



Exotic solid state ion conductor from fluorinated titanium oxide and molten metallic lithium



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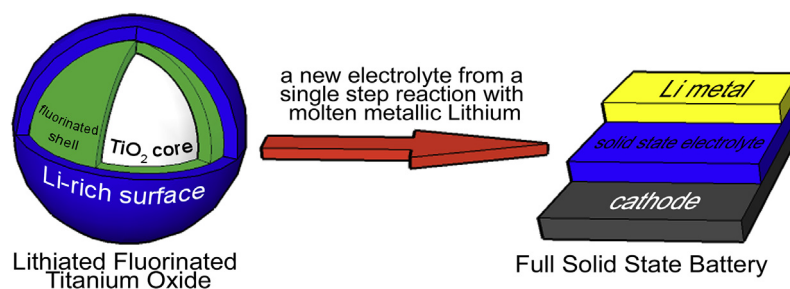
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HIGHLIGHTS

- An inorganic solid-state electrolyte for lithium batteries is prepared through an innovative one-step synthesis.
- The electrolyte shows a high conductivity due to the hopping of Li cations at the interfaces between anatase-based NPs.
- Good prototype performance and full solid-state cyclic voltammetry are demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential for metallic lithium batteries that exhibit high specific capacities has stimulated a large interest within the energy research field. For safety reasons, the use of metallic lithium anodes requires electrochemically stable electrolytes. However, to date there has been limited success in this area. This work introduces a solid, lithium single-ion conductor thus providing new perspectives in the field of solid-state lithium-batteries. This new-concept material (LiFT), obtained by a direct reaction of nanometric fluorinated titanium oxide (FT) with molten metallic lithium, consists of nanoparticles (NPs) with anionic surface groups that are neutralized with lithium cations. The material displays fast lithium ion transport via an efficient migration mechanism occurring at the interfaces between different nanoparticles. The electrolyte comprises 1.34 mol kg^{-1} of Li and a conductivity of $2.8 \cdot 10^{-4} \text{ S cm}^{-1}$ at 25°C is demonstrated. This level of performance, in conjunction with a native electrochemical stability towards lithium, extremely low cost starting materials (TiO_2) and a facile one-pot synthesis, renders this electrolyte very attractive for applications in future full solid-state lithium batteries.

1. Introduction

Lithium ion batteries, LIBs, are promising electrochemical devices

that will likely play a crucial role in future energy technologies [1]. However, to assure their proper application in the emerging markets of road electrification and renewable energy storage, LIBs still require

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improvements in terms of safety, energy density and cost [2,3]. In this respect, the electrolyte, owing to its strong role on determining current density; time stability and safety; is arguably the most important component of the cell. Several classes of electrolytes including: polymer membranes [4]; ionic liquids [5] and inorganic solid-state materials [6] have been proposed in the last ten years, with the solid-state electrolytes, both polymeric and inorganic, exhibiting the best performance in terms of mechanical and chemical properties, especially in conjunction with metallic lithium or Li alloy-based anodes. New full solid-state electrolytes should present a: a) high ionic conductivity, which would enable high rate battery performance; and b) high chemical and electrochemical compatibility with the electrode materials. However, these two points are not achieved in state of the art solid-state electrolytes, which generally suffer of low conductivity at room temperature and poor interfacial properties with the electrodes. In addition, in order to be realistically applied to practical devices, they must also be of low cost and environmentally compatible.

Several classes of solid-state electrolytes have been proposed in the last decades including: Lisicon, Nasicon, Perovskites, Antiperovskites, Garnets and glassy materials [7,8]. Lisicon-like materials typically show high conductivity values (up to $2.5 \times 10^{-2} \text{ S cm}^{-1}$ at 298 K) and suitable contact properties with the electrodes, nevertheless their stability against lithium anode is still an on-going issue [9,10]. Nasicon-based materials, which show conductivity values as high as $6 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K [11] often present titanium reduction problems and generally show poor electrode wettability with high grain boundary resistance. Perovskites materials generally present high RT conductivity [12] ($> 10^{-3} \text{ S cm}^{-1}$ at RT) but poor electrochemical stability and high grain boundary resistance [13]. On the contrary, preliminary work on metastable antiperovskite-based materials, has shown promising features from both a conductivity and electrochemical stability window (ESW) point of view [14]. Finally garnet-base materials present both a high conductivity (up to $1 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K) and good wettability and interfacial properties [15,16]. In this scenario, the herein presented solid-state lithium single-ion conducting material stands as a significant breakthrough in the field. The conductivity in this material arises from an effective lithium ion long range migration process occurring at the interfaces between functionalized nanoparticles. Due to the presence of a fluorinated shell on a TiO_2 core, the proposed electrolyte (LiFT) does not undergo reduction upon contact with molten metallic Lithium during the synthesis process. This unusual behaviour makes this material extremely compatible with a metallic lithium anode of a “Lithium” battery.

2. Experimental section

2.1. Materials

NH_4HF_2 (99.999%), FeTiO_3 (99.9%), metallic Lithium (99.9%) and Ethanol (> 99.8%) were Sigma-Aldrich products. Prior to use, ethanol was further dried by distillation over CaO. All handling, transfer and storage of reagents and products were carried out in Ar inert atmosphere dry boxes.

2.2. Synthesis of the fluorinated titanium oxide (FT) precursor

FT was prepared by reacting FeTiO_3 with an aqueous solution (30% wt) of NH_4HF_2 at 105 °C in a closed vessel for 1 h. The weight ratio between FeTiO_3 and $\text{NH}_4\text{HF}_2(\text{aq})$ was equal to 1:1.75. The resulting mixture was then filtered and the pH raised to 9 by adding $\text{NH}_4\text{OH}(\text{aq})$. The increase in pH led to the precipitation of a white powder that was first dried and then hydrolyzed at 450 °C in presence of steam (20 g min^{-1}) for 2 h. The resulting powder was then dried overnight under vacuum at 100 °C.

2.3. Synthesis of the Lithiated fluorinated titanium oxide electrolyte (LiFT)

LiFT electrolyte was prepared by suspending FT in a large excess of molten metallic lithium in an argon filled glovebox at 220 °C, with molten lithium acting as both a reagent and as a solvent. After cooling, the excess of metallic lithium was removed by reacting with ethanol thus obtaining lithium ethoxide, which is removed through several washing with EtOH. The resulting powder was then dried overnight under vacuum at 100 °C.

2.4. Materials characterization

Elemental analyses were performed using a Spectro Arcos inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The preparation of samples was conducted by reacting a known amount of material with hydrofluoric acid in a CEM MDS-2100 microwave digestion system. High-resolution transmission electron microscopy (HR-TEM) measurements were performed using a 300 kV Jeol 3010 electron microscope equipped with a Gatan slowscan 794 CCD camera. A “GNR Analytical Instruments” eXplorer spectrometer, at a potential of 40 kV and a current of 30 mA applied to a Cu $\text{K}\alpha_1$ source, was used to obtain the X-ray diffraction data. Measurements were carried out in a transmission mode between 5 and 60° every 0.1° sandwiching each sample between two Mylar windows. IR spectra were determined using a Nicolet Nexus spectrometer with a resolution of 2 cm^{-1} in the range 4000–50 cm^{-1} . The MIR spectra were measured in the ATR mode while the FIR spectra measured in the transmission mode. For both cases, the samples were loaded inside an argon filled glove box. For the FIR measurements, two polyethylene windows were used and each spectrum was obtained after averaging 1000 scans. The ionic conductivity measurements were carried out by using a Novocontrol Alpha-A analyzer in the frequency range 10 mHz–10 MHz and in 25–155 °C temperature range, with a temperature control better than $\pm 0.2 \text{ }^\circ\text{C}$, by exploiting a homemade heating-cooling system operating with liquid nitrogen. The sample, in the form of a pellet with known dimensions, was sandwiched between two circular platinum electrodes and placed into a hermetically sealed Teflon cell, assembled in an argon filled glove box and kept under argon for the duration of the test.

2.5. NMR measurements

Both wideline ^7Li and magic-angle spinning (MAS) ^{19}F nuclear magnetic resonance (NMR) spectroscopy were used in this study in order to obtain additional information on the lithium, and the fluorine environments. Measurements were performed on a Varian-S Direct Drive spectrometer operating at 117.1 MHz and 283.5 MHz for ^7Li and ^{19}F respectively. Powdered samples were packed into hermetically sealed 3.2 mm zirconia rotors inside an argon glovebox and ^{19}F spectra were recorded at a spinning rate of 19–25 kHz. Free-induction decays (FIDs) were obtained using a phase cycled $\pi/2$ pulse – acquire – recycle delay sequence, and ECHOs were acquired using a typical phase cycled spin echo pulse sequence ($\pi/2$ pulse – τ – π pulse – τ – acquire). Spectra were gathered by Fourier transformation of the FIDs or trailing half-ECHO signal. $\pi/2$ pulse widths of 4 and 3 μs were used for ^{19}F and ^7Li , respectively, with recycle delays of 2–10 s. Typically, several thousand transients were signal averaged before processing. Static (non-spinning) ^7Li spectra were obtained to assess the effect of temperature on Li^+ motion through linewidth changes. The spectral frequency scales in the corresponding figures, as given in the normalized units of ppm, are relative to the ^7Li and ^{19}F chemical shifts of an aqueous solution of LiCl and CFCl_3 , respectively. A cross polarization (CP) experiment between ^{19}F and ^7Li was performed to probe internuclear distances, with Hartmann-Hahn matching conditions optimized for solid LiF.

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