

# Polymer nanocomposites for lithium battery applications<sup>☆</sup>

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## Abstract

A series of polymer-clay nanocomposites have been synthesized, characterized, and electrochemically tested as possible candidates for polymer electrolytes in lithium ion cells. Only cations are mobile in these materials, rather than both cations and anions, leading to a higher conductivity. The nanocomposites are based on synthetic lithium hectorite (SLH) and different mass ratios of polyethylene oxide (PEO). Transparent films with excellent mechanical strength are obtained with conductivity that is comparable to more traditional polymer electrolytes made with added lithium salts.

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## 1. Introduction

Lithium ion secondary batteries are currently the best portable energy storage device for the consumer electronics market. Improved safety over conventional, fully liquid electrolytes provides a compelling rationale for use of polymer electrolytes in rechargeable lithium batteries, but these polymers often show insufficient conductivity or poor mechanical properties. The dual ion-conducting nature of most polymer electrolytes also poses problems. Investigations of transport properties indicate that cationic transference numbers are nonunity or even negative, indicating substantial transport by anionic complexes, particularly at high salt concentration. Concentration gradients caused by the mobility of both cations and anions in the electrolyte arise during cell operation, resulting in premature cell failure. This is a more severe problem than in conventional liquid electrolytes because of the lower salt diffusion coefficients and the relative immobility of the polymer hosts.

Attempts to design single-ion conductors based on poly-electrolytes with fixed negative charges on the polymer have

met with limited success; conductivities are relatively too low for practical use. Still, the ease of film fabrication, ability to withstand electrode volume changes, and low temperature operation of a well-design polymer-based system provide distinct advantages over many ceramic single-ion conductors. Further research into polymeric or composite single-ion conductors is, therefore, well-justified.

The conductivities of lithium-containing polymer-clay nanocomposites are greatly enhanced over synthetic polymer single-ion conductors because only cations are mobile in these materials. The preparation is simpler, they are self-supporting, and they generally have excellent mechanical properties.

We have prepared a series of nanocomposites containing polyethylene oxide (PEO) intercalated in the layers of synthetic lithium hectorite (SLH) clays. These clays belong to the family of smectite clay minerals. They are composed of two tetrahedral silicate layers sandwiching a central octahedral layer in a so-called 2:1 arrangement. Isomorphous substitutions in the lattice of Li(I) for Mg(II) in the octahedral layers cause an overall negative charge that is compensated by the presence of interlayer, or gallery, cations. A significant amount of interlayer water is also present and the cations are easily exchangeable. A large degree of preferential orientation in films prepared by natural occurring clays tends to occur, due to their large particle size (approximately 1  $\mu\text{m}$ ). This can lead to non-conducting planes being perpendicular to the current path and thus reduce the conductivity. To avoid this problem, we followed a method developed by Carrado et al. [1] which

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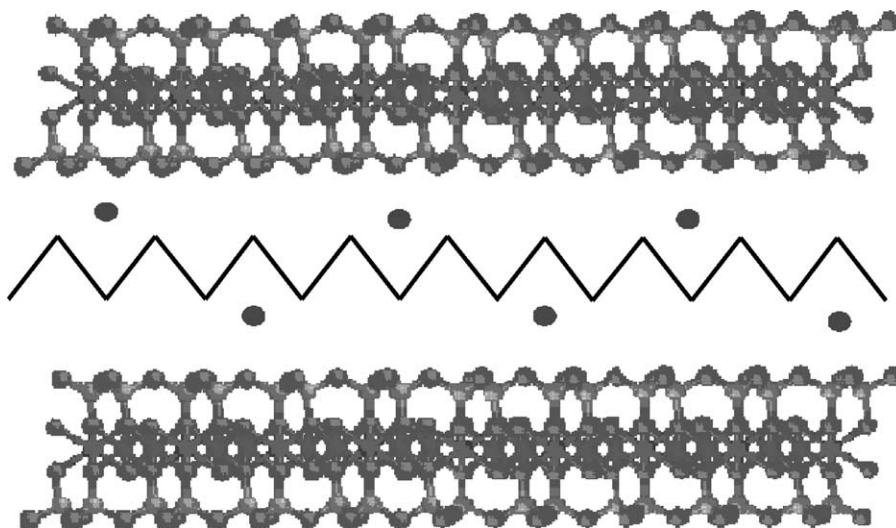


Fig. 1. Schematic representation of lithium hectorite clay. The gallery regions shows one PEO layer and exchangeable Li(I) cations.

involves direct hydrothermal synthesis and crystallization of the clay mineral, that is of smaller particle size, from a gel. Organic molecules can be either incorporated directly from the gel or by subsequent intercalation. Fig. 1 shows an idealized structure of intercalated PEO in the SLH. The circles in the gallery represent Li ions. Organic intercalants need only be water soluble, cationic or neutral, and stable to reaction conditions. Aranda and Ruiz-Hitzky [2] have found that intercalated PEO molecules between silicate galleries impede polymer crystallization, resulting in higher electrolyte conductivity compared to the system without clay.

There has been a considerable amount of work performed by Giannelis and co-workers [3–9] related to the synthesis of nanocomposites derived from PEO and montmorillonite, a naturally occurring aluminosilicate smectite clay. They use, however, a melt intercalation procedure to produce the films. Doeff and Reed have reported the formation of PEO/laponite (a commercially available synthetic hectorite) electrolytes; however their conductivity is low [10]. To the best of our knowledge, PEO:SLH nanocomposites have not been used as polymer electrolytes.

## 2. Experimental

### 2.1. Preparation of SLH, PEO addition, and film preparation

Preparation of the clay can be found in detail in [1]. In brief, precursor clay gels are of the composition:  $1.32 \text{ LiF}$ ,  $5.3 \text{ Mg(OH)}_2$ ,  $8 \text{ SiO}_2$ ,  $n \text{ H}_2\text{O}$ , to correlate with the ideal hectorite composition of  $\text{Li}_{0.66}[\text{Li}_{0.66}\text{Mg}_{5.34}\text{Si}_8\text{O}_{20}(\text{OH},\text{F})_4]$ . A typical reaction begins by suspending the LiF with stirring in water. Separately,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is dissolved in water and mixed with  $2\text{N NH}_4\text{OH}$  to crystallize fresh  $\text{Mg(OH)}_2$ . Prior to use, this brucite source must be washed several times with water to remove excess ions. It is then added wet to the LiF solution.

This slurry is stirred for 15–30 min before addition of silica sol (Iudox HS-30,  $\text{Na}^+$ -stabilized, 30%). The total volume is increased to afford a 2 wt.% solids suspension, and is stirred and refluxed for 40–48 h. Solids are isolated by centrifugation, washed, and air-dried. Colloidal suspensions containing 1 g SLH/100 ml de-ionized water were stirred for 1.5 h. The desired amount of PEO (100,000 average molecular weight) was then added, and the mixture stirred for 24 h. Mixtures contained 0.6, 0.8, 1.0, and 1.2 g of PEO per g of clay. Films were prepared by puddle-casting solutions onto Teflon-coated glass plates and air-drying. Further drying was carried out at  $120^\circ\text{C}$  under an inert atmosphere for at least 48 h.

### 2.2. Physical characterization

X-ray powder diffraction (XRD) patterns of SLH powder and the nanocomposite films were determined using a Rigaku Miniflex, with  $\text{Cu K}\alpha$  radiation and a NaI detector at a scan rate of  $0.5^\circ 2\theta \text{ min}^{-1}$ . Thermogravimetric analysis was conducted using a Xstart 6000 under nitrogen or oxygen at a rate of  $10^\circ\text{C min}^{-1}$ . Differential scanning calorimetry was carried out using a DSC-7, Perkin-Elmer. Lithiated PEO:SLH film was sealed in a DSC pan in a dry glove box under argon gas atmosphere and the sample was run at  $10^\circ\text{C min}^{-1}$  purging nitrogen gas. The ac impedance measurements as a function of temperature were obtained on films in sealed cells with lithium foil as the counter and working electrode, using a Solartron SI 1256 electrochemical interface and 1254 frequency response analyzer.

## 3. Results and discussions

Fig. 2 shows the XRD of the SLH powder. The peaks are indexed as indicated on the graph. The distance between clay sheets is given by the  $d_{001}$  reflection and corresponds to  $12.7 \text{ \AA}$ , which includes one clay lattice unit at  $9.6 \text{ \AA}$ . The

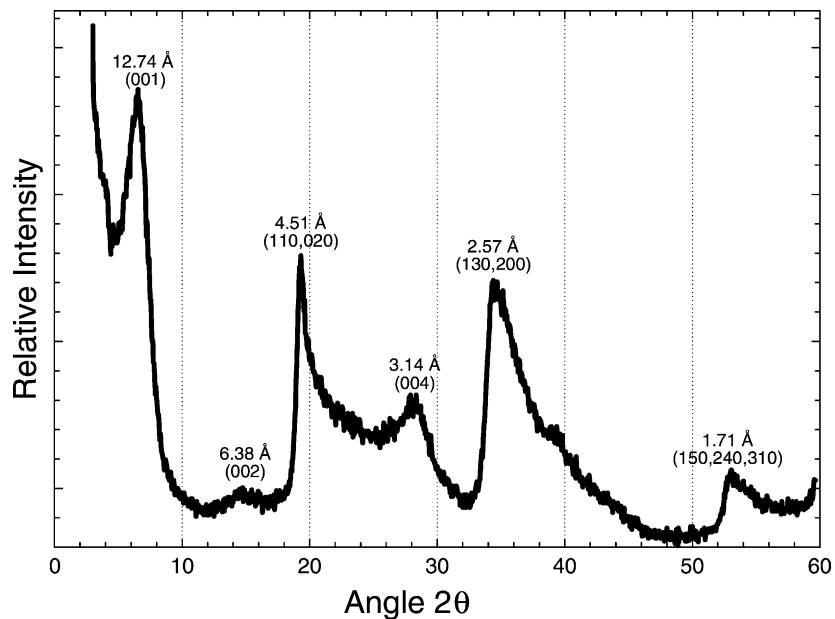


Fig. 2. X-ray powder diffraction pattern of SLH.

gallery region therefore corresponds to 3.1 Å and contains Li(I) cations and water. Because smectites are capable of swelling, this region can easily accommodate one or more layers of PEO [2].

Fig. 3 shows the characteristic DSC behavior of a nanocomposite film prepared by using 1:1 weight ratio of PEO:SLH. The sharp peak at 51.2 °C is an artifact, but the endothermic peak at 63.2 °C, corresponds to melting of crystalline regions of PEO and the amount corresponds to only 1% of polymer. The rest of the polymer is intercalated in the SLH layers. Over this temperature range, the SLH does not exhibit any thermal transitions.

Fig. 4 shows a TGA plot of the nanocomposite sample containing 1:1 nominal ratio of PEO:SLH. The film contains about 3.9% weight of water that evaporated at 81 °C. When pure clay is similarly heated, the only observed peaks are due to this gallery water loss and a dehydroxylation event at 700 °C. The organic PEO is then burned at 206.6 °C (55.5% weight as PEO) and the remaining material corresponds to the SLH. There is only one sharp peak which corresponds to PEO intercalated in the SLH layers.

A series of impedance measurements at different temperatures were obtained. As the polymer nanocomposite was heated from room temperature to 60, 80, 100, 120, and

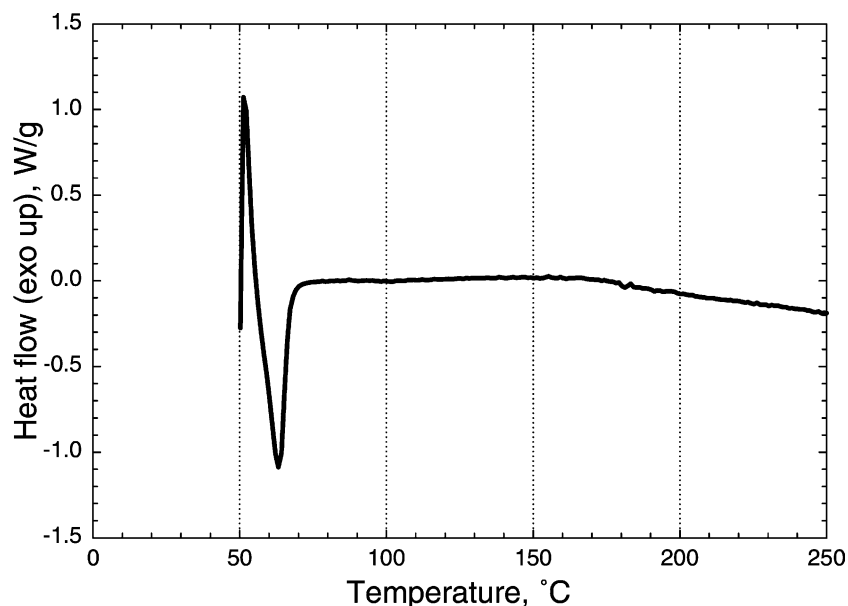


Fig. 3. DSC heating run ( $10\text{ }^{\circ}\text{C min}^{-1}$ ) for the 1:1 PEO:SLH.

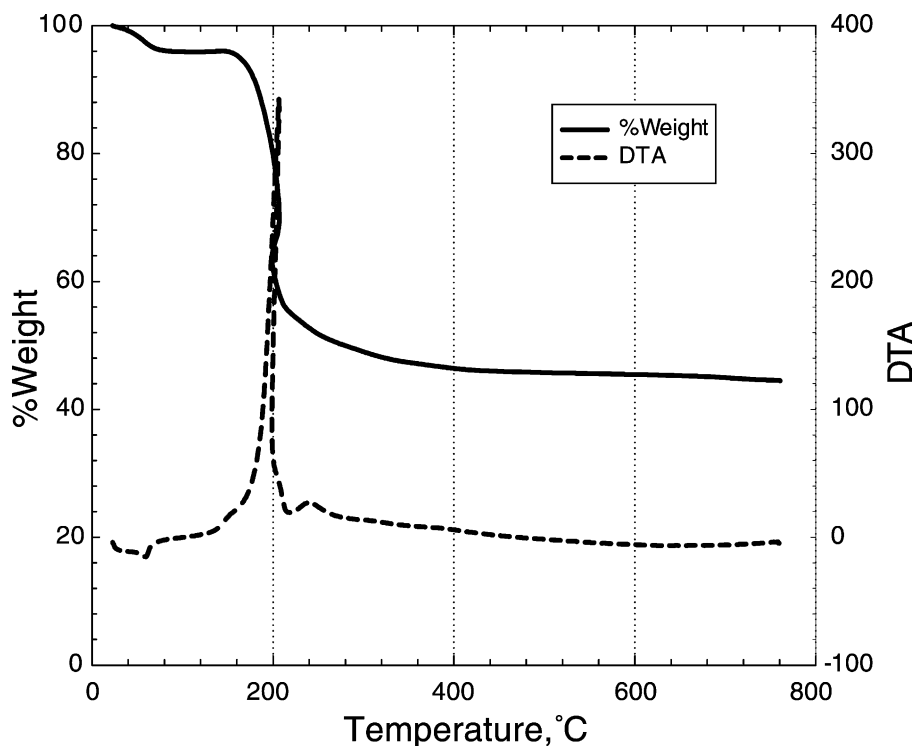


Fig. 4. TGA of a PEO:SLH polymer electrolyte. The run was conducted under oxygen flow at 5 °C min<sup>-1</sup>.

150 °C, the resistivity of the material decreases, hence, the conductivity increases. By using the relationship:

$$\sigma = \frac{l}{RA}$$

where  $\sigma$  is the conductivity,  $l$  is the thickness of the polymer film (63  $\mu\text{m}$ ),  $R$  is the resistance (in  $\Omega$ ), and  $A$  is the surface

area of the film (1.6  $\text{cm}^2$ ), the conductivity of the film (with a nominal composition PEO:SLH 1:1) can be calculated and shown in Fig. 5. The slope of the Arrhenius plot has a value of  $-0.1292 \text{ S cm}^{-1} \text{ }^\circ\text{C}$ . These values display quite high conductivities considering that no Li salt was added to the composite. Others [11] have reported similar values, but they have added a considerable amount of LiX ( $X = \text{CF}_3\text{SO}_3^-$ ,

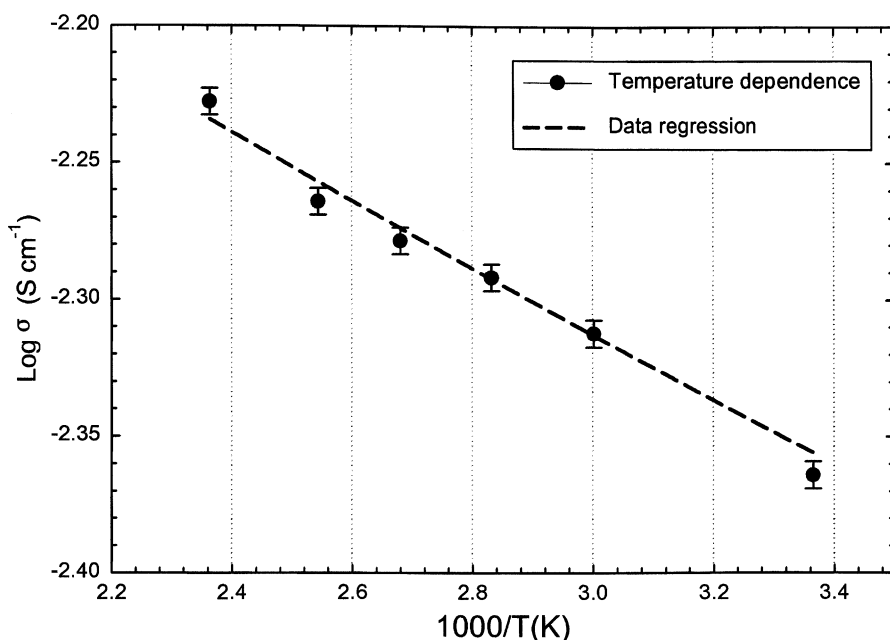


Fig. 5. Conductivity as a function of temperature of the nanocomposite with nominal composition PEO:SLH 1:1 mass ratio.

$\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) and ceramic fillers ( $\text{LiAlO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) to be able to obtain these high conductivities.

#### 4. Conclusions

Transparent films made with SLH and intercalated PEO are obtained with excellent mechanical strength and with conductivity that is comparable to more traditional polymer electrolytes made with added lithium salts. For example, the conductivity of the nanocomposite with a nominal ratio of PEO:SLH 1:1 shows a conductivity of  $4.324 \times 10^{-3} \text{ S cm}^{-1}$ , as indicated in Fig. 5. These values suggested that these materials can be good candidates as polymer electrolytes in solid state lithium cells.

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