Operando analysis of lithium profiles in Li-ion batteries using nuclear microanalysis

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HIGHLIGHTS

- *Operando* observation of Li and F concentrations and distributions in Li-battery.
- Direct visualization and characterization of the electrode/electrolyte interface.
- Elemental characterization of LiFePO$_4$ electrodes.
- Design of an *operando* cell for profiling Li using Ion Beam Analysis techniques.

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ABSTRACT

A wide variety of analytical methods are used for studying the behavior of lithium-ion batteries and particularly the lithium ion distribution in the electrodes. However, the development of in situ/operando techniques proved powerful to understand the mechanisms responsible for the lithium trapping and then the aging phenomenon. Herein, we report the design of an electrochemical cell to profile operando lithium concentration in LiFePO$_4$ electrodes using Ion Beam Analysis techniques. The specificity of the cell resides in its ability to not only provide qualitative information about the elements present but above all to measure quantitatively their content in the electrode at different states of charge of the battery. The nuclear methods give direct information about the degradation of the electrolyte and particularly reveal inhomogeneous distributions of lithium and fluorine along the entire thickness of the electrode. Higher concentrations of fluorine is detected near the electrode/electrolyte interface while a depletion of lithium is observed near the current collector at high states of charge.

1. Introduction

Energy storage will be more essential in the future than it has never been in the past. Lithium-ion technology holds in this area a prominent place on the market for stationary and mobile applications. Nevertheless, its specific capacity and energy density seem to reach their limits and could be insufficient for the long-term. It is first thus essential to understand the aging phenomena in the existing technology in order to improve their electrochemical performance with new electrode/electrolyte materials or to guide future research. Different physical and chemical processes, such as volume changes, phase transitions, side reactions, *etc.* mainly govern the decrease in performance of a lithium-ion battery. The ageing phenomena are highly complicated to characterize [1]. *In situ/operando* measurements allow live monitoring of these phenomena that can be directly link with the battery

electrochemical performance. Major developments of characterization techniques have taken place in the last decade, particularly in the cell design and the electrochemical setups that are compatible with the applied technique. Hark et al. have reviewed the recent development in *in situ* methods for lithium-ion battery research [2]. However, the electrochemical community needs more *in situ/operando* techniques in order to completely understand the aging mechanism involved during the battery operation. Particularly, the development of techniques that enable spatial resolved measurements such as *in situ* TEM and *in situ* X-ray tomography are necessary [3–5].

The Ion Beam Analysis (IBA) techniques are powerful tools to investigate in a non-invasive way the elemental distributions and the composition of a material. To this purpose, the object to be analyzed is probed by a beam of accelerated particles. The interactions of the beam particles with the atoms of the target material induce reaction products

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(X-rays, γ-rays, charged particles), having an energy characteristic of the emitting atom, including light ions such as lithium. The IBA techniques are based on the detection and the analysis of these emitted radiations. Depending on the nature of the detector used, several techniques are available. It is then possible to determine atomic concentration from matrix elements (stoichiometry), in one dimension (depth profiles) or two dimensions (elemental maps). Due to the good sensitivity to the whole periodic table, the IBA techniques have a special impact on materials science and solid-state chemistry physics. However, their application to the characterization of lithium-ion batteries is scarcely known and not enough developed. Only few works have been devoted to this topic.

Tadić et al. [6] were the first to apply IBA techniques to study the gel-polymer interfaces with Li anode and spinel cathode for Li-ion battery. The elemental composition was determined in some intercalation compounds or thin films before and after lithium insertion [7–9]. Several authors have measured the lithium extraction in cathode materials but only by chemical delithiation [10,11]. Recently, Gonzalez-Arrabal et *al.* showed that the lithium distribution in lithium-ion battery is dependent of electrode thickness [12,13]. Habrioux et al. carried out e*x situ* experiments on C-LiFePO$_4$ electrodes at different state of charge (SOC) [14]. All of these works prove the potential of nuclear analysis techniques, especially in studying elemental concentration distributions of each element present in the target with good lateral resolution (in the µm range). More recently, Mima et al. perform *in situ* measurement using X-rays and γ-rays emissions [15]. Two dimensional maps of the lithium and the iron distributions were obtained in the LiFePO$_4$ electrode and the interface between the electrode and the liquid electrolyte. However, they only obtained qualitative elemental maps by combining these two IBA-techniques, no information on the whole elements presents in the electrode or at the interface was shown. On the contrary we report here a specific electrochemical cell which maps *operando* elemental concentration in a lithium-ion battery using micro-Ion Beam Analysis. The design of our cell allows the quantitative determination of the content of all elements present in a LiFePO$_4$ electrode upon charging. Especially, the distribution and concentration of light elements such as lithium and fluorine are presented as function of the state of charge of the LiFePO$_4$ electrode.

2. Experimental section

2.1. Materials preparation

The positive electrode was prepared by coating an Al current collector with a slurry composed of 92 wt% of carbon-coated LiFePO$_4$ (C-LiFePO$_4$), 4 wt% of carbon black and 4 wt% of CarboxyMethyl Cellulose (CMC). The negative electrode was obtained by the same process on a Cu collector with graphite as the active material. Celgard®2400 polypropylene, a Viledon polypropylene foil and 1 M LiPF$_6$ dissolved in 1:1 ethylene carbonate/diethylcarbonate (EC/DEC) were respectively used as separator and electrolyte.

2.2. Experimental procedures

The experimental setup and the designed electrochemical cell for *in situ/operando* measurements using ion beam techniques are represented on Fig. 1. The experiments were carried out at the nuclear microprobe of the CEA - Paris Saclay [16]. The analysis chamber offers a large range of analysis techniques, which are explained in section 2.2.1. A *4-axis* micron-level goniometer provides precise positioning of the samples. Two cameras visualize the sample. The first one is used to get an overview of the sample, while the second is connected to a 400 × confocal optical microscope and gives more precision on the positioning.

2.2.1. Underlying principle of ion beam techniques

Depending on which detectors are placed in the analysis chamber, several IBA methods are available to determine simultaneously the elemental depth profiles or maps. The most common method concerns the detection of the energy of backscattered particles: the Rutherford Back-Scattering (RBS) for the heavy elements or the Particle Enhanced Scattering (PES) for the lightest ones (with the proton beam). Nuclear reactions also occur with light elements, giving rise to the NRA technique (Nuclear Reaction Analysis) which signal adds up to the RBS/PES one. Back-scattering analysis provides the ability to distinguish the atomic masses of elements and their distribution in depth as a function of the detected energy. The others methods are based on the detection of X-rays and γ-rays emissions (respectively PIXE and PIGE for Particle Induced X-ray or γ-ray Emission). The PIXE method is directly comparable with electron probe microanalysis (EPMA) with very similar spectra, except that there is negligible primary bremsstrahlung background due to the much higher particle mass. Consequently, trace element analysis using PIXE has a detection limit orders of magnitude lower than what can be attainable by X-rays spectrometry techniques using electron excitation. As for the PIXE method, where each element has a characteristic X-rays energy, the energy of the γ-emitted during the irradiation is characteristic of one element for the PIGE technique.

Protons beams in the range 1.0–4.0 MeV are preferred for lithium and fluorine analysis, as it offers an optimal compromise of probing techniques, listed hereafter:

- Efficient and well-known EBS cross sections of all elements
- Enhanced PIXE cross sections (compared to other projectiles)
- Available NRA and PIGE reactions for both Li and F.

Regarding Li and F measurements, PIGE technique was selected as it produces well separated spectrum contributions (478 keV and 197 keV γ-rays from ^{7}Li $(p,p'\gamma)^7$Li and ^{19}F $(p,p'\gamma)^{16}$O reactions respectively), while NRA gives rise to very close Li and F contributions (7471.4 keV and 7561.4 keV α particles from ^{7}Li $(p, \alpha_0)^4$He and the ^{19}F $(p, \alpha_0)^{16}$O reactions respectively). Although the RBS and PIXE spectra are not directly used for the lithium content determination, these techniques provide information about all elements present on the analyzed target.

2.2.2. Specific consideration for in situ cell design

Many groups have designed electrochemical cells for *in situ* or *operando* measurements. *In situ* cells have not a single ideal design. Indeed, each cell needs to fit the experimental setup available for the experiment purpose. In this paper, we present the electrochemical cell that we develop with specific requirements for IBA experiments:

- Being able to cycle electrochemically for ten cycles at different rate of charge (from C/5 to C/100).
- Being airtight. IBA techniques are generally performed under vacuum while the charge/discharge of a Li-ion battery is achieved under inert atmosphere.
- Taking account of the geometric space of the analysis chamber.
- Providing a good quality of IBA spectra in 30 min or less with no contributions apart from those of the electrodes/electrolyte materials.

To conduct ion beam measurements on an operating battery, a transparent window needs to be incorporated to the design in order to allow the ion beam to reach the electrode(s)/electrolyte under investigation. Since the interaction between the beam and the window can induce an undesirable background, the exit window must fulfill the following conditions: *(i)* minimum of energy loss and energy straggling; *(ii)* minimum of interfering signal; *(iii)* good resistance to pressure and irradiation. As silicon nitride windows are commonly used to extract ion beam to air, we choose for our electrochemical cell a 200 nm Si$_3$N$_4$ window.