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In situ X-ray diffraction and electrochemical impedance spectroscopy of a nanoporous Li_2FeSiO_4/C cathode during the initial charge/discharge cycle of a Li-ion battery

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HIGHLIGHTS

- An *in situ* XRD cell was fabricated with conductive Kapton film as X-ray window.
- EIS was collected at varying states of charge for nanoporous Li_2FeSiO_4/C cathode.
- Coexistence of a $P2_1/n$ phase and a $Pmn2_1$ phase was observed during the first cycle.
- The XRD data showed that the $Pmn2_1$ phase dominated in the fully discharge state.
- An inductance loop observed in the EIS data confirms the phase transformation.

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ABSTRACT

Understanding of the structural evolution of the cathode during the charge/discharge processes is crucial to describe the Li insertion/de-insertion mechanisms in a Li-ion battery. An *in situ* XRD cell has been specially fabricated to study a nanostructured electrode using a standard laboratory diffractometer. This cell was used to investigate phase transformations of a nanoporous Li_2FeSiO_4/C cathode in the initial charge/discharge cycle by *in situ* XRD as well as analyzing the full Li-ion battery by electrochemical impedance spectroscopy (EIS). The battery was operated in chronocoulometric mode for the *in situ* XRD and galvanostatic intermittent titration technique (GITT) mode for the EIS. Coexistence of two different polymorphs, $P2_1/n$ and $Pmn2_1$ of Li_2FeSiO_4, was observed in the *in situ* XRD patterns. The amount of $P2_1/n$ phase, which was the only phase present before cycling, decreased while the amount of $Pmn2_1$ phase increased during the first cycle. In the fully discharged state the $Pmn2_1$ phase appeared as the main phase. An inductive loop was observed in the impedance spectra which is believed to arise from the formation of a concentration cell ($Li|P2_1/n||Pmn2_1|Li$) from which current flows in opposition to the Li being intercalated/de-intercalated into and out of the $Li_{2-x}FeSiO_4$ electrode.

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1. Introduction

The Li-ion battery is currently the battery technology with the highest energy density, volumetric as well as gravimetric. Since the cathode materials play an important role in the determination of energy density, safety and life cycle of Li-ion batteries, research and development of cathode materials is important for the further improvement of these batteries. Especially, the study of the structural evolution of the cathode during the charge/discharge process is crucial to understand the Li insertion/de-insertion mechanisms and to optimize these materials so as to achieve high performance and cyclability. *In situ* X-ray diffraction (XRD) is widely used to study the correlation between the electrode material's structural and electrochemical behavior [1]. This technique allows for observations of the structural changes of the material while inside a closed *in situ* XRD electrochemical cell, which eliminates the risk of contamination and changes occurring due to chemical reactions that might occur if the cell is disassembled prior to the analysis. Beryllium (Be) foil has been widely used as X-ray window on the cathode side of the *in situ* XRD cell operating in synchrotron source facilities [2–4]. However, the Be window oxidizes and becomes porous at a high operating voltage, and an attenuation of the signal occurs due to the path length varying with the diffraction angle, consequently

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resulting in a poor signal to noise ratio in the collected powder patterns. Hence the *in situ* X-ray cell with Be window is not an ideal design for operating in standard laboratory diffractometers. Especially, for certain types of cathode materials which contain nanoparticles, nanopores, secondary phases, and a carbon-coating, using a Be window will result in poor quality of the XRD patterns. To compensate for the shortcomings of the Be window an X-ray penetrable polymer film can be used as the seal between the cathode and the ambient air. For this purpose electrically conductive Kapton (a polyimide) is a particularly good choice which has been used as XRD window by Meulenkamp et al. [5] because it is chemically inert (except in strongly alkaline solutions), shows no sharp XRD peaks, and is stable at temperatures up to about 325 °C [6].

Another powerful method that can be used to investigate structural changes of the electrode material during cycling is electrochemical impedance spectroscopy (EIS). It is important to note that an electrochemical impedance spectrum contains information about the entire electrochemical cell and not only the cathode as is the case with XRD. However, one important feature of the impedance spectrum which can be used to indicate structural changes is an inductive loop in the low frequency region of the Nyquist plot. The inductive loop is defined as the property of an electric circuit that causes an electromotive force to be generated in it as a result of a change in the current flowing through the circuit [7]. Hong et al. [8] proposed that the volume change in the phase transformation between $LiFe_{0.9}Mg_{0.1}PO_4$ and $Li_{0.1}Fe_{0.9}Mg_{0.1}PO_4$ leads to elastic–plastic deformation and induces a potential hysteresis and an inductive loop when the applied energy is higher than the opposing elastic–plastic accommodation energy. Gnanaraj et al. [9] also observed the inductive loop in the impedance spectra of the graphite electrode during initial cycling, which was attributed to the formation of a $(Li_{1-x}C_6)/C_6$ concentration cell from which current flows in opposition to the Li being intercalated into the graphite. This kind of two-phase concentration-cell-induced inductive loops were also found in Nyquist plots obtained in other initial cycling studies where layered $LiCoO_2$ [10] and spinel $LiMn_2O_4$ [11] were used as cathodes in lithium ion batteries.

Recently, a Li_2FeSiO_4/C composite has been considered a promising candidate as cathode material for Li-ion batteries [12]. However, the structure of Li_2FeSiO_4 undergoes significant changes during the initial charge, from the as-prepared high temperature γ_s ($P2_1/n$) phase to a more stable inverse β_{II} ($Pmn2_1$) polymorph [13]. As a consequence, all the Fe^{2+} and half the Li^+ share one set of tetrahedral sites with the remaining Li^+ occupying a second set of tetrahedral sites. Nytén et al. [14] have monitored the lithium extraction and insertion mechanism in Li_2FeSiO_4 by *in situ* XRD during the first two cycles. Only fully charged ($LiFeSiO_4$) and discharged states (Li_2FeSiO_4) were studied. Some *ex situ* XRD works have also revealed the structural change of Li_2FeSiO_4 during the initial charge and discharge [13,15].

In this study, a modified version of the cell design of Leriche et al. [4] was used for *in situ* XRD experiments, utilizing a conducting Kapton RS™ X-ray film as both the X-ray window and current collector in place of a Be window. Investigations by *in situ* XRD as well as EIS of a nanoporous Li_2FeSiO_4/C cathode was performed to study the structural and electrochemical property changes associated with the gradual change of composition x ($Li_{2-x}FeSiO_4$, $0 \le x \le 1$) and voltage during the initial cycle.

2. Experimental

2.1. Synthesis of nanoporous Li_2FeSiO_4/C

Nanoporous Li_2FeSiO_4/C was synthesized by a wet chemical method previously described [16]. A Li–Fe–Si-PVA solution (with the molar ratio Li:Fe:Si:PVA = 2:1:1:0.8) was prepared and stirred at 60 °C to form a gel, where $Li(CH_3COO)\cdot 2H_2O$ (Sigma–Aldrich, reagent grade), $Fe(NO_3)_3\cdot 9H_2O$ (Sigma–Aldrich, >98%), and tetraethyl orthosilicate (TEOS) (Aldrich, >99%) solutions were used as metal cation precursors. Polyvinylalcohol (PVA) (Aldrich, Mowiol 10–98, Mw = 61,000) was used as complexing and reducing agents during the carbothermal reaction. Gel formation took place after stirring for 6 h in an uncovered beaker. The gel was then covered and aged at 60 °C for 10 h before drying at 130 °C for 3 h. The Li–Fe–Si-containing dried gels were calcined at 450 °C for 1 h in air. The calcined powder was then mixed with an aqueous corn starch (Sigma–Aldrich, reagent grade) solution and ground into a paste in an agate mortar. The powder mixtures (starch content = 27 wt%) were heat treated in a flowing N_2 atmosphere at 650 °C for 10 h.

2.2. Characterization

The structural changes of the nanoporous Li_2FeSiO_4/C composite during the initial cycling were assessed using the *in situ* XRD electrochemical cell. Both a photograph and schematic drawing of the *in situ* XRD electrochemical cell setup are presented in Fig. S1. The cathode was prepared by mixing 90 wt% of the Li_2FeSiO_4/C composite with 8 wt% Supper-P carbon black, and 2 wt% polyvinylidene fluoride (PVDF) (Kynar, reagent grade) as a binder. A slurry was mixed by ball milling, using *N*-methyl-2-pyrrolidene (NMP) (Sigma–Aldrich, >99%) as the solvent. The electrodes were formed by tape casting the slurry onto the conductive surface of the Kapton, followed by drying overnight at 30 °C in a vacuum furnace. The *in situ* XRD electrochemical cell was assembled with the cathode, lithium metal as the anode and a Celgard 2400 film as the separator. The electrolyte used was 1 M $LiPF_6$ (Aldrich, ≥99.99%) dissolved in ethylene carbonate (EC, Sigma, 99%)/diethyl carbonate (DEC, Aldrich, ≥99%) (3:7 volume ratio). Cell assembly was carried out in an argon-filled glove box, where water and oxygen concentrations were 0.1 ppm. The cell was connected to a potentiostat (Voltalab 10) operating in chronocoulometric mode. The cell was charged/discharged instantaneously to 3000 mV, 3100 mV, 3200 mV, and 3250 mV/2500 mV and 1500 mV step by step and held till the charge current decreased to C/200 ($C = 160\ mA\ g^{-1}$) in order to record the XRD patterns close to equilibrium. *In situ* XRD patterns were recorded with a Siemens D5000 diffractometer operating with a Cu Kα radiation (X-ray wavelength

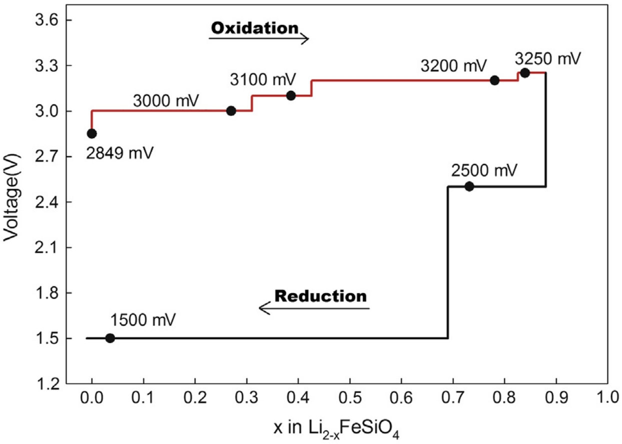

Fig. 1. Chronocoulometric profile for the initial charge and discharge of the nanoporous Li_2FeSiO_4/C cathode using the *in situ* XRD electrochemical cell. The red straight line is the oxidation (charge) profile and the black straight line is the reduction (discharge) profile. The black dots are the starting points for the XRD measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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