Nanocomposite Li-conducting polymer electrolytes based on PEG400 and lithiated fluorinated iron oxide NPs

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Li-conducting polymer electrolytes are fundamental materials for the development of advanced lithium secondary batteries. In general, classical polymer electrolytes (PEs) consist of organic macromolecules (e.g., polyethers) doped with inorganic salts including $LiClO_4$, $LiPF_6$, LiTFSI, among others [1]. These PEs show good room-temperature conductivities (on the order of 10^{-5} - 10^{-6} $S\cdot cm^{-1}$), but low Li^+ transference numbers. One possibility to address this latter issue is to dope PEs with an inorganic nanofiller such as SiO_2, TiO_2 or Al_2O_3. As a result, both the conductivity and the transference numbers may be improved [2].

In this report, an advanced Li-conducting nanofiller based on a lithiated fluorinated iron oxide (LiFI) is proposed and studied. LiFI is used as a doping filler for PEG400 matrices, to obtain a group of nanocomposite PEs of formula $PEG400/[LiFI]_x$. In these latter materials, the counter-ions of Li^+ are bound to the surface of the filler nanoparticles, while a PEG400 matrix promotes the migration of Li^+ cations between polyether coordination sites. LiFI is obtained by reacting molten metallic lithium with fluorinated iron oxide nanoparticles as described elsewhere [3]. The concentration of metals in the $PEG400/[LiFI]_x$ nanocomposite PEs is determined by ICP-AES. The aim of this study is to elucidate: (a) the interactions between the LiFI nanofiller and the PEG400 matrix; and (b) the details of the ion conduction mechanism, with a particular reference to the coordination sites of the charged species and the secondary structure of the PEG400 polymer chains. These studies are carried out by vibrational spectroscopy, DSC, TGA, XRD, solid-state NMR and electrochemical methods. In addition, a detailed study of the ion conduction mechanism is carried out by broadband electrical spectroscopy (BES) in the 10^{-2} Hz - 10 MHz and -150°C to 150°C frequency and temperature ranges, respectively. Fig. 1 reports a typical tend of log(σ) *vs.* 1/T for both the pristine LiFI nanofiller and a $PEG400/[LiFI]_{0.31}$ nanocomposite PE. It is observed that the conductivities: (a) of LiFI at 25°C and 100°C are $1.1\cdot10^{-4}$ $S\cdot cm^{-1}$ and $5.09\cdot10^{-4}$ $S\cdot cm^{-1}$, respectively; (b) of $PEG400/[LiFI]_{0.31}$ at 25°C and 100°C are $3.8\cdot10^{-6}$ $S\cdot cm^{-1}$ and $1.5\cdot10^{-4}$ $S\cdot cm^{-1}$, respectively. These results witness that the obtained electrolytes are very promising materials for application in lithium secondary batteries based on lithium metal anodes.

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FIGURES

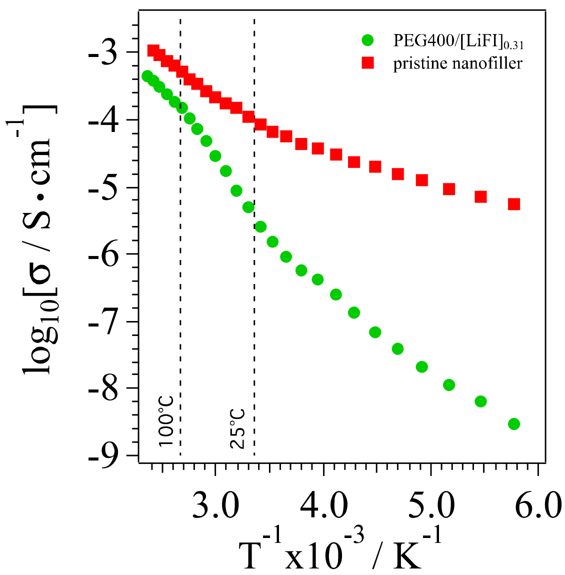

Figure 1. Conductivity of pristine LiFI and $PEG400/[LiFI]_x$ as a function of T^{-1}; x = n(PEG400)/n(Li) = 0.31.