Evolution of LiFePO₄ thin films interphase with electrolyte

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HIGHLIGHTS
● Interphase evolution description on a model LiFePO₄ crystallographic orientation.
● XPS and XRR confirmed the breathing of the electrode/electrolyte interphase behavior.
● Clear depth dependence of composition of the interphase.
● Evolution of the distribution of inorganic and organic species in the interphase.

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ABSTRACT
Many parameters may control the growth and the characteristics of the interphase, such as surface structure and morphology, structural defects, grain boundaries, surface reactions, etc. However, polycrystalline surfaces contain these parameters simultaneously, resulting in a quite complicated system to study. Working with model electrode surfaces using crystallographically oriented crystalline thin films appears as a novel and unique approach to understand contributions of preferential orientation and rugosity of the surface. In order to rebuild the interphase architecture along electrochemical cycling, LiFePO₄ epitaxial films offering ideal 2D (100) interfaces are here investigated through the use of non-destructive depth profiling by Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS). The composition and structure of the interphase is then monitored upon cycling for samples stopped at the end of charge and discharge for various numbers of cycles, and discussed in the light of combined XPS and X-ray reflectivity (XRR) measurements. Such an approach allows describing the interphase evolution on a specific model LiFePO₄ crystallographic orientation and helps understanding the nature and evolution of the LiFePO₄/electrolyte interphase forming on the surface of LiFePO₄ poly-crystalline powder.

1. Introduction

Over the past years, LiFePO₄ has attracted considerable attention in the field of lithium batteries since it was proposed [1] as an alternative to cobalt-oxide based cathode. The initial motives for searching alternative positive electrode materials to lithium transition metal oxides such as LiCoO₂ [2], Li(Ni,Co,Al)O₂ [3] and LiMn₂O₄ [4] already used in commercial applications were the high cost of raw materials, environmental toxicity as well as the limited thermal stability of some of these compounds. The now possible use of LiFePO₄ in large scale and power application such as hybrid electric vehicles (HEV) or electric vehicles (EV) led to a tremendous activity aiming at reducing the particles size [5–8] and/or providing an efficient carbon coating [9–12] in order to overcome the extremely low electronic conductivity of LiFePO₄. The successful synthesis of sub-micronic or nanometric particles allowed enhancing the accessibility of the active material to lithium ions and electrons and reaching theoretical capacity of 170 mAh g⁻¹ with high power capability [8,13–15]. The dramatic increase of the surface/volume ratio is nevertheless proven to induce a preponderant contribution of surfaces exposed to the electrolyte to the chemistry of the whole battery and amplify parasitic reactions, developing a complex surface chemistry, detrimental to the electrochemical performance [16–25]. Within this scope, few studies deal with surface chemistry [26–30] or interphase evolution of LiFePO₄ electrode material [22,31–34] upon its

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operation in a lithium battery as it was considered as chemically inert. Fundamental research is critically needed to uncover the underlying principles that govern these complicated and interrelated processes. Many parameters may control the growth and the characteristics of this interphase, such as surface structure and morphology, structural defects, grain boundaries, surface reactions, etc. However, polycrystalline surfaces contain these parameters simultaneously, resulting in a quite complicated system to study. In order to understand the origin of the interphase formation, it appears necessary to separate the different parameters. Working with model electrode surfaces using different crystallographically oriented crystalline thin films appears as a novel and unique approach to understand contributions of preferential orientation and rugosity of the surface. The study of the model electrode/ electrolyte interphases based on LiFePO4 can then lead to a better understanding of these parasitic phenomena necessary to the optimization of the cycle life of batteries using this material. Moreover, the roles of the preferential orientation, of the crystallographic plane in contact with the electrolyte as well as the rugosity of the surface at a nanometric scale have still to be explored.

In the domain of thin films, it is often possible to describe the architectures of stacked layers by XPS thanks to ion etching, highlighting multi-layered geometries (e.g. layers thickness and stacking order). Although encouraged in earlier studies focused on Li-ion batteries, it is now commonly agreed that Ar+ sputtering on interphases dramatically modifies their composition, due to preferential evaporation and/or re-deposit of extraneous species. To avoid possible interphase modification due to the etching technique, non-destructive depth profiling using Photoelectron Spectroscopy (PES) is rather performed by varying the beam wavelength in order to tune the penetration depth. This approach requires nevertheless access to a synchrotron light source. In the work presented here, we chose to play on another parameter giving access to the depth profiling i.e. detection angle relative to the normal of the surface. In order to rebuilder the interphase architecture along electrochemical cycling, LiFePO4 epitaxial films offering ideal 2D (100) interfaces are here investigated through the use of non-destructive depth profiling by Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS). The composition and structure of the interphase is then monitored upon cycling for samples stopped at the end of charge and discharge after 1, 10 and 20 cycles, and discussed in the light of combined ARXPS and X-ray reflectivity (XRR) measurements. Such an approach allows describing the interphase evolution on a specific LiFePO4 crystallographic orientation and illustrates the possibility to correlate the nature and evolution of the LiFePO4/electrolyte interphase, as probed by XPS on model surfaces consisting in epitaxial crystallographically oriented thin films, to the interphase forming on the surface of LiFePO4 poly-crystalline powder. Data are correlated to results obtained on powders.

2. Experimental

2.1. Thin films synthesis

a-oriented LiFePO4 epitaxial thin films, deposited by PLD on SrTiO3 substrates, were prepared with the following method: a-oriented LiFePO4 epitaxial thin films were grown using a KrF excimer laser with a wavelength of 248 nm under Ar and a pulsed laser deposition (PLD) apparatus (AOV, Inc.) [42]. The substrate used was single-crystalline Nb-doped SrTiO3 (110) (0.5% Nb doped, 10 × 10 × 0.5 mm). The substrates were washed with ultrapure water and annealed at 1000 °C prior to the deposition. The target of the PLD process was synthesized by sintering a mixture of Li2CO3 (Wako, 99%), Fe(II)C2O4·2H2O (Aldrich, 99%), and (NH4)2HPO4 (Wako, 99%) at 900 °C for 24 h. The target contained an excess of lithium and phosphorus (Li:Fe:P = 1.2:1:1.1) to compensate for the loss that occurred during PLD. Synthetic conditions were as follows: argon pressure, p/Ar = 3.3 Pa; distance between substrate and target, d = 70 mm; laser frequency, f = 10 Hz; deposition time, t0 = 30 min; energy density, E = 90 mJ; temperature, t = 600 °C. The orientation of the films was characterized by both out-of-plane and in-plane techniques from thin-film X-ray diffraction data, recorded by a thin-film X-ray diffractometer (ATX-G, Rigaku) with Cu Kα1 radiation.

2.2. Electrochemical cycling

As synthesized LiFePO4 thin films were cycled vs lithium metal in coin cells. The two working electrodes were separated by a Celgard separator soaked with a 1 M solution of LiPF6 in EC-DEC. Batteries were prepared under argon atmosphere in a glovebox. Cells were then cycled using a VMP cyclcer between 2.5 and 4.5 V or using a TOSCAT-3100 (Toyo system, Japan) cycler between 3.0 and 4.2 V as specifically stated in the manuscript. Cells were disassembled after electrochemical cycling, LiFePO4 films were then washed with few drops of dimethyl carbonate and dried overnight under vacuum before characterization.

2.3. XRR

The thickness, density and roughness of the films were determined by X-ray reflectivity (XRR) measurement using a thin-film X-ray diffractometer (ATX-G) in air. The reflectivity spectra were plotted as functions of the scattering vector, Q = 4πsinθ/λ, where λ is the X-ray wavelength (0.1541 nm) and θ is the glancing angle. Models of the surface structure were refined by the data analysis program Parratt32 with the reflectivity calculated by Parratt’s method [44], using the roughness, thickness, and scattering length density (SLD) of each layer as parameters. The X-ray SLD value depends on number of electrons in unit cell, giving information about film composition. Ex-situ XRR analyses were performed to investigate the structural changes of LiFePO4 films induced by electrochemical cycling.

2.4. XPS

X-ray photoelectron spectroscopy (XPS) data have been collected after different cycle numbers using a Kratos Ultra Axis spectrometer. The X-ray source is AlKα working at 1253.6 eV and the surface analyzed Full Width Half Maximum is 0.7 × 0.3 mm. Wide scans were measured with an instrument resolution of 1.9 eV. Narrow scans were performed at Pass Energy 20eV corresponding to a resolution of 0.40 eV. An inert transporter has been used to transfer the samples from the glove box to the spectrometer, to avoid reaction with ambient atmosphere and minimize surface contamination. Semiquantitative XPS analysis has been performed using pseudo-Voigt function constrained by full width at half-maximum (FWHM) ranges typical of each element. The validity of the analyses was confirmed by an experimental M/O ratio close to the theoretical one for the bare pristine compound. Binding energies were fixed at 0.2 ± eV of the given value.

3. Results

3.1. Depth profiling XPS

Non-destructive depth profiling using PES is usually performed by varying the beam wavelength in order to tune the penetration depth 3λcos(θ). For a given chemical bond (e.g. E构造), the kinetic energy of ejected photoelectrons E构造 varies with hv; the harder the X-rays (i.e. the smaller the source wavelength), the longer the escape depth, and the deeper the sample is analyzed. Although this type of study is nowadays increasingly reported [45–47], thanks to technical developments as well as the accessibility of synchrotron radiation, it still requires a tunable radiation source not always available in the laboratory framework.

In this work, we implemented XPS depth profiling by varying the second accessible parameter, i.e. the incident angle, using a Kratos
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