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# Single-ion-conducting nanocomposite polymer electrolytes based on PEG400 and anionic nanoparticles: Part 2. Electrical characterization

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## ABSTRACT

Molecular relaxation and polarization phenomena of twelve single-ion-conducting nanocomposite polymer electrolytes (nCPEs) are studied using Broadband Electrical Spectroscopy (BES). The electrolytes are obtained by combining PEG400 oligomers with increasing amounts of anionic nanofiller comprised of fluorinated-TiO<sub>2</sub> associated with Li<sup>+</sup> cations (LiFT<sup>®</sup>), resulting in [PEG400/(LiFT)<sub>y</sub>] systems with 0 ≤ y ≤ 26.4. This new class of [PEG400/(LiFT)<sub>y</sub>] electrolytes allows us to achieve a significant single-ion conductivity (1.1 · 10<sup>-5</sup> S cm<sup>-1</sup> at 30 °C for n<sub>Li</sub>/n<sub>O</sub> = 0.113) without the addition of lithium salts. To the best of our knowledge, this is the highest conductivity value reported for this class of electrolytes. This study, in conjunction with the results reported in Part 1, leads us to hypothesize a conduction mechanism in terms of two types of long-range charge-transfer processes. The first charge-transfer occurs at the interface between the filler nanoparticles and filler-PEG domains, while the second occurs through the PEG400 matrix with the assistance of polymer segmental motion. The measured Li<sup>+</sup> transference numbers confirm that the studied materials are single-ion conductors.

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## 1. Introduction

The synthesis of new solid-state polymer electrolytes (SPEs) for lithium-polymer batteries is aimed at achieving a high

ionic conductivity without compromising on safety characteristics. Classical polymer electrolytes are based on polyether matrices doped with low dissociation energy lithium salts [1,2]. Two interesting approaches have been proposed to

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overcome the limitations of classic lithium polymer electrolytes and two main categories of hybrids have been extensively studied. The first class is represented by nanocomposite polymer electrolytes (nCPEs), which provide unique opportunities in producing ion-conducting materials capable of satisfying the demanding requirements of the automotive and portable electronics industries [3–6]. nCPEs constitute a widely-studied class of ion-conducting materials [3,7–19]. nCPEs are typically based on a polyether matrix used to dissolve a lithium salt and to suspend an inorganic nanofiller such as SiO<sub>2</sub> [14], TiO<sub>2</sub> [3,4,13,17], Al<sub>2</sub>O<sub>3</sub> [3,9,16], ZrO<sub>2</sub>, ZnO [11], and clay [12]. It was suggested that the inorganic species at the interface with the polymeric chains generated a grain boundary effect, thereby significantly increasing the conductivity [3]. The second class consists of homogeneous monophasic materials where inorganic atoms are introduced directly into the skeleton of polyether macromolecules [20–24]. This latter class includes very promising materials such as the hybrid inorganic–organic polymer electrolytes containing the “ate” complex structure (e.g., aluminate, borate) in the polymer matrix. Indeed, the incorporation of Lewis acid metal sites into the polymer backbone chains facilitates the delocalization of anionic charges, reducing the cation–anion pairing and thus increasing the ionic conductivity [22–24]. A few studies were dedicated to probe the effects of cellulose nanocrystals as an additive to conventional PEs [15,19]. Research efforts in this area were directed toward nCPEs, where it is commonly agreed that adding a nanofiller to a conventional PE leads to an enhancement of the conductivity of the pristine PE [25]. However, the mechanism responsible for the increase of conductivity in nCPEs is still under debate. Thus, different explanations as to the reasons for this increase in conductivity were proposed. One school of thought indicates that Lewis acid–base interactions between the oxygen of the polymer, the filler and the salt result in the kinetic inhibition of the normal tendency of the polymer host to crystallize [3]. Another school of thought focuses its attention on the dielectric interactions between fillers and polymer and between fillers and ions [26].

This paper presents the electrical characterization of a new class of nCPEs prepared by adding a lithium-doped nanofiller to a PEG400-based polymeric matrix. In this ion-conducting material, the only source of Li<sup>+</sup> ions is provided by the

nanofiller and no lithium salts are added. The pristine nanofiller (LiFT) is based on a functionalized fluorinated TiO<sub>2</sub> bearing lithium ions on its surface. Twelve nCPEs with different Li<sup>+</sup> concentrations were prepared to investigate the effect of different nanofiller concentrations on the ionic conductivity of these materials and to elucidate their conduction mechanism. The materials were studied by Broadband Electrical Spectroscopy (BES) and the electrochemical method of Evans et al. [27] to determine the Li<sup>+</sup> transference number. In Part 1 of this investigation, a detailed structural, thermal and vibrational characterization of the materials was reported, and allowed us to highlight three compositional regions (A, B, C), where Li<sup>+</sup> is dissociated from the anionic nanofiller surface and coordinated in different ways by PEG400 chains. Here we present the study of the charge transfer and dielectric relaxation processes, which allow us to hypothesize a satisfactory conduction mechanism for the proposed nCPE systems.

## 2. Experimental

### 2.1. Reagents

LiFT<sup>®</sup> nanopowder [28] with the formula Li<sub>0.128</sub>[(NH<sub>4</sub>)<sub>0.007</sub>-TiO<sub>1.98</sub>F<sub>0.07</sub>] was provided by Breton S.p.a. (Castello di Godego, TV, Italy). PEG400 was Aldrich reagent-grade. The reagents were further purified by standard methods and stored in an Argon glove-box (M-BRAUN; O<sub>2</sub>, H<sub>2</sub>O < 1 ppm) to prevent oxidation by air and exposure to moisture. All transfer and handling operations were carried out under a strictly inert Ar atmosphere.

### 2.2. Synthesis

[PEG400/(LiFT)<sub>y</sub>] nanocomposite polymer electrolytes (nCPEs) with y ranging from 0 to 26.4 (see Table 1) were prepared according to the following procedure. PEG400 and LiFT were dried under vacuum (10<sup>-3</sup> mbar) at 100 °C for 72 h. The absence of water was confirmed by IR spectroscopy. Twelve different concentrations of LiFT-containing nCPEs were obtained by mixing PEG400 with pure nanofiller at room temperature. To achieve a good homogenization of the materials, each sample was sonicated for 30 min. The filler and lithium

**Table 1 – Composition of [PEG400/(LiFT)<sub>y</sub>] nCPEs.  $n_{Li}$ ,  $n_{PEG}$ ,  $n_{Ti}$ , and  $n_O$  are the number of moles of Li, PEG400, Ti and polyether oxygens, respectively.  $c_{Li}$  is the molality of Li.**

	Description	Region	%wt filler	%wt PEG400	$c_{Li}/\text{mol kg}^{-1}$	$x = n_{Li}/n_{PEG}$	$y = n_{Ti}/n_{PEG}$	$r = n_{Li}/n_O$
1	Solid	N/A	100	0	1.34	–	–	–
2	Powder	C	86.3	13.7	1.17	3.418	26.4	0.354
3	Powder	C	66.8	33.2	0.91	1.093	8.40	0.113
4	Viscous paste	B	57.8	42.2	0.78	0.737	5.73	0.0763
5	Viscous paste	B	40.1	59.9	0.55	0.366	2.80	0.0378
6	Viscous paste	B	29.0	71.0	0.39	0.219	1.71	0.0227
7	Viscous paste	A	15.1	84.9	0.20	0.095	0.75	0.00984
8	Viscous paste	A	9.8	90.2	0.13	0.0588	0.46	0.00608
9	Liquid	A	5.7	94.3	0.072	0.0306	0.25	0.00316
10	Liquid	A	2.6	97.4	0.035	0.0142	0.112	0.00147
11	Liquid	A	1.2	98.8	0.016	0.00641	0.0487	0.000663
12	Liquid	A	0	100	0	0	0	0

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