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Structural investigations of $LiFePO_4$ electrodes and in situ studies by Fe X-ray absorption spectroscopy

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Abstract

Fe K-edge X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) have been performed on electrodes containing $LiFePO_4$ to determine the local atomic and electronic structure and their stability with electrochemical cycling. A versatile electrochemical in situ cell has been constructed for long-term soft and hard X-ray experiments for the structural investigation on battery electrodes during the lithium-insertion/extraction processes. The device is used here for an X-ray absorption spectroscopic study of lithium insertion/extraction in a $LiFePO_4$ electrode, where the electrode contained about 7.7 mg of $LiFePO_4$ on a 20 μm thick Al-foil. Fe K-edge X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) have been performed on this electrode to determine the local atomic and electronic structure and their stability with electrochemical cycling. The initial state ($LiFePO_4$) showed iron to be in the Fe^{2+} state corresponding to the initial state (0.0 mAh) of the cell, whereas in the delithiated state ($FePO_4$) iron was found to be in the Fe^{3+} state corresponding to the final charged state (3 mAh). XANES region of the XAS spectra revealed a high spin configuration for the two states (Fe (II), d^6 and Fe (III), d^5). The results confirm that the olivine structure of the $LiFePO_4$ and $FePO_4$ is retained by the electrodes in agreement with the XRD observations reported previously. These results confirm that $LiFePO_4$ cathode material retains good structural short-range order leading to superior cycling capability.

Keywords: Fe K-edge; X-ray absorption near edge spectroscopy; Electrodes

1. Introduction

The emergence of portable telecommunications, computer equipment and, ultimately, electric and hybrid vehicles has created a growing demand for improvements in energy storage devices that are cost effective, operate for a longer time, and are smaller in size and weight [1]. Transition metal oxides have been investigated as active cathode materials because of their high potential versus Li/Li^+ and in many of the materials a large proportion of the lithium can be inserted/extracted reversibly.

Lithium insertion has been investigated in several Fe-containing compounds such as Li_3FeN_2 [2], $LiFe_5O_8$ [3], Fe_3O_4 [4], Fe_2O_3 [5] and $FePS_3$ [6]. These compounds rely on a Fe^{3+}/Fe^{2+} redox couple and hence have a low open-circuit voltage versus Li/Li^+. The substitution of oxygen by a polyanion $MO_4{}^{3-}$ like sulfate or phosphate lowers the Fermi level of the Fe^{3+}/Fe^{2+} redox couple and thereby increases the cell potential [7–9]. This effect is more pronounced for compounds with fewer covalent Fe–O bonds, where M in $MO_4{}^{3-}$ determines the strength of the Fe–O covalency via an inductive effect [10]. Since the demonstration of reversible

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electrochemical lithium insertion–extraction for $LiFePO_4$ in 1997 [11], lithium transition metal phosphates with an ordered olivine structure, $LiMPO_4$ (M = Co, Ni, Mn, Fe, Cu) have attracted much attention as promising new cathode materials for rechargeable lithium batteries [12–15]. One of the most promising candidates for rechargeable lithium cells is $LiFePO_4$, with a theoretical capacity of 170 mAh/g [11] and a voltage of >3.4 V versus Li/Li^+. $LiFePO_4$ is inexpensive, non-toxic, non-hygroscopic and environmentally friendly. It occurs in nature as the mineral triphylite, which has an orthorhombic unit cell (space group *Pmna*) [16] and often contains varying amounts of manganese as in $LiFe_xMn_{1-x}PO_4$. Both Li and M atoms are in octahedral sites with Li located in the 4a and M in the 4c positions. The oxygen atoms are nearly hexagonal closed-packed and the M atoms occupy zigzag chains of corner-shared octahedra running parallel to the *c*-axis in alternate *a*–*c* planes. These chains are bridged by corner- and edge-sharing $PO_4{}^{3-}$ polyanions to form a host structure with strong three-dimensional bonding. The Li^+ ions in the 4a sites form continuous linear chains of edge-shared octahedra running parallel to the *c*-axis in the other *a*–*c* planes. The P_{tet}-O-Fe_{oct} linkage in the structure induces a superexchange interaction that tunes the Fe^{3+}/Fe^{2+} redox energy to useful levels (3.4 V) [11]. The stable nature of the olivine-type structure having a $PO_4{}^{3-}$ polyanion with a strong P–O covalent bond provides not only excellent cycle-life but also a safe system. The fact that all oxygen atoms are not only bonded to Fe but also strongly bonded to phosphorous is advantageous for the safety of the battery since oxygen is less likely to be released at elevated temperature which makes oxygen ignition of the organic electrolyte an unlikely accident. Low utilization due to conductivity problems within the electrode and slow electron transfer kinetics at the iron phosphate retarded its application to start with. Special coatings, small grain size and substitution of part of the iron by other metals are concepts to ameliorate these unattractive properties. When the electrode is fully charged, the reactivity with regard to the combustion reaction with the organic electrolyte is low [15].

Synchrotron based X-ray absorption spectroscopy is a very useful tool to investigate the structural and electronic properties of electrode materials. X-ray absorption near edge spectroscopy (XANES) is an element-specific technique sensitive to the local atomic and electronic structure of the element of interest [17]. XANES and extended X-ray absorption fine-structure spectroscopic (EXAFS) studies have revealed details about the local coordination, site symmetry, oxidation state, and bond character in Mn oxides and Mn-containing molecular compounds [18–21]. In order to study the atomic and electronic structure of these materials and understand the changes occurring upon cycling, we performed in situ Fe XANES and EXAFS on this material. In the last few years the use of XAS in electrochemistry to study battery and fuel cell electrodes has gained momentum [22,23]. Recently XAS has been used to study catalyst on bifunctional oxygen diffusion electrodes containing $La_{1-x}Ca_xCoO_3$, which is used as a catalyst in these electrodes [24,25]. XAS studies on $Li_{1-x}Ni_{0.85}Co_{0.15}O_2$ and $Li_xNi_{0.8}Co_{0.2}O_2$ cathode materials were performed to elucidate the changes in the oxidation state, bond lengths and coordination numbers of these materials [26,27]. Though there have been many cell designs, which until now have been successfully tested for short-term experiments, very few studies exist wherein cells have been used for experiments which extend for several days or even a week. After overcoming many obstacles, a transmission in situ XAS study was performed on nickel oxide electrodes by McBreen et al. [28] to observe the change in structure during electrochemical oxidation. Due to the known limitations of in situ investigations e.g. difficult cycling set-up and complicated multi-element assembly of a working cell, these experiments are more complicated compared to ex situ measurements. A few workarounds have been developed by cycling and disassembling cells at appropriate electrochemical conditions, in this case a post mortem analysis is possible and the results may be substantially altered by examining states of the material which are not present under operating conditions. Upon charging and discharging a cell the lithium ions are extracted and inserted from the electrode material and this reaction is seriously limited by diffusion and may take hours to reach equilibrium. Since we are interested in studying the changes in the electrode material which may depend on the number of charge and discharge cycles, the experiments can last as long as several weeks or even months. Here we used an in situ cell that is reusable and utilizes kapton X-ray windows, is convenient to assemble in the glove box, and is portable. The effective design of the in situ cell allows us to cycle the cell for several weeks without any noticeable traces of corrosion of the lithium metal counter electrode. For a complete description and design of this novel electrochemical XAS cell the reader is referred to Deb at al. [29]. In contrast to the earlier work [29] where we have only considered the initial and the final states during charging, for our discussion here we have shown the results for the various states during the charging cycle, and have clearly shown how this promising material is changing during cycling. This has been done by studying the changes in the short-range order of the Fe–O and Fe–P distances at various stages of the charging cycle.

2. Experimental procedures

The $LiFePO_4$ powder used in this study was synthesized using the starting materials $Fe(NO_3)_3.9H_2O$ (iron nitrate, Aldrich), $Li(CH_3COO)_2.2H_2O$ (lithium acetate, Aldrich), H_3PO_4 (phosphoric acid, Sigma) and $HOCH_2COOH$ (glycolic acid, Aldrich). The metal compounds were first dissolved in phosphoric acid and deionized water. This solution was mixed until homogenous and was added to glycolic acid (1:2 metal:glycolic acid ratio). Ammonium