MS40 Operando and in situ crystallographic studies

MS40-05

Local order structural studies during electrochemical (de)intercalation by operando PDF analysis of the systems $LiMoO_2$ and $NaMoO_2$

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Abstract

The electrochemical (de)intercalation of alkaline ions in a battery is a very powerful technique to determine the phase diagrams in MO_2-A*M*O_2 lamellar systems (where A is an alkaline ion and *M* is a 3d or 4d transition metal ion) by combining *in situ* X-ray scattering probes and electrochemistry. In MoO_2-$AMoO_2$ (A = Li or Na) systems, many phase transitions occur during the deintercalation of alkali ions. It was proposed that these phase transitions arise in part from the rearrangement of molybdenum sites within the MoO_2 sheets formed from MoO_6 octahedra. [1,2]

In order to validate this hypothesis, operando Pair Distribution Function (PDF) analysis experiments have been performed during electrochemical cycling using $A_{2/3}MoO2$ phases as positive electrode materials in batteries. These experiments were performed on the XPDF beamline (I15-1) of the Diamond synchrotron. As PDF analysis from X-ray scattering data are particularly sensitive to heavier elements, it proved possible to follow the evolution of Mo-Mo bond lengths during the intercalation and deintercalation of alkaline ions in both the Li_xMoO_2 and Na_xMoO_2 systems.

As an example, Figure 1 illustrates the evolution of operando battery PDF G(*r*) curves obtained during intercalation and deintercalation of sodium ions in Nax*M*oO_2. The analysis of G(r) for interatomic distances between 2.4 Å and 3.3 Å, largely dominated by Mo-Mo distances, clearly shows that these distances evolve continuously during cycling. This indicates that the molybdenum atoms shift slightly from the centre of their MoO_6 octahedron to form molybdenum "clusters". We have identified several types of "clusters" according to the alkaline content, *i.e.* according to the average degree of oxidation of the molybdenum ions. Figure 2 illustrates the "zig-zag" chain clusters of molybdenum forming in $Na_{0.5}MoO_2$ (Figure 2a) and "diamond" type clusters stabilizing the structure of the compound $NaMoO_2$ (Figure 2b).

In this work, the complex structural phase diagrams of these materials will be reviewed, and using these new results, it will be shown how operando PDF measurements under electrochemical cycling can provide new insight into the role of short Mo-Mo bond formation during (de)intercalation in the Li_xMoO_2 and Na_xMoO_2 systems.

References

[1] L. Vitoux, M. Guignard, M. R. Suchomel, J. C. Pramudita, N. Sharma, C. Delmas "The Na_xMoO_2 Phase Diagram ($1/2 \leq x < 1$) : An Electrochemical Devil's Staircase" *Chemistry of Materials* **2017**, 29, 7243-7254.

[2] L. Vitoux, M. Guignard, J. Darriet, C. Delmas "Exploration of the Na_xMoO_2 phase diagram for low sodium contents ($x \leq 0.5$)" *Journal of Materials Chemistry A* **2018**, 6, 14651-14662.

Figure 1:

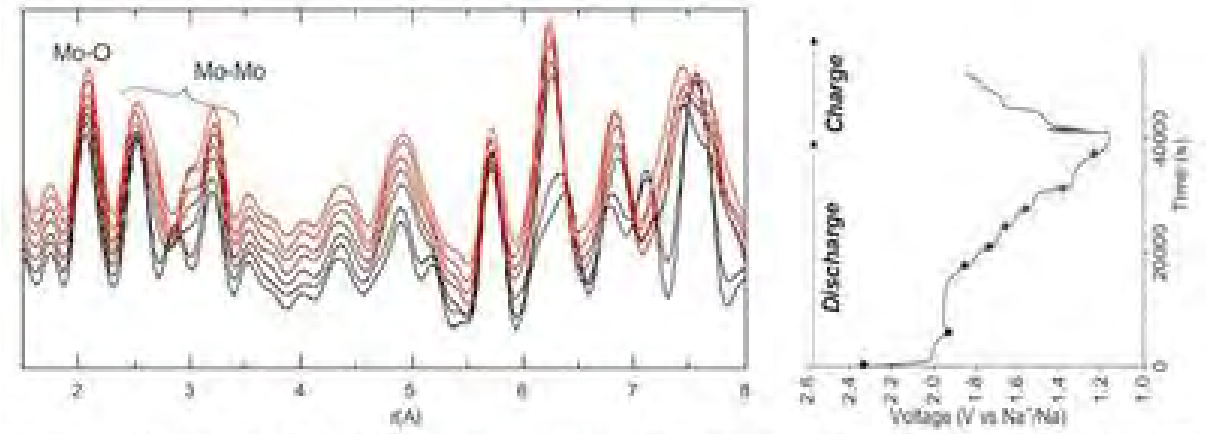

Figure 1: Operando Pair Distribution Function G(r) curves (left) for the system Na_xMoO_2 measured during the electrochemical intercalation and deintercalation of Na^+ (right).

Figure 2:

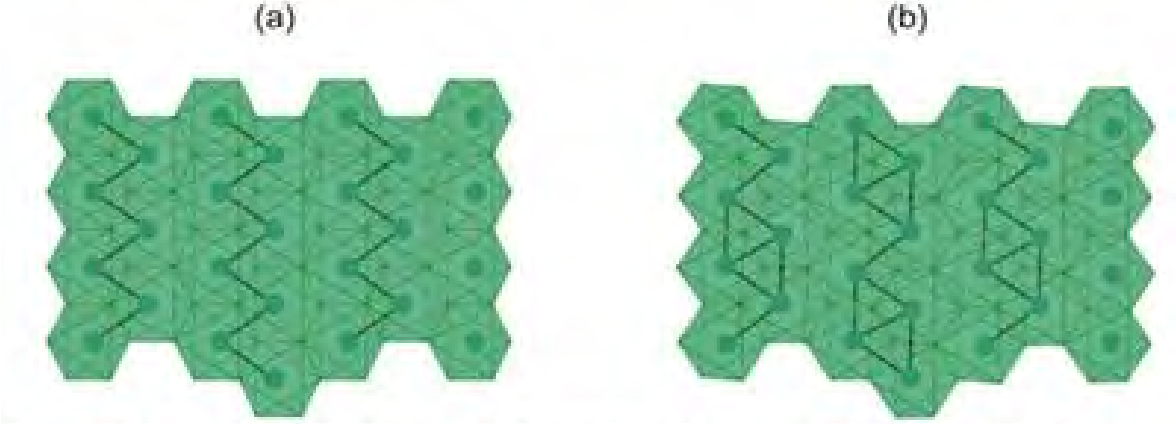

Figure 2: Projection of $(MoO_2)_n$ sheets formed by edge-sharing MoO_6. Only Mo atoms are shown to highlight clustering. Black lines represent short (< 2.8 Å) Mo-Mo bonds in (a) "zig-zag" type clusters for $Na_{0.5}MoO_2$ and (b) "diamond" type clusters for b) $NaMoO_2$