The identification of any commercial product or trade name does not imply endorsement or recommendation by NIST. The policy of NIST is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document, however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements. wt% is used throughout this manuscript and is identical to mass fraction.

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