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Published in:
Journal of Applied Crystallography

Link to article, DOI:
10.1107/S1600576718007756

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Intercalation of lithium into disordered graphite in a working battery

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Intercalation of lithium into disordered graphite in a working battery

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The structural transformations occurring during the intercalation of lithium into disordered graphite in a working battery were studied in detail by \textit{operando} X-ray powder diffraction (XRPD). By using a capillary-based micro-battery cell, it was possible to study the stacking disorder in the initial graphite as well as in lithiated graphites. The micro-battery cell was assembled in its charged state with graphite as positive electrode and metallic lithium as counter electrode. The battery was discharged until a stage II compound (LiC\textsubscript{12}) was formed. The \textit{operando} XRPD data reveal that the graphitic electrode material retains a disordered nature during the intercalation process. A \textit{DIFFaX+} refinement based on the initial \textit{operando} XRPD pattern shows that the initial graphite generally has an intergrown structure with domains of graphite 2H and graphite 3R. However, the average stacking sequence of the initial graphite also contains a significant concentration of AA-type stacking of the graphene sheets. \textit{DIFFaX+} was further used to refine structure models of a stage III type compound and the final stage II compound. The refinement of the stage II compound showed that it is dominated by A\textsubscript{A}/C\textsubscript{11}AA\textsubscript{A}/C\textsubscript{11}A-type stacking, but that it also contains a significant concentration of A\textsubscript{A}/C\textsubscript{11}AB\textsubscript{B}/C\textsubscript{12}B-type slabs in the average stacking sequence.

1. Introduction

Lithium-ion batteries (LIBs) are today crucial to the operation of most new commercial portable devices and electrical vehicles. An increased fundamental understanding of the electrochemical reactions and the structural and microstructural changes occurring in the electrode materials during battery operation is, however, still needed in order to be able to optimize the LIB technology even further. Graphite is used as the negative electrode material in the majority of the secondary Li-ion batteries produced today. It has been known for many years that lithium may intercalate into the graphite structure during charging of the battery. The intercalation causes an expansion of the basal spacing between the graphene sheets in the graphite structure (da Costa \textit{et al.}, 1994; Cryst & McCusker, 1991; Xu \textit{et al.}, 2017). The maximum amount of lithium it is possible to intercalate into graphite is one lithium atom per six carbon atoms (LiC\textsubscript{6}). This gives a theoretical specific capacity of 372 mAh g\textsuperscript{-1} for graphite as electrode material. Two polymorphs of well ordered graphite exist, graphite 2H and graphite 3R, with hexagonal AB-(space group \textit{P}6\textsubscript{3}\textit{mmc}) and rhombohedral ABC-type (space group \textit{R}3\textit{m}) stacking of graphene sheets, respectively. Graphite 2H is slightly more thermodynamically stable than graphite 3R, but
the energy difference is very small. Thus, most naturally occurring graphites have a disordered or intergrown structure with domains of graphite 2H and 3R stacked along a common c axis (Shi, 1993; Shi et al., 1996; Herstedt et al., 2003; Dittrich & Wohlfahrt-Mehrens, 2001). Several different lithiated graphite phases are formed as intermediates during the charging and discharging of the battery. LiC₆ is, besides graphite, the most well described phase in the intercalation process. LiC₆ is reported to crystallize in space group P6/mmm, with a stacking sequence of AαAα (α denotes the position of the plane composed of the lithium atoms) (Guerard & Herold, 1975; Kganyago & Ngoepe, 2003). The degree of intercalation may also be associated with a stage number, which describes the number of graphene layers between two layers of intercalant. Thus, LiC₆ is a stage I compound and LiC₁₂ is a stage II compound. A series of other somewhat less well defined lithiated graphite phases, e.g. LiC₃₆, LiC₃ₐ, LiC₂₇, LiC₂₄ and LiC₁₆, have also been reported (Dahn et al., 1990; Billaud & Henry, 2002; Etacheri et al., 2011; Yao et al., 2004). These phases are somewhat grouped and referred to as part of the non-stoichiometric Li₁₋ₓC₁₂, Li₁ₓC₉ or LiₓC phases. The relationship between the stage number and the chemical composition has generally been debated. LiC₁₄ is occasionally called a stage III compound (Jiang et al., 1995), whereas others refer to it as a dilute stage II or stage 2L compound with an in-plane ordering of one lithium atom per nine carbon atoms in the intercalated layer (Flandrois & Simon, 1999; DiVincenzo et al., 1984; Billaud et al., 1996). The chemical composition of stage III is also suggested to be in the range of LiC₂₋₅ LiC₃₀ (Yao et al., 2004; Flandrois & Simon, 1999). The chemical composition of stage IV is reported to be in the range from LiC₂₄ to LiC₄₄− LiC₅₀ (Flandrois & Simon, 1999; Ohzuku et al., 1993). Regarding the space group of the intermediate phases, there seems to be an agreement in the literature that LiCₓ crystallizes in P6/mmm with AαAαAα-type stacking (Imai & Watanabe, 2007; Woo et al., 1983; Guerard & Herold, 1975; Billaud et al., 1996). The diluted stage II compound LiC₁₈ is reported to have a stacking sequence of AαBβB (Woo et al., 1983; Billaud et al., 1996), with the suggested space group P6₃mc (Missyul et al., 2017). As for the stage III compound, the stacking sequence was suggested to be AαABAαACAAαA or AαABAαABAαA (Billaud et al., 1996; Billaud & Henry, 2002). Alternative models based on modulation mechanisms using a ‘twist bilayer’ approach have also been proposed to describe the ordering in LiₓC₆ (x < 0.5) (Senyshyn et al., 2013).

In the present work, we study the intercalation of lithium into disordered graphite during discharging of a working battery with graphite as the positive electrode and metallic lithium as the negative electrode. Operando X-ray powder diffraction (XRPD) was used to study the structural transformations and refine changes in the stacking disorder of the graphitic electrode material using our capillary-based micro-battery cell (Johnsen & Norby, 2013). DIFFaX+ (Leoni et al., 2004) refinements provided valuable information about stacking sequences and stacking disorder in the disordered graphite and the lithiated graphites formed by electrochemical intercalation of lithium into a disordered graphite.

2. Experimental details

2.1. Capillary-based micro-battery cell

A micro-battery cell with a disordered graphite electrode was assembled according to the procedure described by Johnsen & Norby (2013). A droplet of the electrode was dip-coated on the tip of a copper wire with a diameter of 0.15 mm. A slurry of graphite (Fluka, product No. 78391), PVDF binder (polynylidene fluoride) and NMP (N-methylpyrrolidone) was used for the dip-coating, resulting in a droplet with a diameter of approximately 0.6 mm. A detailed description of the steps in the production of a capillary-based micro-battery cell is given by Johnsen & Norby (2013).

2.2. Operando X-ray powder diffraction

Operando XRPD experiments were performed at beamline 1711 at MAX-lab in Lund, Sweden. The micro-battery cell was placed in an electrical insulating sample holder frame and mounted on a goniometer head. The battery was connected to a Reference 600 Plus potentiostat from Gamry Instruments, which was used for galvanostatic discharge of a battery with a constant current of 5 μA (the voltage was set to have a lower limit at 1 mV). Powder diffraction data were collected while discharging the micro-cell battery. The experimental setup used a Titan CCD detector from Oxford Diffraction (2048 x 2048 pixels) with a diameter of 165 mm, a sample-to-detector distance of 73.01 mm, a wavelength of 1.103 Å, a slit size of 0.2 x 0.2 mm and an exposure time of 60 s. The data were converted to conventional one-dimensional powder patterns using the program FIT2D (Hammersley, 2016).

2.2.1. Data analysis. TOPAS-Academic 4.1 (Coelho Software, Brisbane, Australia; http://www.topas-academic.net; Coelho, 2018) was used to extract peak positions and half-width parameters. A pseudo-Voigt function was used to describe the peaks. DIFFaX+ (v2.500 Beta 10, 7 June 2010), which is based on the DIFFaX code (Treacy et al., 1991), was used to model and refine the disordered layered structures.

3. Results and discussion

The graphite/Li micro-battery cell was assembled in its charged state, where graphite is the positive electrode and lithium metal is the negative electrode. Fig. 1 shows the operando XRPD patterns of the graphite electrode as a function of time during the first galvanostatic discharge process. A relatively low discharging current of 5 μA was chosen to minimize the risk of formation of chemical gradients in the graphite electrode material during the intercalation process. Previous studies have shown that a current of 5 μA is sufficiently low to avoid long-range chemical inhomogeneity in the graphitic electrode material inside a micro-battery cell (Johnsen & Norby, 2013). Fig. 1 reveals the apparent changes in the diffraction patterns of the graphitic electrode material as the intercalation reaction progresses during the discharging process. The diffraction patterns clearly show that the broad diffraction peaks of the pristine graphite compound are succeeded by other broad diffraction peaks of the different
lithiated graphite compounds. The broad characteristic of the diffraction peaks appears to be retained during the entire intercalation process. Fig. S1 (in the supporting information) shows the formation of a diffraction peak at a position corresponding to the position of the 001 reflection of LiC$_{12}$ ($P\bar{6}mnm$, $c \approx 7.0$ Å) during the first galvanostatic discharge process.

The changes in the XRPD patterns were studied in detail using single-peak fitting as well as whole-pattern refinement of the data. Fig. 2 shows the changes in the cell potential and $d$-spacing values of the diffraction peak corresponding to the 002 diffraction peak of graphite $2H$ (and the 003 diffraction peak of graphite $3R$), at 2$\theta \approx 18.5^\circ$, as a function of discharging time. The diffraction peak (reflecting the interplanar distance) is from now on referred to as the ‘002$_{2H}$’ peak, even though it strictly speaking has different indices for the different stages in the intercalation process. The ‘002$_{2H}$’ diffraction peak was treated as a single peak and described as a pseudo-Voigt function in the fitting process. The quotations marks around $d$ spacing in the legend of Fig. 2 indicate that this assumption may not be completely true in the entire discharging process, as will be discussed later. The gaps in the $d$ spacing curve are due to beam dumps in the storage ring of the synchrotron, and the ripples in the $d$-spacing values and potential curves are due to instability in the power supply at MAX-lab. Solid electrolyte interphase (SEI) layers are known to be formed at the graphite electrode during the first discharging process (or first charging process if graphite acts as negative electrode material) (Yamaguchi et al., 1998; Aurbach, 1995; Peled, 1998). The $d$ spacing does not usually change during the formation of the SEI layer for more well ordered graphite compounds as lithium is not intercalated into the graphite structure during the process. Thus, the small apparent increase in the $d$ spacing (shown in Fig. 2) could perhaps indicate that lithium does get intercalated into the structure of this disordered graphite. An operando XRPD study using an ECC-Opto-Std battery cell from EL-CELL GmbH with Fluka graphite as positive electrode material and metallic lithium as negative electrode material was conducted to elucidate the question further. The study shows that the $d$ spacing of the ‘002$_{2H}$’ diffraction peak is nearly constant during the formation of the SEI layer (Fig. S2 in the supporting information). Thus, the small apparent increase in the $d$ spacing of the graphite in the micro-battery cell is probably mainly related to the instability in the power supply at MAX-lab. The $d$ spacing starts to increase at a cell potential of approximately 0.65 V in the ECC-Opto-Std battery cell when the battery is being discharged very slowly.

The structure of the initial disordered graphite phase was studied in detail using DIFFaX+. A cell containing two graphene sheets was used for the DIFFaX+ refinement (Table 1). The second graphene sheet in the cell is stacked (2/3, 1/3) in the $ab$ plane with respect to the first sheet, giving an AB-type stacking of the graphene sheets in the cell. The cell is hexagonal ($a = b = 2.4478$, $c = 6.7120$ Å, $\alpha = \beta = 90$, $\gamma = 120^\circ$) but is described in the triclinic space group $P1$. A three-layer model was used to refine the structure of the disordered graphene phase. The three layers are identical with a cell content as shown in Table 1 (Fig. S3 in the supporting information shows a sketch of the layers). Table 2 shows nine possible layer transition vectors for the three layers defined in Table 1, e.g. a (0, 0, 1) stacking vector for the 1-1 layer transition. As the double layers in the cell are AB stacked, a stacking sequence with only 1-1-type stacking forms graphite $2H$, whereas 1-3-type stacking followed by 3-3-type stacking...
forms graphite 3R. A pseudo-Voigt function was used for the refinements over a 2θ range of 16.0–44.0° using one refined half-width parameter (W) and one fixed peak-shape parameter (the mixing parameter). The scale factor, the overall isotropic displacement parameter (Biso) and 12 Chebyshev background parameters were also refined, together with the seven stacking probabilities. The probability of 2-1- and 3-2-type stacking was fixed to zero in order to reduce the complexity of the model. The refined stacking probabilities are shown in Table 2 (t = 1 min). Fig. 3 shows the DIFFaX+ refinement plot of the initial disordered graphite. The asterisk symbol in the figure shows the position (2θ ≈ 31°) of a low-intensity diffraction peak originating from the 111 reflection of the copper current collector. The DIFFaX+ refinement gave the following agreement factors: Rf = 0.99%, Rap = 1.39%, Rexp(background) = 1.91% and GOF = 1.40.

The stacking probabilities from the DIFFaX+ refinement clearly show that the initial disordered graphite has an intergrown structure dominated by domains of both graphite 2H and graphite 3R, but also that it contains sequences in the stacking of the graphite sheets that are different from those observed in graphite 2H and graphite 3R. If one starts from layer one, there is a 10 (1)% probability of having 1-2-type stacking which will form an ABBC stacking sequence of the individual graphene sheets. The stacking sequence contains BB-type stacking where the graphene sheets are stacked directly on top of each other, which forms a honeycomb structure with hexagonal prisms of carbon atoms. The BB-type stacking is on the local scale identical to AA-type stacking, which is expected when lithium is intercalated into graphite where AA-type slabs are formed (α denotes the position of the plane composed of Li atoms). Thus, one could imagine that it would be most energetically favourable for the intercalation of lithium atoms to start between the AA-type stacked graphene sheets. This would not require an in-plane sliding of the layers. If one starts from layer two, the probability of having 2-2-type stacking is 52 (7)% which will also on the local scale form an AA-type stacking of graphene sheets. A 1-2-type stacking followed by a 2-2-type stacking will form an ABBCCA stacking sequence of graphene sheets. Thus, the refined stacking probabilities indicate that the AA-type (AA, BB and CC) stacking partly tends to cluster.

A previous study of intercalation of lithium in a more well ordered graphite revealed significant changes in the apparent full width at half-maximum (FWHM) of the ‘002 2H’ diffraction peak during charging and discharging of the micro-battery cell because of the coexistence of multiple phases (stages) (Johnsen & Norby, 2013). Fig. S4 (in the supporting information) shows the changes in the apparent FWHM of the ‘002 2H’ diffraction peak of the disordered graphite during discharge of the battery. The changes in the apparent FWHM are relatively small, which indicates that the lithiated graphite very much retains a disordered nature. Thus, there is no indication of formation of well ordered lithiated graphite phases during the intercalation process. Also, the asymmetry of the ‘002 2H’ diffraction peak only changes slightly during the intercalation process.

DIFFaX+ was also used to attempt to refine the structure of a ‘stage III’ compound with an interlayer spacing of approximately 3.48 Å (t = 1205 min). A three-layer model where each of the cells consists of three layers of graphene and one layer of lithium was used for the refinement. The graphene layers are stacked AAAB, AAAC and BABA in the three cells, respectively (Fig. S3 in the supporting information shows a sketch of the layers). The cells are hexagonal (a = b = 2.456, c = 10.441 Å, α = β = 90, γ = 120°) but described in the triclinic space group P1. The refinement is based on a
simplified model where lithium is statistically distributed within the \( ab \) plane. Table S1 (in the supporting information) shows the layer transition vectors and the refined stacking probabilities for the refinement. Fig. 4 shows the DIFFaX+ refinement plot of the ‘stage III’ compound \((t = 1205 \text{ min})\). The DIFFaX+ refinement gave the following agreement factors: \( R_p = 1.37\% \), \( R_w = 2.12\% \), \( R_{p(\text{background})} = 3.06\% \) and \( \text{GOF} = 2.16 \). The sharper diffraction peak at \( 2\theta \approx 31.6^\circ \) in Fig. 4 originates from an impurity in the Fluka graphite, probably SiC. The two-dimensional diffraction images from the area detector revealed the existence of diffraction spots from larger crystals at a \( d \) value comparable to the position of the sharper diffraction peak. Fig. 4 shows that most of the features in the diffraction pattern (except for the diffraction peaks of the impurity and the current collector) are described by the refined structure model. Some of the estimated standard deviations of the refined stacking probabilities are relatively large (Table S1 in the supporting information). Thus, somewhat different structure models give more or less the same goodness of fit. However, the refinement does clearly demonstrate that slabs of \( AaAB \) and \( AaAC \) stacked directly on top of each other cannot fully describe the stacking disorder in this ‘stage III’ compound. A model that also included stage II and stage IV domains was needed. The slightly more asymmetric shape of the \('002_{2H}\) diffraction peak supports the need to include the additional domains. The refinement shows that the structure is significantly more disordered than the ‘stage III’ compound in our previous study (Johnsen & Norby, 2013), which was formed from a more well ordered graphite.

The structure of the final stage II compound was also studied using DIFFaX+. Two cells were used for the DIFFaX+ refinement: one cell (CELL1) containing one graphene layer and one layer of lithium with a chemical formula of \( \text{LiC}_6 \) (Table 3), and one cell (CELL2) containing only one graphene layer (Table 3 minus the \( \text{Li1} \) site). The cells are hexagonal \((a = 4.267, b = 4.267, c = 3.691 \text{ Å}, \alpha = 90, \beta = 90, \gamma = 120^\circ \) (space group: \( P\text{1} \)). The structure of the final stage II compound was also studied using DIFFaX+. Two cells were used for the DIFFaX+ refinement: one cell (CELL1) containing one graphene layer and one layer of lithium with a chemical formula of \( \text{LiC}_6 \) (Table 3), and one cell (CELL2) containing only one graphene layer (Table 3 minus the \( \text{Li1} \) site). The cells are hexagonal \((a = 4.267, b = 4.267, c = 3.691 \text{ Å}, \alpha = 90, \beta = 90, \gamma = 120^\circ \) (space group: \( P\text{1} \)). The structure of the final stage II compound was also studied using DIFFaX+. Two cells were used for the DIFFaX+ refinement: one cell (CELL1) containing one graphene layer and one layer of lithium with a chemical formula of \( \text{LiC}_6 \) (Table 3), and one cell (CELL2) containing only one graphene layer (Table 3 minus the \( \text{Li1} \) site). The cells are hexagonal \((a = 4.267, b = 4.267, c = 3.691 \text{ Å}, \alpha = 90, \beta = 90, \gamma = 120^\circ \) (space group: \( P\text{1} \)). The structure of the final stage II compound was also studied using DIFFaX+. Two cells were used for the DIFFaX+ refinement: one cell (CELL1) containing one graphene layer...
ret al. Billaud (LiC12) was formed. The charged state and discharged until a stage II compound lithiated graphites. The micro-battery cell was assembled in its stacking order/disorder in the initial graphite as well as in lary-based micro-battery cell, it was possible to study the intercalation process. By using our specially designed capil-elefon electrode material retained a disordered nature during the occurring during intercalation of lithium into disordered stage III domains in the stacking sequence. Thus, the initial graphite also contains a significant concentration of AAAB/BB-type slabs in the average stacking sequence.

4. Conclusion

This operando XRPD study of the structural transformations occurring during intercalation of lithium into disordered graphite in a working Li–C battery revealed that the graphitic electrode material retained a disordered nature during the intercalation process. By using our specially designed capillary-based micro-battery cell, it was possible to study the stacking order/disorder in the initial graphite as well as in lithiated graphites. The micro-battery cell was assembled in its charged state and discharged until a stage II compound (LiC12) was formed. The DIFFaX+ refinement based on the initial operando XRPD pattern showed that the initial disordered graphite had an intergrown structure dominated by domains of graphite 2H and graphite 3R, but also that it contained sequences in the stacking of the graphene sheets different from those observed in graphite 2H and graphite 3R. For example, there was a 10 (1)% probability of having 1-2-type stacking forming an ABBC-type slab of graphene sheets. Thus, the initial graphite also contains a significant concentration of AAAB/BB-type slabs in the average stacking sequence.

Acknowledgements

The authors would like to acknowledge Anders W. Jensen for assisting in the assembling of the micro-battery cell. The staff of beamline I711 at MAX-lab, Sweden, are gratefully acknowledged for experimental assistance.

Funding information

The research leading to these results has received funding from the European Union’s Seventh Framework Programme (FP7/2007–2013) under grant agreement 608575. DANSCATT is acknowledged for covering travel expenses in relation to the synchrotron experiment.

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