



Identify OH groups in TiOF_2 and their impact on the lithium intercalation properties



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ABSTRACT

A detailed investigation on the chemical composition of the cubic form of titanium oxyfluoride-based compound reveals the presence of OH groups substituting the oxide/fluoride sublattice. The substitution of oxide by hydroxyl groups induces the presence of titanium vacancies (\square) which were characterized by ^1H and ^{19}F solid-state NMR. ^1H NMR shows that OH groups are present as bridging Ti-OH-Ti or terminal OH groups, i.e. sitting close to a titanium vacancy Ti-OH- \square . The electrochemical properties *vs.* Li^+/Li indicates that the presence of OH groups prevents the intercalation of lithium in the upper voltage region (1.2–3 V *vs.* Li^+/Li). Indeed, a partial dehydroxylation of the framework enables to improve the reversibility of the lithium insertion/de-insertion processes. Since the presence of OH groups in this type of compounds is usual and depends on the synthesis method employed, this work enables to rationalize the different electrochemical behaviors reported in the literature and further highlights the importance of a good knowledge of the chemical composition with regard to the physico-chemical properties.

1. Introduction

Solution-based synthesis of transition metals oxyfluorides relies on hydrolysis/fluorolysis and condensation reactions [1,2]. Accordingly, certain transition metal such as titanium or niobium can accommodate up to three types of anions, i.e. O^{2-} , OH^- and F^- , yielding complex compositional and structural features [3–10]. In specific conditions, the formation of oxo species can be prevented thus enabling the stabilization of hydroxyls groups. In particular, the use of acidic aqueous medium has yielded a hydroxyfluoride compound derived from TiOF_2 . The substitution of divalent oxide by monovalent OH groups led to the formation of a significant amount of titanium vacancies, i.e. $\text{Ti}_{0.75}\square_{0.25}\text{F}_{1.5}(\text{OH})_{1.5}$ [10].

Titanium oxy-(hydroxyl)-fluoride compounds have been shown to be of particular interests for a broad variety of applications spanning energy storage [11–17], optical properties [18] and photocatalysis [19–21]. The precise knowledge of the chemical composition and structural features of these compounds is of paramount importance to understand their physico-chemical properties. For instance, the lithium insertion properties of Ti-based oxyfluoride compounds in the 1.2–3 V region depend on the material's preparation methods [11–17]. In the present article, we employ a variety of analytical and spectro-

scopic tools to characterize OH groups in the cubic form of TiOF_2 . Finally, we investigate how OH groups can alter the electrochemical reaction *vs.* Li^+/Li .

2. Material and methods

2.1. Synthesis

Hydroxylated TiOF_2 was synthesized using a microwave-assisted solvothermal method. A solution containing 27 mmol of titanium tetraisopropoxide (TTIP, Sigma-Aldrich), 47.22 mL of isopropanol (Sigma-Aldrich) and 4.78 mL (F/Ti molar ratio of 4) of hydrofluoric acid (40 wt%, Rectapur) was placed in a sealed Teflon line container. The solution was then heated at 90 °C for 30 min with a ramp of 13 °C/min yielding a transparent solution. The precipitation was then obtained by solvent removal using a microwave heating at 75 °C for 30 min under a nitrogen stream. The obtained powder was washed twice with ethanol. Finally, the sample was dried at 90 °C under vacuum.

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2.2. Characterization methods

X-ray diffraction was carried out by using a Rigaku Ultima IV diffractometer with a Cu K α radiation ($\lambda=1.5418$ Å).

The thermogravimetric analysis (TGA) was performed using Setaram Setsys. The sample was heated from room temperature up to 350 °C under a helium atmosphere (heating rate 5 °C/min).

Thermal treatments of the hydroxylated TiOF₂ were performed in a tubular oven under vacuum for 10 h with a heating rate of 2 °C min⁻¹.

2.3. Solid-state NMR spectroscopy

¹H and ¹⁹F solid-state magic angle spinning (MAS) NMR experiments were performed on a Bruker Avance III spectrometer operating at 7.0 T (¹H and ¹⁹F Larmor frequencies of 300.1 and 282.2 MHz, respectively), using a 1.3 mm CP-MAS probe head. The room temperature ¹H and ¹⁹F MAS spectra were recorded using a Hahn echo sequence with an interpulse delay equal to one rotor period. The 90° pulse lengths were set to 2 μ s and 1.55 μ s and the recycle delays were set to 10 s and 20 s, for ¹H and ¹⁹F, respectively. ¹H and ¹⁹F spectra are referenced to TMS and CFCl₃, respectively and they were fitted by using the DMFit software [22]. ¹⁹F solid state NMR was used to quantify the fluorine content on the TiOF₂ samples by using reference samples [7–9]. ¹⁹F solid-state MAS NMR (Hahn echo) spectra were also recorded for YF₃ and LaF₃ and the masses of each sample in the rotor were measured. The fits of the spectra allow to determine the integrated intensities (I) for each sample. Since, for each sample, the recycle delays were chosen to ensure that the amount of signal detected is maximum (420 s for YF₃ and 120 s for LaF₃), we assume that the integrated intensities are proportional to the number of scans (256 for the TiOF₂ samples and 16 for YF₃ and LaF₃) and to the molar quantity of fluorine atoms (n) in the rotor. This assumption is verified since the calculated I/n ratio for YF₃ and LaF₃ are equal. The intensities per scan of the NMR signals of the TiOF₂ samples, I₁, and of YF₃ (or LaF₃), I₂, allow to calculate the fluorine wt% in the TiOF₂ samples using the following formula where m and M are the mass and the molar mass, respectively:

$$\frac{I_1}{I_2} = \frac{n_F(\text{TiOF}_2)}{\frac{3m_{\text{YF}_3}}{M_{\text{YF}_3}}}$$

$$F_{\text{wt.}\%} = \frac{m_F(\text{TiOF}_2)}{m_{\text{TiOF}_2}} = \frac{n_F(\text{TiOF}_2)M_F}{m_{\text{TiOF}_2}} = \frac{3m_{\text{YF}_3}}{M_{\text{YF}_3}} \frac{I_1}{I_2} \frac{M_F}{m_{\text{TiOF}_2}}$$

2.4. Electrochemical characterization

Electrodes were prepared by hand-milling of active material (80 wt %), acetylene black (10 wt%) as conductive agent and polyvinylidene difluoride (10 wt%) previously dissolved in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) as the binder. The resulting paste was coated onto a copper foil using a doctor blade. The electrode was dried in an oven at 75 °C overnight to evaporate NMP solvent and then cut into chips with a diameter of 1 cm and a typical mass of active material of 2 mg. The chips were outgassed in a vacuum furnace at 110 °C overnight and stored inside a glove box under argon atmosphere for battery assembly. The electrochemical characterization vs. lithium was carried out in a lithium metal half-cell. A solution of LiPF₆ dissolved in EC/DMC (LP30, Merck) was used as the electrolyte. The cells were tested in the voltage range of 1.2–3.0 V using a current density of 26.3 mA g⁻¹. The used current density corresponds to a 0.1 C rate referring to the 263 mAh.g⁻¹ theoretical capacity of TiOF₂ based on the reaction of one mol of Li in 10 h.

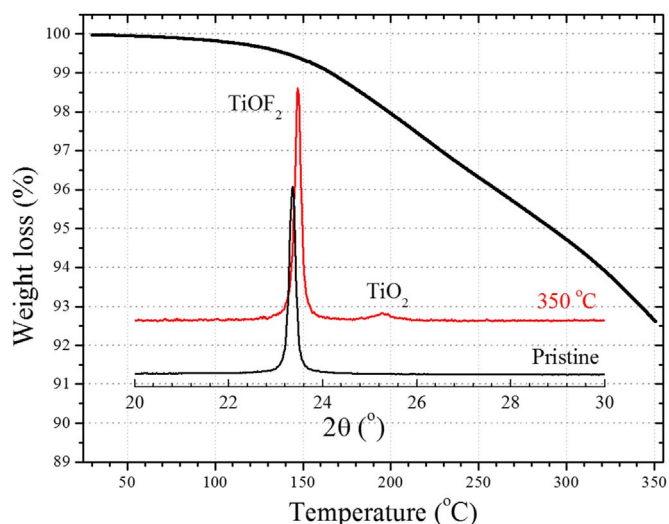
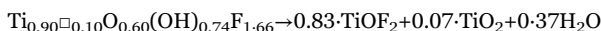


Fig. 1. Thermogravimetric analysis performed under He. Inset: XRD patterns of the sample before and after TGA analysis..

3. Results and discussion

The X-ray diffraction pattern of the as-prepared compound can be fully indexed using a cubic cell characteristic of TiOF₂ (space group Pm-3 m). The lattice parameter was refined to 3.8076(1) Å, which is close to that reported by Vorres and Donohue, that is 3.798(5) Å [23]. The fluoride content was quantified by ¹⁹F solid state NMR as described in the experimental section. The fluorine wt% is 32.3 which is slightly lower than expected for pure TiOF₂, i.e. 37.3 wt%. Such a difference accounts for a deviation of the oxydifluoride composition emphasizing the presence of OH groups. The latter was quantified using TGA. The TG curve (Fig. 1) shows a continuous weight loss of 6.88 wt% from 140 to 350 °C, characteristic of OH groups departure in water form (2OH⁻→O²⁻+H₂O). It should be noted that beyond 350–400 °C, gaseous TiF₄ can form yielding an oxide phase having the anatase type structure [10]. X-ray diffraction analysis performed on the powder recovered after the TGA shows the presence of a small amount of anatase TiO₂ indicating that the dehydroxylation reaction has occurred yielding anionic partitioning. Assuming that both F⁻ and O²⁻ can be substituted by OH⁻, the substitution of O²⁻ yields a negative charge deficiency counterbalanced by the creation of titanium vacancies. The general composition of hydroxylated TiOF₂ can then be written as Ti_{1-x}□_xO_{1-4x}(OH)_{4x+y}F_{2-y}, where □ represents a titanium vacancy. Based on ¹⁹F solid state NMR and TG analyses, the following composition Ti_{0.90}□_{0.10}O_{0.60}(OH)_{0.74}F_{1.66} was established. The decomposition path can be summarized as follows:



The local environments of the fluorine atoms were investigated by ¹⁹F solid state MAS NMR (Fig. 2). The spectrum was reconstructed using four lines located at ~12, 20, 146 and 182 ppm (Table 1) emphasizing different types of local environments for the F atoms. Within pure TiOF₂, an anion is surrounded by two titanium atoms. The occurrence of titanium vacancies induces additional coordination modes for the anions. Assuming random distributions of vacancies and Ti on the (1a) titanium and of O, F and OH on the (3d) anionic Wyckoff sites, the probabilities of occurrence of the various anionic environments are 81% for Ti-X-Ti, 18% for Ti-X-□ and 1% for □-X-□ (where X=O, F or OH). The last case can obviously be ruled out leading to probabilities of occurrence equal to 80% for Ti-X-Ti and 20% for Ti-X-□. The main lines (relative intensities equal to 82%) located at ~12 and 20.3 ppm are assigned to bridging fluorine atoms Ti-F-Ti. The lines located at higher chemical shift values, i.e. ~146 and 182 ppm (relative intensities equal to 18%), are assigned to fluorine atoms close to

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