

In situ processing of fluorinated carbon–Lithium fluoride nanocomposites

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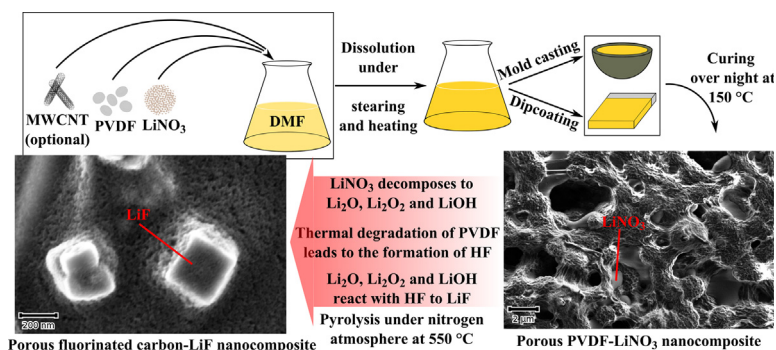
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HIGHLIGHTS

- Fluorinated carbon - lithium fluoride powder and thin films are *in situ* fabricated.
- Polymer matrix is present before pyrolysis and fluorinated carbon after pyrolysis.
- Lithium nitrate particles with up to 1 μm size are observed before pyrolysis.
- Lithium fluoride particles with a mean size of 200 nm are detected after pyrolysis.
- Thermodynamic mechanisms and formation of intermediate products are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium fluoride (LiF) and fluoride additives in carbon-based materials are currently under research as electrode materials for energy storage applications. Herein we demonstrate a simple and novel method for the *in situ* fabrication of fluorinated carbon–LiF nanocomposites both as powder and as supported thin films. The starting solution of polyvinylidene fluoride (PVDF) and lithium nitrate (LiNO₃) in *N,N* Dimethylformamide is poured into a mould or applied to a thermally resistant substrate as a thin film. Pre-tempering and further pyrolysis at 550 °C yield LiF doped amorphous and fluorinated carbon (AC) powder or film. The precursor solution can be additionally modified with multi-walled carbon nanotubes (MWCNT) to yield porous AC–MWCNT–LiF–nanocomposites. Structural and morphological characterization (scanning electron and energy dispersive X-ray spectroscopy, X-ray diffraction as well as solid-state ⁷Li magic angle spinning nuclear magnetic resonance spectroscopy) show a fine dispersion of faceted LiF–nanoparticles in the carbon matrix or decorating the MWCNTs. The formation mechanism involves the thermally activated reaction of Li-ions with the fluorine of the polymer during pyrolysis thus allowing an *in situ* nanocomposite to be obtained. Finally the electrochemical capacitance properties in a two-electrode set-up using LiNO₃ in ethylene glycol as electrolyte are reported and discussed in comparison to LiF-free electrodes.

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1. Introduction

Porous materials are of a paramount importance for energy applications. Their microstructures may be tailored using myriad processes, including tape and gel-casting [1,2], de-alloying [3], templating and many more [4]. In particular, the design of 3D-carbon-based materials with

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controlled pore size and their doping with different elements can boost their energy storage capabilities, e.g. as supercapacitors [5,6], or improve their properties for other applications such as the desalination of water [7,8]. Carbon-based materials containing lithium fluoride (LiF) and different metals are being investigated as electrode (mainly cathode) materials for Li-ion batteries. Fluoride additives lower the initial loss in specific capacity as well as energy density and improve cycling performance of Li-ion batteries [9,10]. LiF is also well known as an interesting material for optical applications, e.g. as radiation detector material [11,12] or in organic solar cells [13]. A possibility to achieve the so-called prelithiation (adding of a Li-source into the electrode material to compensate the loss after the first cycle) of Li-ion batteries is the use of nanocomposites consisting of LiF and carbon materials that are doped with different metals, e.g. Co and Fe [9,14–16]. Sun et al. [9] describe a processing method of LiF/Fe and LiF/Co based on the chemical reactions of molten lithium and CoF_3 or FeF_3 powder. The active materials of LiF/Co or LiF/Fe obtained are then mixed with carbon black and polyvinylidene fluoride (PVDF) as binder to achieve electrode materials [9]. Other processing methods consist of the pyrolysis at 700 °C of a mixture of LiF and cobaltocene or ferrocene [14,15]. The crystallite size of LiF used for the production of these nanocomposites seems to affect capacity with a favourable effect of smaller crystallite size [17]. Pure LiF can be produced using hydrofluoric acid together with an aqueous solution of lithium hydroxide or carbonate [13,18,19] as well as using evaporation methods to achieve LiF films [20,21].

In the present study, we introduce a simple and novel method for the *in situ* fabrication of fluorinated carbon-LiF nanocomposites starting from a solution. The method is akin to gel-casting and is template free, allows nevertheless to process both porous LiF-nanocarbon-nanocomposites in the form of powder and supported thin films. In a previous work we have demonstrated a versatile method for the processing of porous PVDF and nanocarbon films starting from a precursor solution of PVDF that was modified with ammonium nitrate (NH_4NO_3) [22,23]. Carbon materials produced in this way are slightly fluorinated after the pyrolysis and so the question then has arisen as to whether a similar approach could result in making *in situ* nanocomposites of nanocarbon and metal fluorides, e.g. by replacing ammonium nitrate in the PVDF precursor solution with metal nitrates. An obvious system to start with is the nanocarbon-LiF nanocomposite, taking advantage from PVDF as the fluoride source, and using lithium nitrate (LiNO_3) as the lithium source. With this strategy the formation of the *in situ* nanocomposite is expected during pyrolysis of the organic phase that sets fluorine free which then reacts with lithium ions to form LiF (the free energy of formation of this compound is exothermic, see below). For this purpose, PVDF and LiNO_3 are dissolved in *N,N*-Dimethylformamide (DMF) yielding a clear precursor solution that can be applied to any thermally resistant substrate as a thin film using solution deposition methods, e.g. dip-coating, or poured into a mould to obtain bulk materials. Self-ordering of the salt-solvent droplets in the polymer matrix and subsequent evaporation of the solvent during tempering generate a porous polymer structure with a fine distribution of LiNO_3 -nanoparticles. Further pyrolysis under a nitrogen atmosphere at 550 °C leads to the formation of a fine distribution of LiF-nanocrystallites in a matrix of amorphous and fluorinated carbon (AC). We demonstrate also that the precursor solution can be easily modified with multi-walled carbon nanotubes (MWCNT) to generate AC-MWCNT-LiF-nanocomposites.

2. Experimental

2.1. Reagents

N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) were obtained from Carl Roth, Germany. Goodfellow supplied polyvinylidene fluoride granule. Lithium nitrate and multi-walled carbon nanotubes (>90% carbon basis) were purchased from Sigma-Aldrich, Germany.

2.2. Preparation

For the preparation of the precursor solution, first 20 wt% of PVDF is dissolved in DMF under stirring and heating (65 °C). Upon dissolution of PVDF (ca. 1 h) 8 wt% of LiNO_3 is added and the whole is stirred for further 2 h until the solution becomes clear. The prepared solution is poured into a mould or applied by dip coating (other solution deposition methods are also possible, e.g. spin or tape coating) to a thermally resistant substrate, in our case mill-finish stainless steel, as a thin film. Additionally we use a versatile and recently reported [24,25] method for the precursor solution modification with MWCNTs to achieve nanocomposites containing a MWCNT network. For this purpose, first 1 wt% of MWCNT is added to DMF followed by dissolution of PVDF and finally LiNO_3 as described above. Curing was conducted over night at 150 °C, and pyrolysis was performed under flowing nitrogen at 550 °C for 60 min.

2.3. Characterization

The microstructure and morphology of the materials were analysed using a high-resolution scanning electron microscope (SEM, Ultra Plus, ZEISS, Germany), equipped with an energy dispersive X-ray spectroscopy (EDS) package (INCAx-act, Oxford Instruments, UK). The structure was characterized using Raman scattering (Raman microscope, Senterra, Bruker, Germany) and X-ray diffraction (XRD, X'Pert Pro diffractometer PANalytical, Holland). Raman spectroscopy was performed at a laser wavelength of 785 nm in a backscattering configuration using a CCD detector in the wave number range from 70 to 3700 cm^{-1} with a spectral resolution of 3–5 cm^{-1} . XRD measurements were done in grazing incidence diffraction mode with constant $\theta = 1^\circ$ using monochromatic $\text{Cu K}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$ and a scanning range between 20° and 70° (2 θ). Fourier transform infrared (FT-IR) spectroscopy was performed on a PerkinElmer Frontier ATR-FTIR spectrometer (Waltham, USA) at a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1} . In addition, single pulse ^7Li solid-state nuclear magnetic resonance (SS NMR) was performed on a 600 MHz Agilent NMR spectrometer using a triple resonance 3.2 mm magic angle spinning (MAS) NMR probe and are referenced to 1.0 M LiCl ($\delta(^7\text{Li}) = 0.0 \text{ ppm}$). The relaxation delay was optimized for each sample to ensure full relaxation. Spinning speeds in the range of 15 to 17 kHz were employed. The electrochemical performance of the supported films was investigated in a two-electrode setup in 1 M LiNO_3 in ethylene glycol (EG) using an electrochemical workstation (ZAHNER IM6e, Kronach, Germany). The specific capacitance C_{sp} (F g^{-1}) of the prepared supercapacitors was calculated from cyclic voltammetry (CV) curves using Eq. (1) [26,27]:

$$C_{sp} = \frac{A_I}{2 \cdot \Delta V \cdot \frac{dV}{dt} \cdot m} \quad (1)$$

where m is the mass of both electrodes in g, dV/dt the scan rate in V s^{-1} , A_I the integrated area in VA of the CV curve in 1 cycle and ΔV is the voltage window in V. The mass of the prepared films was calculated by difference of the substrate weight measurements before coating and after pyrolysis, using a high precision balance (ABT 320-4M, Kern, Germany). For the specific surface capacitance, the geometrical surface area was used instead of the mass.

3. Results and discussion

3.1. Structural investigations

The presence of LiNO_3 makes the materials highly hygroscopic after tempering at 150 °C. This manifests by a thin watery film that appears on the porous polymer surface already after a short time at laboratory atmosphere. The FT-IR spectra of Fig. 1a show in comparison to the pure PVDF film an additional broad vibration peak centred at

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