Spectrochimica Acta Part B 85 (2013) 62–70

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Surface and in-depth characterization of lithium-ion battery cathodes at different cycle states using confocal micro-X-ray fluorescence-X-ray absorption near edge structure analysis

Magnus Menzel [a], Annalena Schlifke [a], Mareike Falk [b], Jürgen Janek [b], Michael Fröba [a,*], Ursula Elisabeth Adriane Fittschen [a,*]

[a] Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
[b] Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany

ARTICLE INFO

Article history:
Received 28 November 2012
Accepted 5 April 2013
Available online 12 April 2013

Keywords:
Confocal
Micro-XRF
XANES
Li-ion battery
Cathode

ABSTRACT

The cathode material $LiNi_{0.5}Mn_{1.5}O_4$ for lithium-ion batteries has been studied with confocal micro-X-ray fluorescence (CMXRF) combined with X-ray absorption near edge structure (XANES) at the Mn-K edge and the Ni-K edge. This technique allows for a non-destructive, spatially resolved (x, y and z) investigation of the oxidation states of surface areas and to some extent of deeper layers of the electrode. Until now CMXRF-XANES has been applied to a limited number of applications, mainly geo-science. Here, we introduce this technique to material science applications and show its performance to study a part of a working system. A novel mesoporous $LiNi_{0.5}Mn_{1.5}O_4$ material was cycled (charged and discharged) to investigate the effects on the oxidation states at the cathode/electrolyte interface. With this approach the degradation of Mn^{3+} to Mn^{4+} only observable at the surface of the electrode could be directly shown. The spatially resolved non-destructive analysis provides knowledge helpful for further understanding of deterioration and the development of high voltage battery materials, because of its nondestructive nature it will be also suitable to monitor processes during battery cycling.

1. Introduction

1.1. Spatially resolved analysis of solid state

Characterization of solid state matter is indispensable in all scientific approaches where systems in their original state are to be studied e.g. functional synthetic materials like catalysts, bioorganic and inorganic compounds like roots, teeth, bone or geological samples. Because of their nondestructiveness and relatively high information depth (several μm), X-ray related methods are at the forefront e.g. XRD (X-ray diffraction for crystal structure), XRF (elemental occurrence) and XAFS (X-ray absorption fine structure for structure and valence). The use of focusing X-ray optics also allows for spatially resolved analysis, initially in x and y [1]. In-depth analysis can be achieved by a stepwise grinding of the material. Though, this is not always favored e.g. if the samples are precious or brittle or in-situ analyses are to be performed. Here nondestructive techniques capable to give 3D information are favorable e.g. confocal micro-X-ray fluorescence (CMXRF), that was first described by Ding, Gao and Havrilla [2], and the more frequently used tomography technique. The spatial resolution of the latter has been improved over the recent years, to well below micrometer dimensions at newest synchrotron radiation sources. Unfortunately, tomography studies are hampered regarding rather large and non-opaque samples like the battery cathodes studied here. And, if entire systems or representative parts of the battery cathode are to be characterized, spatial resolution of several micrometers is favorable because it can be accomplished in reasonable time. In this case CMXRF setups are advantageous.

1.2. CMXRF and CMXRF-XANES

The performance of CMXRF was highlighted recently [3]. Two sets of X-ray optics enable spatial selectivity both laterally and in depth. One X-ray optic focuses the primary beam, which excites the sample material within its path. The second optic in front of the detector accepts only photons originating from that volume, which is defined by the overlapping foci of both sets of optics [4]. Combined with crystal monochromators and high brilliance source available at synchrotron facilities it is possible to measure X-ray absorption near edge structure (XANES) spectra of a defined volume of the sample capable of elucidating the chemical species of an element. CMXRF XANES has been used in a limited number of studies looking at inclusions in

---

* Corresponding authors. Tel.: +49 40 42838 2332.
E-mail addresses: froeba@chemie.uni-hamburg.de (M. Fröba), ursula.fittschen@chemie.uni-hamburg.de (U.E.A. Fittschen).

0584-8547/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sab.2013.04.001

diamonds by Silversmit et al. [4,5] and on geological material by Denecke et al. [6].

Here we introduce CMXRF-XANES to the analysis of functional material, namely Li-ion battery cathodes made from the high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$. The spatially resolved approach enables studying different parts and different layers of the cathode material exclusively, which offers more specific information than bulk XANES and bulk XRD studies which were available before. The nondestructive nature allows for further analyses of cathode degradation e.g. XRD, SEM (Scanning electron microscopy).

The cathode under investigation in our experiments is built from mesoporous material especially designed to ensure high mobility of charge carriers in Li-ion batteries. However, they also show poor cycle stability.

1.3. Li-ion battery cathode material

The demand for energy storage is increasing, especially high energy densities for the use in electric vehicles or the storage of the only partly predictable power sources wind and sunlight. Rechargeable lithium-ion batteries offer one of the highest energy densities and have been the subject of intensive research in recent years to push this technology beyond the great impact they had on consumer electronics.

1.3.1. High voltage spinel

Improving the cathode material is essential, since it is the primary factor in regard to energy density, rate capability and cost of Li-ion batteries. One promising cathode material is the high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ in the space group $Fd\overline{3}m$ which was studied here. This material shows a random distribution of Mn and Ni ions, which is caused by Mn^{3+}-ions substitution generated by a small oxygen deficiency. It displays a remarkable discharge voltage plateau at around 4.7 V and the material is inexpensive and environmentally benign [7,8].

The oxidation state of manganese is one of the crucial criteria for the capacity at a high voltage and the stability against corrosion. The oxidation of Mn^{3+} to Mn^{4+} is responsible for the 4.1 V plateau, the capacity at 4.7 V is attributed to the Ni^{2+}/Ni^{4+} couple [7,9–11].

1.3.2. Corrosion of the material

However at this high voltage a possible corrosion between the electrolyte and the cathode surface is a major concern, especially at elevated temperatures (60 °C) [12]. Oxidization of the electrolyte has been identified as one major reason for severe performance loss of the high voltage spinel after several hundred cycles. Additionally, redox reactions of Mn have been reported to contribute to performance loss. The conducting salt $LiPF_6$, most commonly used, can readily decompose reacting with trace amounts of water and form HF that is continuously attacking the cathode material [13–16].

The disproportion reaction from Mn^{3+} to Mn^{2+} and Mn^{4+} of $LiMn_2O_4$ catalyzed by aqueous acidic solutions was found by Hunter [17]. Similar reactions occur during electrochemical cycling [18,19]. It could be shown that HF formed from the electrolyte accelerates this reaction in the battery [15].

Local formation of λ-MnO_2 out of Mn^{4+} on the cathode is discussed by Aurbach et al. [13] though this does not indicate higher Mn^{4+} concentrations at this location. None of these studies were capable of monitoring the change of valence of Mn in the solid state material. Consequently, a direct detection of Mn valence would prove the proposed processes and add additional knowledge to understand the multidimensional processes taking place in cycled batteries.

1.4. XANES on battery material

As mentioned before, determination of valence of solid state matter can be accomplished using XANES. Several cathode materials have been investigated using XANES [20–25]. In-situ XANES experiments have shown the different oxidation states and their correlation to the high voltage [26] and the dynamical structure behavior of Mn ($Li_{1+y}Mn_{2-y}O_4$) as a function of both Li content and Li deintercalation [27]. However, the setups used in those studies allow only for analysis of the bulk material. Because electrolyte–cathode reactions occur at the interface, valence alteration exclusively in this region can be expected and analysis of this region would be highly interesting.

Spatially resolved XANES analyses of Ni metal cathode were recently shown by Meirer et al. using full field transmission X-ray spectrometry and a charge-coupled device (CCD) detector [28]. Excellent spatial resolution was achieved with this setup (down to 30 nm). Nonetheless, difficulties may be experienced analyzing material having complex matrix or composition. Usually, CCD detectors count all incoming fluorescence and do not allow for energy dispersive detection. Therefore, depending on the edge of interest, other components included in the material will add significantly to the background e.g. Mn in the $LiNi_{0.5}Mn_{1.5}O_4$ (spinel studied here) when analyzing the Ni K edge, Mn and Co in $LiNi_{0.21}Mn_{0.21}Co_{0.58}O_2$ studying the Ni Kedge, and Cr in $LiMn_{0.8}Cr_{0.2}O_2$ when studying the Mn K edge.

Additionally, samples need to be either transparent or thin to be suitable for transmission analysis. The electrode studied in this work did not qualify for transmission analysis, as the electrode system consisting of the cathode material prepared on an Al or Cu current collector was not transparent.

1.5. CMXRF-XANES in-depth analysis

None of the XANES studies above monitored processes leading to degradation of the cathode but rather expected changes in valence from the battery operation. Degradation first occurs at the interface of electrode and electrolyte and eventually progresses on into deeper layers of the material. The combination of CMXRF and XANES allowed us to exclusively probe the surface and to some extent also deeper layers of this electrode system. In-depth XANES is hampered by absorption. In the CMXRF-XANES by Silversmit et al. [4] surface and subsurface regions in material transparent to X-rays (e.g. diamond was polished down close to the inclusion) were analyzed. In the study by Denecke et al. [6] distortion of the detected 3D Micro-XANES spectra due to absorption effects is not discussed. It is described that the monitored Nd inclusion was found on top of an Fe rich region. Just recently, Luehl et al. published a study, showing that absorption effects can be dealt with by fundamental parameter modeling on reference material [29]. The model is based on quantification procedure for 3D Micro-XRF setups developed by Malzer and Kanngießer [30] in combination with a quantification procedure for stratified materials [31]. The model requires a detailed knowledge of sample parameters e.g. density and composition. The $LiNi_{0.5}Mn_{1.5}O_4$ cathodes are formulations from either mesoporous or bulk material having binder and conductive carbon added to it prepared onto a current collector. Therefore, density and composition of the electrode usually vary to some extent. Accordingly, we have followed a different approach. To be able to detect valence of Mn in depth of the cathode material, we extended the XANES scan well beyond the edge (400 eV) and normalized all spectra to the upper end of the post edge line, which is assumed to be not affected by absorption evaluated by analysis on bulk MnO_2. However, the error for the determination of the valence in depth is also increasing due to the higher uncertainty for the post-edge line fitting.

With this approach we can show that the newly developed cathode material shows valence changes after successive cycling exclusively at the surface and probably retain original Mn valence in depth.

Our work proves CMXRF-XANES to be extremely useful to study performance of material, especially where the material is part of a working system and valence changes are involved. For this as well as for other materials it is necessary to use a nondestructive method to be able to study the material, before, during and after use.