Short communication

XRD evidence of macroscopic composition inhomogeneities in the graphite–lithium electrode

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Abstract

In situ and ex situ X-ray diffraction (XRD) measurements were carried out on lithiated graphite electrodes at different states of charge. Data were collected from both sides of electrode. We found macroscopic inhomogeneities in the lithium concentration along the electrode thickness even when the electrode was allowed to rest for 24 h. The electrode side facing the lithium counter electrode in the coin type half-cell displays higher lithium concentration as compared to the side opposed to the XRD window. Residual stage 2 compound is found in the supposedly fully lithiated and fully delithiated electrode. It seems that the differences in the chemical potential between stage 2 and stage 1 is too small to average the lithium composition through chemical diffusion at ambient temperature in reasonable times.
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1. Introduction

Changes in the crystal structure of an electrode material designed for lithium ion battery application affect both the thermodynamics and the kinetics of the electrode reaction. The study of such changes is essential for understanding the electrode's key characteristics such as charge and discharge capacity and stability during out-of-equilibrium conditions such as under high rate, overcharge (high voltage) or overdischarge and at high temperature (i.e. self-discharge) [1–4]. In situ investigation techniques such as XRD are very convenient when determining the crystallographic evolution of electrode materials upon lithiation and delithiation cycles [2–4]. Usually the test cells are discharged under a slow rate and then equilibrated for several hours before each measurement [5]. This common procedure ensures that equilibrium within the electrode is reached so the XRD measurement is representative of the electrode state of charge. X-rays however may not probe the full electrode thickness as the beam intensity is attenuated due to absorption and other inelastic scattering.

In this article a highly crystalline natural graphite electrode is studied by in situ and ex situ XRD during lithiation and delithiation. It is known that graphite undergoes several structural transitions during the course of lithium intercalation, called "stages". The intercalation stage refers to the number of graphene layers between two adjacent lithium layers stacked in a periodic fashion. Dilute stage 1 forms at very low lithium concentration. A series of stage transitions then take place as stage 4, stage 3, liquid-type stage 2, stage 2 and stage 1 successively form [6]. The onset of stage transitions take place at well defined compositions (x in Li_xC_6) that fixes the chemical potential of lithium. A period of rest time after an additional amount of lithium is intercalated promotes equilibrium and a uniform lithium composition. Such a composition reflects the electrode overall state of charge.

In this work we took advantage of the limited penetration depth of X-rays to find evidence of composition inhomogeneities within graphite–lithium electrode thickness by in situ and ex situ XRD measurements.

2. Experimental

Graphite composite electrodes were made by casting a mixture in acetone of 15 wt.% PVDF (Atofina, France, #2801) as a mechanical binder, 10 wt.% carbon black (Superior Graphite Co., USA, ABG05) as the electronic percolator and 75 wt.% natural graphite (Superior Graphite Co., USA, SO-3-24-1) in

a Teflon mold. The film was cut into 12.7 mm diameter electrodes, which weighed typically 10 mg, then dried under vacuum overnight at 80 °C and transferred into a glove box filled with argon, without being exposed to air. The thickness of the electrodes was measured to be about 100 µm.

Two types of CR 2016 coins cells were assembled in the glove box. For ex situ XRD measurements, standard cells containing a lithium counter electrode, 1 molar $LiPF_6$ in EC:DMC (1:1) electrolyte (Mitsubishi Chemicals Co., Japan) and a Celgard 3401 microporous polypropylene separator were made. The cells were cycled twice between 0 V and 1.5 V versus Li^+/Li using a $C/5$ rate, then discharged to a given lithium concentration and opened in the glove box the next day. XRD data were collected using an air sensitive sample holder with a Kapton window and a Philips X'pert diffractometer with the Cu Kα radiation within 10 min after the cells were opened.

For in situ measurements, a 4 mm × 8 mm window was machined into the CR2016 coin cells covers, covered with a thick Kapton window (76 µm), rendered conductive by the vapor deposition of a thin copper layer (∼100 nm). The cells were then cycled using various slow rates ranging from $C/20$ to $C/60$ on an Arbin MSTAT cycler. During the cycles, 5 min XRD scans were collected at regular time intervals with an Inel CPS 120 using the Co Kα radiation and a 120° position sensitive detector. A diffraction angle scale conversion was made to convert diffraction angles data from Co Kα to corresponding Cu Kα. The cycling was not usually stopped during the scans, as the rate is slow enough to neglect the change in composition during the XRD measurement.

3. Results

3.1. In situ XRD

Fig. 1 shows in situ results for lithium concentrations ranging from $x \sim 0.3$ to $x = 1$ in Li_xC_6, which include the voltage area where the stage 2 ($Li_{0.5}C_6$) to stage 1 (LiC_6) transition takes place. The cell was discharged under a $C/20$ galvanostatic rate. In Fig. 1a the strongest peaks of stage 2 (0 0 2) and stage 1 (0 0 1) appear at $d = 3.52$ Å and 3.69 Å, respectively, in agreement with the literature [2]. It can be noted that no residual graphite is present in this composition range as the strongest (0 0 2) peak of graphite at ∼26.6° could not be detected. In Fig. 1b the $Li_{0.5}C_6$ (0 0 4) and LiC_6 (0 0 2) peaks show the same trends. A slight shift to lower angles is observed in the stage 2 (0 0 2) peak in Fig. 1a, which may be related to 'stage 2-liquid' to 'stage 2-solid' transition in the $0.3 < x < 0.5$ composition range. Based on diffraction peak intensities the (0 0 1) and (0 0 2) peaks of stage 1 could be detected only for compositions higher than $x \sim 0.7$. This result is quite surprising because the corresponding discharge curve changes plateau at $x = 0.5$, which is where stage 1 is expected to start forming. An hysteretic behavior is observed when the cell is delithiated: the stage 1 fraction (Fig. 2) calculated from the integrated intensities of the XRD peaks remains relatively large and could still be observed below $x = 0.5$, which corresponds to the end of the stage 1 composition domain. In order to check whether the presence of stage 1 below $x = 0.5$ compo-
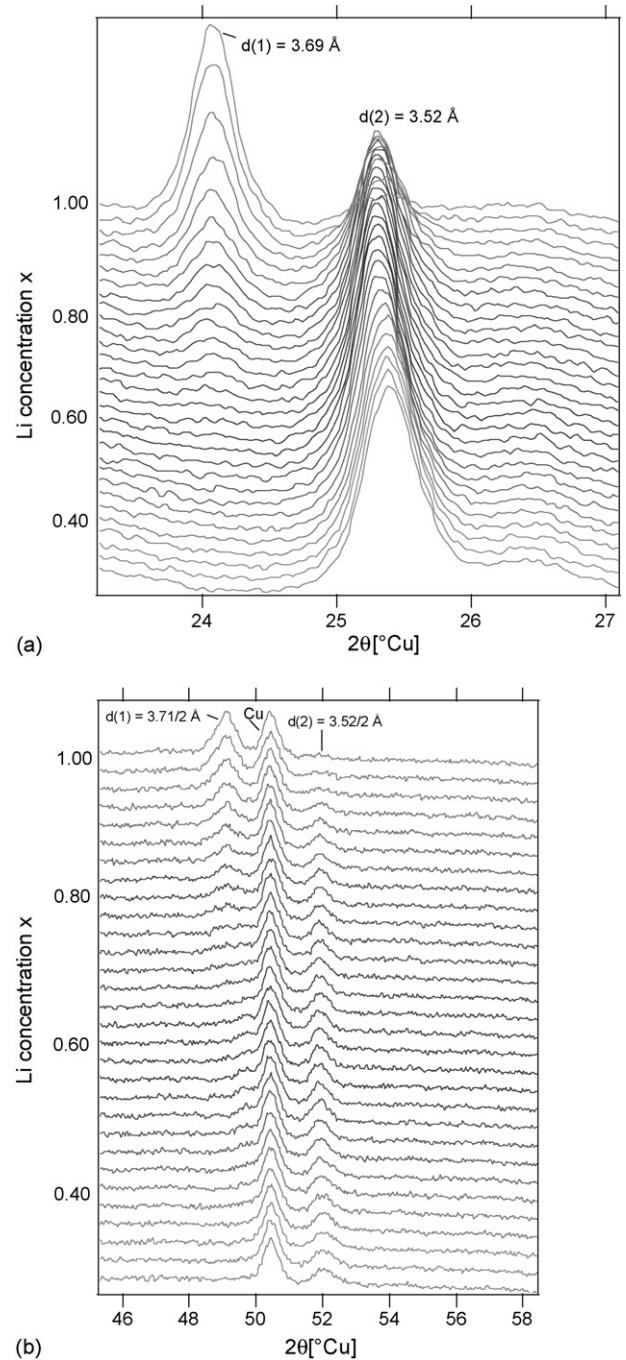

Fig. 1. In situ XRD patterns of the (0 0 2) (a) and (0 0 4) (b) regions of graphite, for lithium concentration 'x' in Li_xC_6 ranging from 0.3 to 1 during discharge.

sition results from a kinetics effect, the cell was intermittently discharged using a $C/10$ rate for 1 h and then was rested for 4 h. Fig. 3 shows the phase fraction of stages 2 and 1 based on peak areas during the 4 h rest. No visible relaxation is observed after this rest period, apart from the two last discharges, where the stage fractions evolve after the current is turned off. This indicates that the observed electrode composition remains mostly stable after 4 h.

A delay in the (0 0 1) peak of stage 1 in the $0.5 < x < 0.7$ composition range during lithiation may be due to kinetic processes such as nucleation and growth. The later may also explain
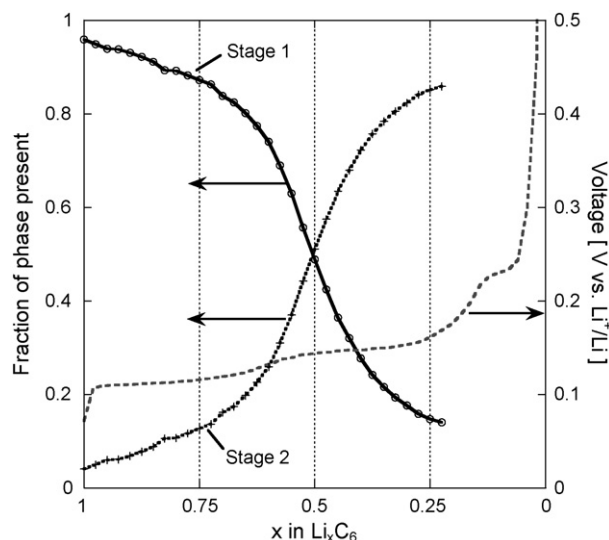
Fig. 2. Fraction of stage 1 and 2 present during a *C*/20 charge (left axis) and the corresponding voltage profile (right axis). Below $x \sim 0.25$ higher stages (2L, 3, 4) appear.

the hysteretic behavior during lithiation and delithiation. Delay could also result from the formation of disordered phases along with stage 2. In fact we reported a sharp increase in entropy at $x \sim 0.5$ during the lithiation process, which may originate from lithium disordering in the empty layers at the early steps of the stage 2 to stage 1 phase transition [7].

3.2. Ex situ XRD

Ex situ measurement on the same kind of composite electrodes was performed. When opened in the glove box the two sides of an electrode discharged to $x \sim 0.83$ were different colors. The side facing the lithium electrode (side A) was golden,

Fig. 4. XRD data collected on both side of an electrode discharged to $x \sim 0.75$ in Li_xC_6. The side closest to the current collector (stainless steel side) has been shifted by 20,000 for clarity.

indicating a rich stage 1 phase [8]. The opposite side (side B) displayed a mixed purple and golden color, suggesting a mixture of stage 2 and stage 1. Fig. 4 shows the ex situ XRD patterns of the two sides of an electrode discharged to nominal $x \sim 0.75$ after 24 h rest. Based on the relative intensities of the LiC_{12} and LiC_6 phases peaks, side A has a composition close to nominal while that of side B is only $x \sim 0.56$. This surprising result was found with several nominal compositions between $x = 0.5$ and 1. Moreover, a fully delithiated cell at 1.5 V versus Li showed on both sides of the electrode residual amounts of stage 1 and stage 2 compounds in similar amounts of about 1% and 4%, respectively (Fig. 5). Residual stage 1 and 2 materials probably come
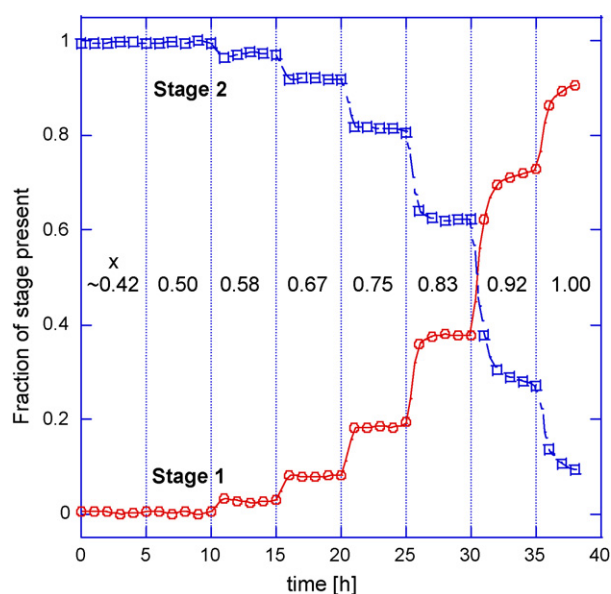

Fig. 3. Stage 1 and 2 phase fractions during an intermittent 1 h discharge followed by 4 h rest. Each plateau represent the rest period after the discharge.
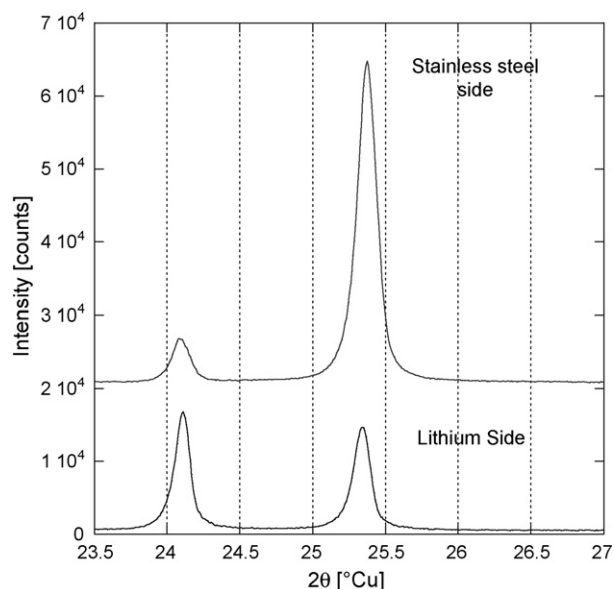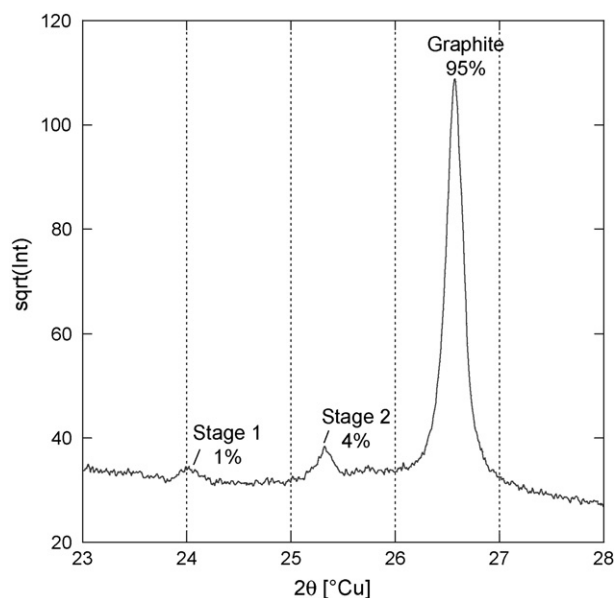

Fig. 5. XRD pattern of a cell delithiated up to 1.5 V vs. Li^+/Li, showing the residual peaks of stage 1 and 2.

from a small fraction of graphite particles that lose electrical contact with the rest of the electrode during the first cycles and consequently will no longer participate in the electrochemical process.

4. Discussion

The discrepancy between the theoretical and observed composition for stage 1 formation can be related to X-ray beam attenuation effects. Indeed the X-ray must cross the full sample before being diffracted from the sample crystallites near the counter electrode. The observed results are mostly representative of the side of the electrode closest to the window (side B). Therefore the overall composition of the graphite–lithium electrode obtained by coulometry can be different from the one observed with XRD owing to the presence of a lithium concentration gradient within the electrode, as confirmed by both ex situ and in situ XRD measurements. The hysteresis with composition delays in the stage 1 formation and disappearance observed by in situ XRD may also result from this gradient. This also causes incomplete lithiation of graphite, as seen on Fig. 3, where the final stage 1 fraction is about 0.9. This result was double checked by an ex situ XRD experiment on a fully charged cell, which showed a composition of about 0.85 on the current collector side. When the side closest to lithium is filled with lithium, the potential measured goes to 0 versus Li^+/Li, meaning the end of the electrochemical discharge, but some graphite galleries on the other side still are not filled.

These inhomogeneities in the electrode bulk, visible even after long equilibration times, suggest that the difference of chemical potential between stage 2 and stage 1 compounds is too small to drive the lithium from one particle to another to homogenize the composition at room temperature. Composition gradients that naturally appear during the dynamical process of

lithiation are then frozen when the discharge current is stopped, leaving the area of the electrode closest to the lithium anode with a larger lithium concentration than the more remote region on the current collector side.

5. Conclusion

Ex and in situ XRD measurements on the graphite–lithium electrode showed macroscopic inhomogeneities in composition along the electrode thickness. Even after one day of equilibration at room temperature the lithium concentration gradient is still present. The interpretation of in situ XRD results should be made very carefully in accordance with the cell geometry and characteristics. The dynamic of this electrode during charge and discharge also seems rather complex, especially in the lithium-rich stage 1 and 2 phases.

Acknowledgments

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