



Single-Ion-Conducting Nanocomposite Polymer Electrolytes for Lithium Batteries Based on Lithiated-Fluorinated-Iron Oxide and Poly (ethylene glycol) 400



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ABSTRACT

A poly(ethylene glycol) 400 (PEG400) matrix doped with different amounts of a fluorinated Fe₂O₃-based nanofiller (LiFI) featuring a Li⁺-functionalised surface gives rise to nanocomposite polymer electrolytes (nCPEs) that demonstrate single-ion conduction. A family of nCPEs with general formula [PEG400/(LiFI)_y] and $y = n_{\text{Fe}}/n_{\text{PEG400}}$ ranging from 0 to 8.15 are prepared; they are characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), High-Resolution Thermogravimetric Analysis (HR-TGA), Differential Scanning Calorimetry (DSC), and Fourier-transform vibrational spectroscopy in both the medium (MIR) and far (FIR) infrared. The Li⁺ transference number, t_{Li^+} , is determined and Broadband Electrical Spectroscopy (BES) is used to elucidate the electrical response of the materials in terms of polarization and relaxation events. The combination of the information obtained by all the aforementioned techniques enables us to present a possible conduction mechanism for these nCPEs single-ion conducting systems.

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1. Introduction

In the past three decades several classes of Polymer Electrolytes (PEs) have been proposed for implementation in a variety of applications ranging from energy-conversion devices (e.g., secondary batteries, fuel cells, DSSCs), to supercapacitors, sensors, actuators among others [1]. In general, PEs should allow a facile and selective migration of only the desired ions; the best PEs show a high ionic conductivity and transference numbers close to 1 [2]. These features, together with an enhanced chemical and electrochemical stability and adequate mechanical properties, could lead to the development of secondary lithium batteries capable of an improved performance and cyclability with respect to the current state of the art [3,4].

Classical PEs consist of: (a) a polymeric matrix, typically based on polyethers, dissolving (b) a lithium salt with a very low lattice energy (e.g., LiClO₄). In these systems, Li⁺ cations are typically coordinated by the ethereal oxygen atoms of the polymeric matrix [5]. However even if this class of materials presents a sufficiently

high RT conductivity, it typically shows a very low transference number (0.1–0.2). It was proposed that hybrid electrolytes could improve the performance of classical PEs by introducing heteroatoms such as Al, Zr, B, Si, that are able to form a weak coordination network for Li cations [6]. Several examples have been proposed such as: Zeolitic Inorganic–Organic Polymer Electrolyte (Z–IOPE) [7,8], three-Dimensional Hybrid Inorganic–Organic Networks (3D–HIONS–APE) [9] and Hybrid Gel Electrolytes (HGs)[10]. In addition, multiphase materials such as Organically Modified Ceramics as Polymer Electrolytes (ORMOCERS–APE) [11] and Nanocomposite Polymer Electrolytes (nCPEs) [12] have been proposed. Indeed, it was first demonstrated by F. Croce et al., [13] that combining an inorganic nanofiller with a classical PE greatly enhances both the conductivity and the transference number. This result was attributed to the interactions between inorganic and organic moieties, which modulate the concentration of mobile Li⁺ cations. Following this approach, a variety of nanofillers have been explored including: (a) inorganic oxides (Al₂O₃, TiO₂, Fe₂O₃, ZnO, SiO₂) [14,15,16,17,18]; (b) carbon nanotubes [19]; (c) cellulose whiskers [20]; (d) clays [21,22] among many others. Recently, an innovative class of nCPEs was proposed by Di Noto et al. [12,23]. In this class of materials, fluorinated metal oxide nanoparticles undergo a surface lithiation process and are subsequently

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dispersed in a polyetheral matrix [24]. The latter is able to readily dissociate Li^+ cations from the surface of the filler nanoparticles, which behave as the counterions. The Li^+ cations coordinated by the polyetheral matrix are much more mobile with respect to the filler nanoparticles; consequently, the materials belonging to this class of nCPEs are effectively single-ion conductors [23].

In this paper, a family of nCPEs based on Lithium-functionalized Fluorinated Iron oxide (LiFI) nanoparticles dispersed in PEG400 is proposed. The nCPEs are labelled “[PEG400/(LiFI) $_y$]”. This approach extends the applicability of lithiated transition metal fluorinated oxides [24] as efficient nanofillers for the preparation of nCPEs, demonstrating that transition metals other than Ti can be included in the inorganic fluorinated oxide phase, thus paving the way for further investigations in this line of research. No lithium salt is added during the preparation of this family of nCPEs; instead, the “free” charge carriers are provided only by the lithiated nanofiller. The interplay between structure, thermal stability, thermal transitions and electric response of [PEG400/(LiFI) $_y$] is investigated by an integrated approach combining the information obtained by techniques such as High-Resolution Thermogravimetric Analysis (HR-TGA), Differential Scanning Calorimetry (DSC), Fourier-transform spectroscopy in both medium (MIR) and far (FIR) infrared and Broadband Electrical Spectroscopy (BES). Finally, on the basis of these results a mechanism for the long-range charge transfer mechanism is proposed.

2. Experimental

2.1. Reagents

LiFI nanopowders (NPs) are received from Breton S.p.A. (Castello di Godego, TV, Italy). The chemical composition of LiFI nanopowders, as determined by ICP-AES, is $\text{Li}_{0.30}[\text{Fe}_{2.09}\text{F}_{0.09}\text{O}_{2.91}]$; the particle size is 20 ± 2 nm. Poly(ethylene glycol) with a molecular weight of 400 units (PEG400) is purchased from Aldrich. All the reagents undergo purification by standard methods [25]; in addition, PEG400 is dried at 100°C under vacuum for one week. All the reagents are handled and stored under an Ar atmosphere in a M-BRAUN dry box (O_2 and $\text{H}_2\text{O} < 1$ ppm), thus preventing contamination by moisture and/or oxygen.

2.2. Preparation of [PEG400/LiFI] $_y$ nCPEs

Dry PEG400 is mixed with suitable amounts of LiFI nanopowders, yielding three [PEG400/LiFI] $_y$ nCPEs with y ranging from 0 to 8.15. nCPEs are thoroughly homogenized by sonication, using a Bandelin HD 2200 Sonoplus probe sonicator operating at 20 kHz. Sonication is performed by applying an ultrasonic pulse with a duration of 0.2 s followed by a rest time of 0.8 s for a total time of 30 min. nCPEs are prepared, handled and stored under an Ar atmosphere in a glove box. Table 1 reports the chemical composition of the nCPEs, which is evaluated on the basis of the Li assay measured by ICP-AES and corroborated by HR-TGA.

2.3. Instruments and methods

An Inductively Coupled Plasma Atomic Emission Spectrometer ICP SPECTRO Arcos with EndOnPlasma torch is used to collect ICP-AES measurements adopting the method of standard additions. The samples undergo mineralization in hot aqua regia; the emission lines taken into consideration are: $\lambda(\text{Li}) = 670.780$ nm; $\lambda(\text{Fe}) = 259.940$ nm. High-Resolution thermogravimetric measurements are collected from room temperature to 950°C under a 100 sccm dry air stream by means of a TGA 2950 thermobalance (TA Instruments). The weight resolution is $1 \mu\text{g}$; the heating rate is varied from 50 to $0.001^\circ\text{C min}^{-1}$, on the basis of the first derivative of the weight loss. The measurements are carried out on ca. 5 mg of sample, which is loaded onto a platinum pan in an Ar atmosphere. A MDSC 2920 instrument (TA Instruments) equipped with a liquid N_2 cooling system is used to carry out DSC analyses in the temperature range between -130 and 150°C , adopting a heating rate of 3°C min^{-1} . DSC samples with a known weight are sealed in an aluminium pan. A Nicolet Nexus spectrometer is used to acquire FT-MIR and FT-FIR spectra in the wavenumber range between 4000 and 50 cm^{-1} . All the FT-IR samples are prepared under an Ar atmosphere in a dry box and sealed to prevent exposure to the open atmosphere during the measurements. A multiple internal reflections 186-0174 accessory (PerkinElmer) is loaded with each sample; then, FT-MIR spectra are collected in the Attenuated Total Reflectance (ATR) mode. FT-FIR samples are sandwiched between two polyethylene windows. The experiments are conducted in transmission, and spectra obtained by averaging 1000 measurements. The electrical response of the samples is determined by BES, adopting a Novocontrol Alpha-A analyzer in the frequency and temperature ranges from 10 mHz to 10 MHz and -150 to 150°C , respectively. A homemade cryostat with a N_2 gas jet heating and cooling system is used to control the temperature, achieving an accuracy higher than $\pm 0.2^\circ\text{C}$. nCPEs are sandwiched between two circular platinum electrodes mounted inside a sealed cylindrical Teflon cell; a separator consisting of optical fibers with $d = 0.126$ mm is used to keep the electrodes apart and set precisely the thickness of the samples under measurement. All the nCPE samples are prepared under an Ar atmosphere in a glove box, thus preventing exposure to the open atmosphere. The electrode-electrolyte interface is used to evaluate the geometrical cell constant; no corrections for the thermal expansion of the cell are introduced. The transference number of Li^+ cations (t_{Li^+}) is determined in accordance with the method proposed by Evans et al. [2]. The nCPEs are sealed under an Ar atmosphere in a glove box in a Teflon measurement cell between non-blocking Li foil electrodes with a diameter of 13 mm; the distance between the electrodes is ca. 0.25 mm. The cell assembly is thermostated at 60°C ; impedance spectra are collected from 0.1 Hz to 1 MHz with a potential amplitude of 10 mV; chronoamperometric profiles are determined with an applied potential of 10 mV. Both measurements are collected with a multichannel potentiostat/galvanostat manufactured by BioLogic.

Table 1
[PEG400/(LiFI) $_y$] composition.

Sample#	wt% LiFI	wt% PEG400	$c_{\text{Li}}/\text{mol kg}^{-1}$	$x = n_{\text{Li}}/n_{\text{PEG400}}$	$y = n_{\text{Fe}}/n_{\text{PEG400}}$	$r = n_{\text{Li}}/n_{\text{O}}$
1	100	0	3.89	–	–	–
2	61.7	38.3	2.40	2.51	8.15	0.259
3	5.1	94.9	0.20	0.08	0.27	0.0087
4	0	100	0.00	0	0	0

The number of moles of Li atoms, PEG400, Iron and Oxygen atoms are labeled as n_{Li} , n_{PEG400} , n_{Fe} and n_{O} respectively.

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