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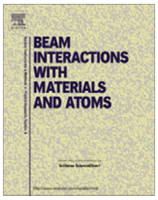

Li distribution characterization in Li-ion batteries positive electrodes containing $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ secondary particles ($0.75 \leqslant x \leqslant 1.0$)

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ABSTRACT

The elemental distribution of as-received (non-charged) and charged Li-ion battery positive electrodes containing $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ($0.75 \leqslant x \leqslant 1.0$) microparticles as active material is characterized by combining μ-PIXE and μ-PIGE techniques. PIGE measurements evidence that the Li distribution is inhomogeneous (existence of Li-rich and Li-depleted regions) in as-received electrodes corresponding with the distribution of secondary particles but it is homogeneous within the studied individual secondary micro-particles. The dependence of the Li distribution on electrode thickness and on charging conditions is characterized by measuring the Li distribution maps in specifically fabricated cross-sectional samples. These data show that decreasing the electrode thickness down to 35 μm and charging the batteries at slow rate give rise to more homogeneous Li depth profiles.

1. Introduction

The development of efficient storage technologies for electrical energy plays an important role mainly in the progress of portable consumer electronics and electric vehicles. Nowadays, Li-ion batteries are attractive candidates for these applications since they can provide high energy and high power densities. 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.

Basically, Li-ion batteries consist of a positive and a negative electrode separated by an electrolyte layer, which must be an ionic conductor and electronic insulator. Once positive and negative electrodes are linked by an external circuit, spontaneous electrochemical reactions take place, in which chemical energy is transformed into electrical energy, namely, the discharge process takes place. For the reverse reaction, an electric current has to be applied. These reactions involve the lithium-ion diffusion between the positive and the negative electrodes [1]. Therefore, the performance of a Li-ion battery strongly depends, among other factors, on the characteristic of the electrodes and in particular on the Li-ion diffusion capabilities on it. Because of this reason the study of the Li distribution in the positive electrode is one of the main points of concern in further battery development.

However, Li characterization is not a trivial task, in particular, if depth resolution is required. The Li distribution in regions close to the sample surface can be inferred from electron spectroscopy techniques [2–4]. However, the basics of these techniques hamper to carry out precise Li distribution characterization mainly because of two reasons: (i) the total amount of Li cannot be accurately characterized, (ii) as a result of electron-matter interaction they can only be used for characterization in the near surface region with low spatial resolution. Some other material analysis methods such as laser induced breakdown spectroscopy or atomic absorption have also poor sensitivity to measure the Li concentration. Synchrotron Radiation (SR) has been also applied to characterize Li distribution by measuring the absorption edge shift of Co, Ni, and so on, using the X-ray absorption fine structure techniques (XAFS), although the Li determination measurement is indirect [5,6].

Ion beam analysis (IBA) techniques [7] are powerful tools which permit direct, nondestructive and accurate quantitative elemental concentration characterization, including light ions such as Li [8,9]. Moreover, the use of μ-beam scanning procedures allows studying elemental concentration distributions with high lateral resolution (in the μm range).

In this paper we investigate the Li and Ni distribution for as-received and charged positive electrode containing $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ($0.75 \leqslant x \leqslant 1.0$) microparticles as active material by

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using particle induced γ-ray emission (PIGE) and particle induced X-ray emission (PIXE), respectively. Li distribution maps of individual secondary particles (active material) are shown. The dependences of the Li distribution on electrode thickness as well as, on the charge process parameters are presented.

2. Experimental set-up

We have measured Li ion battery positive electrodes with thickness of 35 μm and 105 μm, which consist of $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ($0.75 \leqslant x \leqslant 1.0$) micrometer size particles as active material [10–12] mixed with artificial carbon and binder (note that no electrolyte in the sample), where the weight percentages are 85% for active material, 10% for carbon and 5% for binder. This positive electrode is coated on an Al current collector of 20 μm thick.

For fabricating charged samples, the above described positive electrode is attached to an electrolyte and a Li metal negative electrode for charging. Then, the current is applied. The specific charge conditions are summarized in Table I. After charge, the battery is quickly dissembled, typically within 3 min, and the liquid electrolyte is dried out to quench the Li-diffusion. In this way, the Li depth distribution after the charge is preserved. Then, the positive electrode was dissembled and cut to observe its cross section. It is worthwhile to mention that the drying process is intended not to substantially influence the Li distribution in the electrolyte. Thus, the Li distribution in the electrolyte prior to and after the drying process is assumed to be the same.

The Li and Ni spatial distributions are simultaneously characterized for as-received (prior to any charge cycle) and charged (under different conditions) positive electrode cross sections by μ-PIGE and μ-PIXE, respectively. PIGE measurements were carried out by using the ^{7}Li(p, p′γ) ^{7}Li nuclear reaction. Measurements were carried out at the microbeam line of TIARA-JAEA [13]. For the measurements a H^+ beam at an energy of 3.0 MeV was used. The beam current was selected to be 300 pA. The total accumulated charge per map was around 0.48 μC. The beam current was measured in a conductor foil located at the sample holder. The beam diameter, full width at half maximum, was 1.5 μm and the total scan areas were $\leqslant 200 \times 200$ μm^2. The scanning step was 128 of the total scan range, providing 128 × 128 space points for each image. Measurements were carried out in high vacuum at a pressure range of 10^{-5} mbar in order to achieve a good beam spatial resolution. Nevertheless, because of the microbeam halo effects and the lateral straggling of the beam penetrating into the samples, the lateral resolution of the microbeam scans is somewhat larger than the beam diameter. The characteristic emitted γ- and X-rays were collected by a HPGe and by a Li-doped Si detector located at 0° and at 140° to the beam direction, respectively. Under these conditions, typical measuring times were around 30 min. We note that these experimental conditions avoid beam-induced lithium diffusion. Indeed, several spectra were sequentially measured on the same measuring area up to a dose of three times higher than that used in real experiments and no ion beam-induced lithium diffusion was detected. The data acquisition system uses the Microsoft Visual BASIC and runs on the Windows-based PC platform.

For measuring the cross sectional distributions of Li in the electrodes, the electrode cross sections were polished for 10 h by using a focused Ar beam at an energy of 6 keV prior to the ion beam analysis. The beam current of the JEOL SM-09010 Cross Section Polisher was 120 μA. Special precautions were taken during the cutting process to prevent the diffusion of light elements, in particular Li. Indeed in order to be sure that the cutting process does not influence the Li distribution, measurements are carried out for the samples cut from two opposite directions. No significant difference between them was observed. The morphology of the electrode was characterized by means of electron scanning microscopy (SEM) using a HITACHI S-4300 microscope.

3. Results and discussion

A brief overview of the studied samples together with the charge conditions is listed in Table I.

3.1. Elemental composition characterization

The elemental distribution is characterized by μ-PIGE and μ-PIXE techniques. Typical μ-PIGE and μ-PIXE spectra for an as-received and a charged positive electrode are shown in Fig. 1a and b, respectively. The nuclear reactions which contribute to the observed gamma ray spectra are also shown in the table in Fig. 1. These data illustrate that the samples are composed of the active material elements: Ni, Co and Al. Some other elements such as F and O are binder constituents. As illustrated in Fig. 1a (inset), the Li yield is higher for the uncharged than for the charged electrode, whereas the Ni yield (Fig. 1b) is almost the same in both of them. From these data the Li/Ni ratio is estimated to be 1.10 for the as-received electrode and 0.94 for the charged one.

It is worthwhile to mention that according to TRIM Monte Carlo [14] simulations, the 3 MeV proton beam penetration depth is calculated to be 58 μm by assuming an electrode density of 2.1 g/cm^3. Thus, the resulting γ-ray yields are sums of yields from the sample surface up to the depth of 58 μm.

SEM images of the as-received electrode, depicted in Fig. 2a, show a high density of micro-particles randomly distributed at high density with arbitrary shapes and sizes ranging from 5 to 10 μm. μ-PIGE (Fig 2b) and μ-PIXE (Fig 2c) maps, estimated from the defined region of interests, reveal that the micro-particles contain Li, Ni, Co and Al (Co and Al maps are not shown). Thus, they are $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ secondary particles. By comparing SEM, μ-PIGE and μ-PIXE images, complete correspondence between these images is deduced.

3.2. Li distribution within the secondary particle

One important parameter to be controlled in further development of Li-ion batteries is the homogeneity of the Li distribution within individual secondary particles. Previous works carried out on $LiCoO_2$, $LiNiO_2$ and $LiFePO_4$ evidence that these positive electrodes present two-phase transitions during Li intercalation and Li extraction, which give rise to an asymmetric Li distribution (Li-rich and Li-depleted regions) within the individual particles of active material [15]. This two-phase transition is very undesirable

Table I
Brief overview of sample codes, thickness and charge parameters for the analyzed electrodes.

Sample code	Thickness (μm)	Charge current density (mA/cm^2)	Charge time (min.)
SP1-20-0-0	20	0	0
SP2-20-0-0	20	0	0
SP3-20-0.005-6000	20	0.005	6000
SP4-20-0.005-6000	20	0.005	6000
PE105-6-15	105	6	15
PE35-2-15	35	2	15
PE105-0.6-150	105	0.6	150

*The sample code (SPX-T-D-t) corresponds to SP: individual secondary particle, X: particle number, T: sample thickness, D: charge current density, and t: charge time. The sample code (PE-T-D-t) corresponds to PE positive electrode, T: sample thickness, D: charge current density, and t: charge time.