

Electrochemical discharge mechanism of fluorinated graphite used as electrode in primary lithium batteries

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Abstract

In order to better understand the low faradic yield of low temperature fluorinated graphite used as electrode in primary lithium batteries, a study of the discharge mechanism has been performed. The evolution of some physico-chemical parameters such as C–F bond nature and structure of the fluorocarbon matrix has been determined by X-ray diffraction, solid state ^{19}F NMR and EPR as a function of the depth of discharge. The influence of residual catalytic species on electrochemical properties will be also discussed.

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Keywords: A. Inorganic compounds; C. X-ray diffraction; D. Electrochemical properties; D. Electron paramagnetic resonance (EPR); D. Nuclear magnetic resonance (NMR)

1. Introduction

Fluorine containing electrode materials generally exhibit high oxidation–reduction potential in combination with a lithium electrode. To increase the specific capacity (Ah kg^{-1}), these materials should be associated with light elements such as carbon. Specific capacity should increase with the fluorine content in these materials. Therefore, carbon fluorides CF_x with x close to unity have been actively studied as cathode materials in high energy density lithium batteries [1,2]. Two types of synthesis are usually performed to form graphite fluorides: the oldest called high temperature synthesis (the obtained compound is denoted CF(HT)) [3], consists in a direct fluorination of graphite at $600\text{ }^\circ\text{C}$ under fluorine atmosphere, the second, denoted low temperature synthesis (CF(LT)) [4], proceeds in a catalytic fluorination by volatile fluorides at temperature lower than $100\text{ }^\circ\text{C}$. Similar fluorination level than CF(HT) can be attempted if the volatile fluorides used during the catalytic fluorination are IF_5 together with HF [4].

Improved electrochemical performances were achieved when the graphite fluoride synthesis was performed at room temperature, in the presence of a gaseous mixture composed of a volatile fluoride, such as IF_5 , HF and F_2 . Such cathode materials develop the same capacity (close to 600 Ah kg^{-1})

than commercial ones composed of CF(HT) but at higher voltages (3.0 V vs. Li^+/Li for CF(LT), 2.4 V for CF(HT)). 42% increase of specific energy as well as lower kinetic limitations during the electrochemical reduction have been already registered for such low temperature graphite fluorides [5]. However, the faradic yield of these compounds is low and a study of the discharge mechanism is necessary to better understand both this faradic yield, and the evolution of catalyst residues upon discharge. Such information should allow the electrochemical performances to be improved. So, the evolution of the physico-chemical characteristics of the electrode has been investigated as a function of the depth of discharge owing to XRD, NMR and EPR measurements.

2. Experimental

Graphite fluoride compounds were obtained by the reaction at room temperature of graphite with a gaseous mixture of HF, F_2 and IF_5 , as volatile fluoride [4]. The chemical composition, obtained thanks to chemical analysis, is $\text{CF}_{0.89}\text{I}_{0.02}\text{H}_{0.06}$ for this product. Then, it has been treated under N_2 at $300\text{ }^\circ\text{C}$ during 3 h in order to eliminate undesirable impurities, such as HF molecules and FHF^- ions. This sample will be called CF(LT)-300N2.

Powder X-ray diffraction (XRD) measurements were performed using a PHILIPS XPERT diffractometer working with a $\text{Cu K}\alpha$ radiation. Static ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature on a Bruker AVANCE DSX 300 spectrometer operating at

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282.36 MHz. The external reference was CF_3COOH (-78.5 ppm vs. CFCl_3). Electron Paramagnetic Resonance (EPR) spectra were obtained with a Bruker EMX digital X band ($\nu=9.653$ GHz) spectrometer. Diphenylpicrylhydrazil (DPPH) was used as calibration reference to determine both the resonance frequency and the densities of spin carriers (Ds). For electrochemical tests, graphite fluoride electrodes were composed of the sample $\text{CF}(\text{LT})\text{-300N2}$ (about 80% by weight, w/w), graphite (10%, w/w) to insure electronic conductivity and polyvinylidene difluoride (PVDF, 10%, w/w) as binder. The electrode was then mounted in a two electrodes cell where the electrolyte was composed of a 1 mol L^{-1} solution of LiClO_4 dissolved in propylene carbonate (PC). A microporous PVDF film containing the electrolyte was sandwiched between the graphite fluoride electrode and a lithium metal foil. Galvanostatic discharge (reduction) at 10 A kg^{-1} were carried out at ambient temperature between the OCV and 1.5 V versus Li^+/Li . Practical capacity detailed in this article has been obtained for a cell cut-off at 2 V.

Different depths of discharge have been applied for a primary lithium battery with $\text{CF}(\text{LT})\text{-300N2}$ as cathode. After the discharge, the cathode material was dried under dynamic vacuum, ground and put into a XRD apparatus in the argon-filled glove box. After the recording of the XRD patterns, the electrode was placed into a ^{19}F NMR glass tube in the argon-filled glove box and then sealed in order to investigate the discharge using NMR and then EPR. Some of the samples were then exposed to air atmosphere to evaluate the stability of the spin carriers. The depths of discharge studied are 5, 10, 15, 20, 50, 75 and 100%.

3. Results and discussion

3.1. XRD pattern evolution with the depth of discharge

Fig. 1 shows the X-ray diffraction patterns of $\text{CF}(\text{LT})\text{-300N2}$ discharged at 10 A kg^{-1} in LiClO_4 1 M dissolved in PC for different depths of discharge. The intensities of these diffraction patterns have been normalized as regard with the 002 line of graphite at $26^\circ 36'$ (graphite is added during the electrode preparation). So we assumed that there is no change due to the formation of a new intercalation compound at this special position. The peak at 2θ close to 14° is assigned to (001) reflection of graphite fluoride matrix. A broad peak at 23° is present only for low depth of discharge ($<20\%$) and is related to species intercalated into the host matrix such as iodine fluoride species (GIC-IF_n : $n=5, 6$ and 7 for IF_5 , IF_6^- and IF_7^-) [4]. For higher depth of discharge, another broad line appears at about $20^\circ 5'$ which may correspond to the formation of an intercalation compound such as CF_xLi_y , already reported but never evidenced for $\text{CF}(\text{HT})$ [6,7] or for $\text{C}_{7.4}\text{F}(\text{MgF}_2)_{0.06}$ [8]. As the position of this peak is similar to the one obtained for a sample composed of 50 w/w PVDF and 50 w/w graphite, we can then not exclude a low contribution of PVDF diffraction to this peak but it cannot explain both the high diffraction intensity and the linewidth of the recorded peak.

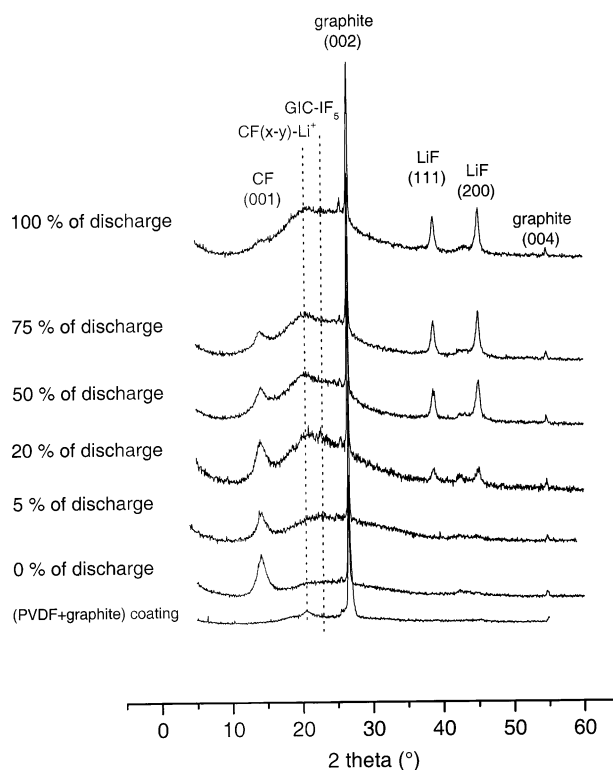


Fig. 1. X-Ray diffraction patterns of $\text{CF}(\text{LT})\text{-300N2}$ discharged at different depths of discharge.

The lines at 39 and 45° are attributed to LiF , indicating the partial decomposition of the intercalation compound produced by discharge.

For low discharge level ($<20\%$), the fluorographite matrix seems to be unchanged because both the linewidth and the intensity of the main reflection (001) are not significantly modified. Only few LiF particles are formed. Experimentally, we observe a color change of the electrolyte which turns from transparency to yellow for 20% of depth discharge and it could be interpreted as the reduction of the iodine fluoride species into iodine which is soluble in propylene carbonate.

For higher discharge level ($>20\%$), more the discharge level increases, more the C–F matrix is decomposed (the reflection at about 14° decreases continuously) and more the LiF formation occurs. The intensity of the $20^\circ 5'$ line is unchanged whatever the depth of discharge indicating that the intercalation compound CF_xLi_y is formed during the first steps of the discharge process (nevertheless higher than 5% of discharge) and its content reaches a maximum at 20% of reduction without significant modification when the depth of discharge is higher than 20%.

The end of the discharge seems to be governed by the de-structuring of the graphite–fluoride matrix rather than an effect of iodine fluoride species which were eliminated during the first step of the reduction. In order to confirm this last hypothesis, ^{19}F NMR experiments were carried out on each sample.

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