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Meso-scale characterization of lithium distribution in lithium-ion batteries using ion beam analysis techniques

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HIGHLIGHTS

- Elemental characterization of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiFePO_4$ electrodes.
- Li distribution characterization in the mesoscopic scale by IBA techniques.
- IBA techniques allow estimating active particle density contributing to Li intercalation.
- We relate the Li distribution inhomogeneity and battery performance.
- We show advantages of ion beam analysis techniques for electrode characterization.

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ABSTRACT

The performance of a Li-ion battery (LIB) is mainly governed by the diffusion capabilities of lithium in the electrodes. Thus, for LIB improvement it is essential to characterize the lithium distribution. Most of the traditionally used techniques for lithium characterization give information about the local scale or in the macroscopic scale. However, the lithium behavior at the local scale is not mirrored at the macroscopic scale. Therefore, the lithium characterization in the mesoscopic scale would be of help to understand and to connect the mechanisms taking place in the two spatial scales. In this paper, we show a general description of the capabilities and limitations of ion beam analysis techniques to study the distributions of lithium and other elements present in the electrodes in the mesoscopic scale. The potential of the $^{7}Li(p,\alpha_0)^{4}He$ nuclear reaction to non-invasively examine the lithium distribution as a function of depth is illustrated. The lithium spatial distribution is characterized using particle induced γ-ray (μ-PIGE) spectroscopy. This technique allows estimating the density of the active particles in the electrode effectively contributing to the Li intercalation and/or de-intercalation. The advantages of the use of ion beam analysis techniques in comparison to more traditional techniques for electrode characterization are discussed.

1. Introduction

The supply and the management of energy are particularly at the center of our daily concerns and stand for a socio-economic priority. Nowadays, Lithium ion batteries (LIBs) are considered to be ideal candidates for many mobile and stationary applications. In particular, the requirement to decrease the green house gas emissions produced from transport stimulates the development of Li-ion batteries to power hybrid and fully electric vehicles. They are attractive candidates for these applications as they can provide high

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energy and high power densities offering the possibility to charge/discharge them many times.

The performance of a Li-ion battery is mainly governed by its energy density, power, capacity, charge and discharge rates as well as, its lifetime. Even if the Li-ion battery technology became notably better over the last two decades, technological breakthroughs seem to be necessary to further increase the energy density, the charge rate, the safety and the longevity of Li-ion batteries. Further improvements in battery development require careful clarification of the underlying physical and chemical processes, in particular, better understanding of the diffusion capabilities of the Li-ion in the electrodes. Thus, for developing advanced Li-ion batteries it is essential to use, especially in situ and non-invasive, characterization tools and methodologies, knowing the capabilities and limitations of each of them.

Modern batteries contain a wide range of metallic, organic and inorganic components with dimensions of interest ranging from local (sub-nm) up to the cm range. Consequently, the use of suitable techniques to investigate the different scales is crucial. However, most of the presently used techniques are oriented to obtain information about the lithium behavior in the local scale and/or in the macroscopic scale (≥mm range). As an example, the lithium atoms in a crystal have been observed by using newly developed transmission electron microscopy techniques [1] and the lithium distribution in the millimeter scale has been imaged by means of neutron radiography [2]. Though, in most cases, the lithium behavior at the local scale is not mirrored at the macroscopic scale. Therefore, the lithium characterization in the mesoscopic scale (μm range) would be of help to understand and to connect the mechanisms taking place in these scales.

Ion beam analysis (IBA) techniques are powerful tools which permit direct, non destructive and accurate quantitative elemental concentration characterization, including light ions such as lithium. Ion beam analysis techniques were developed in the early 1960s, as the Van de Graaff accelerators used for nuclear physics research were not able to produce the higher energies required in this field and new uses were devised for them. Thus being directly derived from nuclear physics, nowadays ion beam analysis techniques are well-established techniques widely employed in many different fields of knowledge, ranging from fundamental physics to fine arts, with special impact on materials science and solid state physics. Ion beam analysis techniques are based on the detection and analysis of the products emitted from the different processes induced when an energetic ion strikes on a target. They comprise a whole family of techniques including those based on scattering by target nuclei (Rutherford Backscattering Spectrometry, RBS, and Elastic Recoil Detection Analysis, ERDA), resonant and non-resonant nuclear reactions (RNRA and RNA, respectively), particle-induced γ-ray emission (PIGE) and particle-induced X-ray emission (PIXE), among others. A comprehensive description of ion beam analysis techniques can be found in Ref. [3]. Two breakthroughs to improve the ion beam analysis techniques capabilities for material analysis are the development of: (i) μ-beam scanning procedures and (ii) of external beams. The development of μ-beam scanning procedures in the 50's has enabled extension of ion beam analysis with additional spatial information, which allows measuring the elemental distribution over specific small areas of a sample. In the μ-probes, ions are raster scanned over the sample, thus enabling the extraction of 2D maps of structural and compositional information from the sample. Since the first "true" microprobe developed by Cookson and Pilling in 1970 in which they obtained a beam spot of 15 μm, with 15 nA [4], a lot of work has been carried out to improve spatial resolution by decreasing beam spot size. Nowadays, to the best of our knowledge, the spot beam size can be as small as few hundreds of nanometers, with 50–100 pA intensities [5].

In this paper we show a general description about the capabilities and limitations of ion beam analysis techniques to characterize the elemental composition and in particular the lithium content and distribution in the mesoscopic scale in Li-ion batteries. First, in Section 2.1, we review the state of the art of the use of ion beam analysis techniques for Li-ion batteries studies, showing some examples in which (p, p) and (p, γ) nuclear reactions have been successfully applied for lithium characterization, emphasizing their capabilities to carry lithium depth-profiling and lithium spatial distribution studies, respectively. Next, in Section 2.2, we indicate the precautions needed when designing an ion beam analysis experiments for lithium characterization. In Section 4.1, we illustrate the potential of the $^{7}Li(p,\alpha_0)^{4}He$ nuclear reaction to examine the lithium distribution, without destroying the sample. In Section 4.2, we show the capabilities of particle induced γ-ray (μ-PIGE) spectroscopy to characterize the lithium spatial distribution. In Section 4.3 we discuss about the possibility of carrying out a fully 3D characterization of the lithium distribution in electrodes by using nuclear reaction analysis techniques. In Section 5 we present the advantages of using ion beam analysis techniques for the characterization Li-ion batteries over more traditional techniques. Finally in Section 6 we describe the main limitations of the use of IBA for the characterization of Li-ion batteries.

2. Nuclear reaction analysis for Li characterization in lithium-ion batteries

Although the capabilities of nuclear reaction analysis techniques are amply known, to the best of our knowledge, their application to the characterization of Li-ion batteries has not been sufficiently exploited. Indeed, only few works have been devoted to this topic. For example Tadic *et al.* [6,7] have monitored changes in the elemental distribution at gel/polymer battery interfaces, Berger *et al.* [8] have characterized the elemental composition of ternary graphite-Li-Ca intercalation compounds, Beddy *et al.* [9] have characterized the lithium content of $LiNiVO_4$ films before and after lithium insertion, Swiatowska-Mrowiecka *et al.* [10] have studied the dosing of intercalated lithium and determined the composition of lithiated MoO_3 thin films, Andrade *et al.* [11] have measured the Li extraction of $LiMn_2O_4$ by chemical delihitation, Habrioux *et al.* [12] determined the lithium composition in C-$LiFePO_4$ as a function of its state of charge and Mima *et al.* [13] have characterized the lithium distribution in Li-ion battery positive electrodes containing $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ secondary particles ($0.75 \leq x \leq 1.0$) as a function of electrode thickness and charge parameters. The main conclusion from these works is that the specific capabilities of nuclear reaction analysis techniques are very powerful to investigate Li-ion batteries and in particular, to measure the Li distribution in electrodes which in combination with other techniques (X-ray absorption spectroscopy, X-ray tomography, scanning probe microscopy, transmission electron microscopy) contribute to understand the lithium intercalation/de-intercalation processes. All these works were focused on very specific aims. However, to the best of our knowledge a general description of the capabilities and limitations of nuclear reaction analysis techniques for Li-ion battery studies has not been presented so far. This is what we show in the following.

2.1. Capabilities of the nuclear reaction techniques for Li characterization

One of the key issues in Li-ion battery research is the knowledge of the lithium distribution as a function of depth, since these data allow obtaining information about the lithium diffusion in the electrodes, which is closely related to the performance of the