

Advanced in situ characterization methods applied to carbonaceous materials

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Available online 31 May 2005

Abstract

This paper is an overview of the progress recently achieved in our laboratory in the development and application of four in situ methods; namely X-ray diffraction (both synchrotron-based and standard), Raman microscopy, differential electrochemical mass spectrometry (DEMS), and infrared spectroscopy. We show representative results on graphite electrodes for each method as an illustration, in particular (i) the influence of the lithium intercalation and graphite exfoliation on the shift of the (002)-reflection of graphite, (ii) Raman single point and mapping measurements of graphite surface, (iii) gas evolution during solid electrolyte interphase (SEI) formation on graphite electrodes, and (iv) the development of infrared spectra during the SEI formation in γ -butyrolactone based electrolytes.

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Keywords: Lithium-ion battery; Graphite electrode; In situ X-ray diffraction; In situ Raman mapping; In situ mass spectrometry; In situ infrared spectroscopy

1. Introduction

In lithium-ion batteries, carbonaceous materials are used in both electrodes. In the negative electrode the carbonaceous material stores lithium ions [1]. Nowadays, artificial graphite is used in advanced batteries [2]. It is the preferred material on account of low cost, low irreversible charge capacity, outstanding cycling stability, and ability to provide very high currents [3]. (Micro)structural parameters [4] have a strong influence on the lithium intercalation mechanism into carbons and affect their electrochemical behavior [5]. Moreover, the electrode potential of lithiated carbon is far beyond the thermodynamic stability window of the most commonly used organic electrolytes. Hence, the electrolyte (either liquid or gelled) is reduced forming at the surface of the negative electrode material a layer called the solid electrolyte interphase (SEI) [6]. In most cases gas is formed at the carbon/electrolyte interface at the same time [7–9]. Fortunately, the SEI, once formed, normally prevents further reductive electrolyte decomposition and gas formation. A clear identification of the SEI composition and its formation mechanism(s) is important for thorough understanding and optimization of lithium-ion

batteries. The SEI layer consists of decomposition products of electrolyte salt and solvent(s) [1,6,10–17]. Models assume that the SEI is composed of two major constituents described as inorganic and organic interpenetrating layers [1]. The composition of the inorganic layer is fairly well understood. But complete understanding of the organic layer remains a challenge because of the inevitable exposure of the SEI film to air and/or vacuum which occurs when using common analytical methods. This results in a loss of volatile (organic) components, shrinkage of the film, and even in changes in the chemistry of the film. Hence, the use of in situ analytical tools is advantageous. In the following text, an overview will be presented of the progress achieved in our laboratory in the development and application of suitable in situ methods during the last five years since our first overview was published [18]. For each method, the corresponding electrochemical cell will be depicted and a representative result will be reported.

2. In situ X-ray diffraction

Due to the reversible lithium intercalation into graphite the interlayer distance between the graphene layers increases moderately (10.3% was calculated for LiC_6) [1,4,19]. In

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contrast, in the case of irreversible processes one can observe either strong lattice expansion (due to solvated intercalation [20]) or no lattice change (due to cracking of the particles and electrical isolation of most of the active mass by SEI films due to strong electrolyte decomposition [21]). In situ X-ray diffraction (XRD) is a powerful tool to monitor the structural evolution of active battery materials during cycling without the risk of contamination or degradation of the materials. In the particular case of lithium intercalation into graphite the XRD method provides information on the reversibility of the intercalation process. However, great care must be exercised in designing the cell. This is because XRD probes the bulk of the particles while their potential is determined by the lithium concentration at the particle surface. Thus, rapid equilibration of the entire insertion electrode should be achieved in a well-designed cell. Consequently, the current density distribution over the surface of the working electrode should be uniform, while the internal resistance of the cell should be minimized.

The use of synchrotron light is particularly suited because the X-ray beam shows a very high intensity and its wavelength can be tuned. The PSI synchrotron is unique in this context because of its very high beam stability, admitting for long time measurement series without difficulties in data analysis. The high intensity of the beam allows the use of a standard electrochemical arrangement without compromising the electrochemical properties of the cell. In our case we use “coffee-bag” type cells (Fig. 1) with copper grids as current collectors for both, the graphite working electrode and the lithium counter electrode. (For experiments on positive electrode materials an aluminum grid current collector is used.) The collection is very fast; one diffraction pattern can be normally recorded within 5–20 s. As an example we present in Fig. 2 a synchrotron in situ X-ray diffraction study on a standard graphite electrode in a standard battery electrolyte, 1 M LiPF₆ in EC/DMC (1:1, w/w). Indeed, the (002)-reflection of graphite shifts to lower reflection angles during lithium intercalation. The observed line shift confirms the intercalation of naked lithium ions without their solvation shells into the graphite indicating a highly reversible intercalation process.

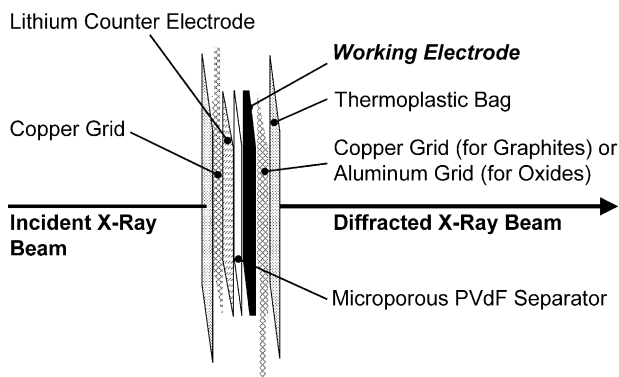


Fig. 1. The electrochemical cell for in situ X-ray diffraction using synchrotron light.

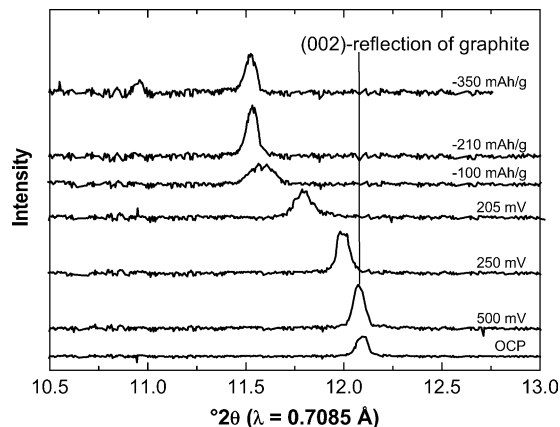


Fig. 2. In situ synchrotron X-ray diffraction patterns of standard graphite; electrolyte 1 M LiPF₆ in EC/DMC (1:1, w/w); all quoted potentials are vs. Li/Li⁺; OCP = open circuit potential.

Apart from the very fast spectra collection, the synchrotron-based technique faces two major challenges, the availability of the beam and the very high cost of the synchrotron beam time. A number of X-ray diffraction studies can be performed with a standard laboratory diffractometer as well. However, the cell must be modified and the time necessary for recording one diffraction pattern is significantly longer. Our in situ cell (Fig. 3) has an internal arrangement which resembles that of a coin cell. Thus, the current density on the working electrode is uniform. The material of the cell body is PEEK (poly ether ether ketone) polymer which is stable in all relevant electrolytes. The beam attenuation due to the PEEK material is minor in comparison to the X-ray absorption in the electrolyte solution. Moreover, there are no diffraction patterns from the PEEK but a broad band at ca.

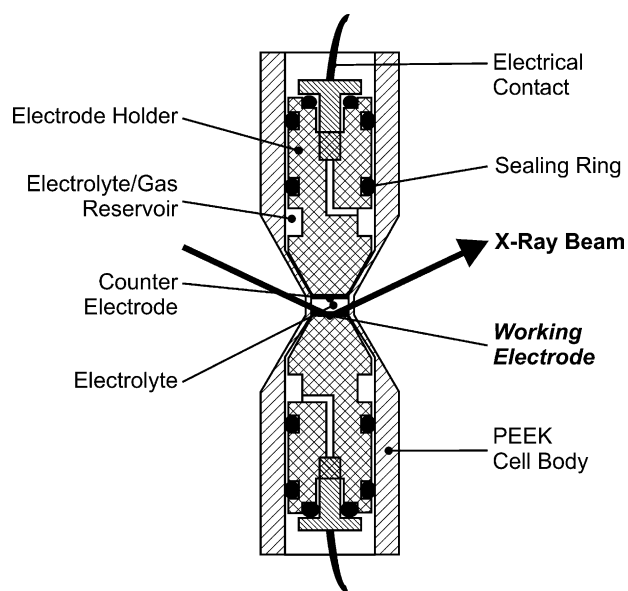


Fig. 3. The electrochemical cell for in situ X-ray diffraction using a standard laboratory diffractometer.

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