Spectrochimica Acta Part B 94–95 (2014) 22–26

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Sulfur X-ray absorption fine structure in porous Li–S cathode films measured under argon atmospheric conditions

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ARTICLE INFO

Article history:
Received 27 June 2013
Accepted 4 March 2014
Available online 15 March 2014

Keywords:
X-ray absorption spectroscopy
Lithium sulfur battery
Material characterization
Electrochemical characterization
Synchrotron radiation

ABSTRACT

In this paper we present the first results for the characterization of highly porous cathode materials with pore sizes below 1 μm for Lithium Sulfur (Li–S) batteries by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. A novel cathode material of porous carbon films fabricated with colloidal array templates has been investigated. In addition, an electrochemical characterization has been performed aiming on an improved correlation of physical and chemical parameters with the electrochemical performance. The performed NEXAFS measurements of cathode materials allowed for a chemical speciation of the sulfur content inside the cathode material. The aim of the presented investigation was to evaluate the potential of the NEXAFS technique to characterize sulfur in novel battery material. The long term goal for the characterization of the battery materials is the sensitive identification of undesired side reactions, such as the polysulfide shuttle, which takes place during charging and discharging of the battery.

The main drawback associated with the investigation of these materials is the fact that NEXAFS measurements can usually only be performed ex situ due to the limited in situ instrumentation being available. For Li–S batteries this problem is more pronounced because of the low photon energies needed to study the sulfur K absorption edge at 2472 eV.

We employed 1 μm thick Si_3N_4 windows to construct sealed argon cells for NEXAFS measurements under ultra high vacuum (UHV) conditions as a first step towards in situ measurements. The cells keep the sample under argon atmosphere at any time and the X-ray beam passes mainly through vacuum which enables the detection of the low energy X-ray emission of sulfur. Using these argon cells we found indications for the presence of lithium polysulfides in the cathode films whereas the correlations to the offline electrochemical results remain somewhat ambiguous. As a consequence of these findings one may state that measurements for battery material characterization are preferably to be performed completely in situ with the electrochemical measurements taking place simultaneously in order to obtain clear and unambiguous results.

1. Introduction

Development of methods for storage of electrical energy has become highly important in recent time [1–3]. Among different concepts for energy storage rechargeable batteries those based on lithium ions deserve particular attention [4,5]. In fact, lithium is the lightest metal and has the highest oxidation potential among the metals allowing an energy density much higher than Ni–Cd rechargeable batteries, for example. Currently, Li-ion batteries based on $LiMnO_2$, $LiFePO_4$ and $LiCoO_2$ cathodes as well as graphite anodes are in practical use [6–9]. These Li-ion batteries provide very high Coulombic efficiency and good cycling sufficiently well allowing for practical applications. However, they suffer from an insufficient energy density of around 400–500 W h/kg.

Li–S batteries are the emerging class of rechargeable batteries, which potentially can provide an energy density 4 to 5 times higher than the energy density of Li-ion batteries [10–13]. Although the lithium–sulfur system operates at a comparably low average potential of 2.1 V against Li+/Li, it shows a high theoretical specific energy of 2600 W h/kg due to the extraordinary theoretical specific capacity of 1675 mA h/g of sulfur. Moreover, in advantage to MnO_2 and CoO_2, which are relatively expensive (MnO_2 ca. 3 $/kg; CoO_2 40 $/kg) sulfur is extremely

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http://dx.doi.org/10.1016/j.sab.2014.03.001
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cheap (<1 $/kg), non-toxic and is produced as a side product of coal and oil conversion. On the other hand, sulfur itself is electrically insulating and therefore composite cathodes, which consist of sulfur and porous conductive materials such as carbon, are used.

One of the main problems limiting a broader use of Li–S batteries is the rapid decay of capacity mainly due to so-called polysulfide [14] shuttle. Understanding of physico-chemical process related to polysulfides is essential to solve this problem. In this paper, we report the use of NEXAFS spectroscopy to address these analytical requests from material research and development.

NEXAFS spectroscopy has proven as a versatile and non-destructive analytical method to measure the chemical species, e.g. for various sulfur species [15]. In the case of transition metals NEXAFS techniques have been applied successfully to perform in situ measurements [16–21] of Li-ion batteries. To enable the in situ detection of the sulfur absorption fine structure, thin windows with a thickness of a few micrometers are required because of the strong attenuation of the characteristic X-rays with low energy. The first in situ experiment investigating the sulfur fine structure of Li–S batteries has been performed by Gao et al. [22] and recently Cuisinier et al. [23] have performed the first NEXAFS measurements of a Li–S carbon cathode film simultaneous to charge and discharge cycling. Cuisinier et al. have been successful in identifying the polysulfide formation by NEXAFS spectroscopy during the charge and discharge of their Li–S material. To obtain the necessary reference spectra they used reference samples characterized by NMR and XRD.

In the frame of the project the results of which we are reporting here, such an effort regarding the preparation of reference samples was not possible. Hence, we decided to use theoretically obtained reference spectra for the identification of the lithium polysulfides. Even though the employed theoretical models do not fully account for the potential impact of the solvent, we found chemical shifts similar to the experimental findings of Cuisinier et al. [23].

2. Experiment

2.1. Li–S cathode material

The cathode material system was a porous carbon film fabricated by using colloidal crystal array templates of PMMA beads with different diameters ranging from 190 nm to 740 nm. The cathodes were prepared using particle-based template methods. Briefly, PMMA particles with different diameters ranging from 190 nm to 740 nm were assembled to form a closely packed opal-like structure. The resorcinol–formaldehyde resin precursor solution was soaked into porous colloidal crystal arrays to fill interparticle interstices. The resin was carbonized that leads to the formation of a porous carbon inverse-opal scaffold. The material was prepared as thick cathode films with a mean thickness of about 50 μm and was used to assemble battery cells for electrochemical characterization.

2.2. Electrochemical characterization

Electrodes (with a total S ratio of 55 w%) were prepared by slurry technique for the electrochemical characterization. The resulting electrodes were composed of a nano-structured carbon–sulfur composite material (82 w%), PVdF binder (8 w%) and Super P® Li (10 w%) on a Ni-foil current collector. A Swagelok® T-cell was used as a testing device using lithium as counter and reference electrode while the carbon–sulfur electrode served as working electrode. The charge/discharge measurements were recorded using a Maccor Series 4000 battery tester applying a C-rate of 0.1C between 1.5 V and 3.0 V vs. Li/Li+. For the preparation of samples at different states of charge cyclovoltammetric measurements were carried out using a Biologic MPG-2 battery tester. Therefore the scanning rate was set to 0.5 mV/s with vertex potentials at 1 V and 3.2 V vs. Li/Li+. The measurement was stopped at the fully discharged state at 1 V and at the fully recharged state at 3.2 V after one and ten cycles respectively. A 1 M solution of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a mixture of 1,2-Dimethoxyethane/1,3-Dioxolane (1/1, v/v) served as electrolyte. Further details about the electrochemical measurements have been compiled in the recently submitted manuscript of Agrawal et al. [24].

The electrochemical results show a high initial capacity but a rather poor cycling stability of the material. A strongly reduced capacity after several recharge cycles was obtained, see Fig. 1.

2.3. Near edge absorption fine structure spectroscopy

The experiments have been carried out in an ultra high vacuum (UHV) chamber [25] at the PTB Four Crystal Monochromator (FCM) beamline [26] located at the synchrotron facility BESSY II in Berlin. The vacuum conditions allow for both the efficient excitation and detection of sulfur with X-ray energies of 2.3 keV to 2.5 keV. In addition, UHV conditions are required because of the window-less and cooled detector used for this experiment. The FCM beamline provides X-ray radiation with high spectral purity and high flux in the energy range of 1.75 keV to 10.5 keV. The UHV chamber allows for total reflection, grazing incidence and conventional 45°/45° beam geometries. The emitted fluorescence radiation is detected by an energy-dispersive Silicon Drift Detector (SDD) under 60° with respect to the incidence X-ray beam, see Fig. 2. For the NEXAFS measurements a 30°/30° beam geometry was chosen and the energy of the monochromator was tuned across the sulfur K absorption edge. The fluorescence radiation emitted by the samples was recorded by the SDD. The typical recording time per incident energy step was 15 s and the step size was 0.25 eV.

To probe the chemical state of the sulfur content inside the cathode films, NEXAFS measurements were carried out with freshly prepared cathode films and with cathode films after the electrochemical characterization. For this purpose we recently designed an UHV compatible thin window argon cell with a 1 μm thick free-standing Si_3N_4 membrane used as X-ray window. The transmittance of the window is about 65% for X-rays in the energy region of the sulfur K absorption edge. In an argon glove box the cathode films were placed into the argon cell directly after the disassembly of the battery half-cell. Afterwards the argon cells were sealed. This procedure ensures that the cathode films were always handled under argon atmospheric condition. The argon cell preserves this condition for the transport of the samples and the measurements in the UHV chamber.

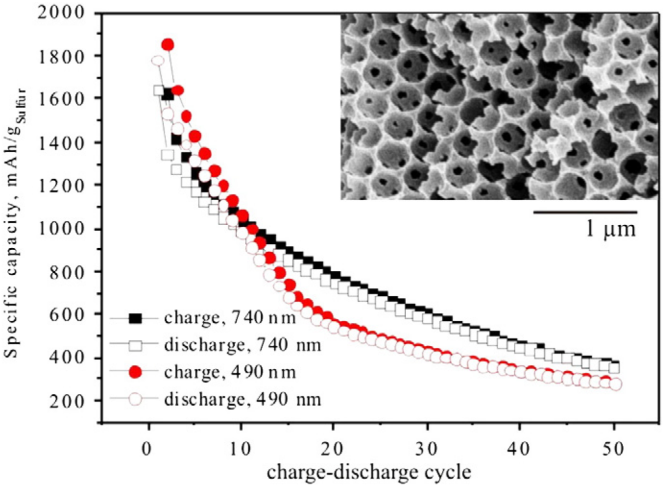

Fig. 1. Structure of porous carbon (inset) obtained using particle-template method and electrochemical properties of cathode based on this structure.