Lithium-ion diffusion pathways within new battery-cathode materials

Li-ion batteries form a basic component on which our world of mobile electronics and communication is built. And they are increasingly used in high power applications such as electric vehicles and the storage of electricity from solar and other renewable power sources.

In these batteries, the cathode is a lithium-containing compound. During a battery's charging and discharging, Li+ ions are alternately extracted from and reinserted in the cathode as they move through the electrolyte to the anode and back. The cathode material must sustain wide variations of its Li+ ion content over many cycles. To date, the best performing cathode materials, combining good cyclability and high charging capacity (LiCoO2, LiFePO4…), are layered compounds. The Li+ ions are arranged in specific 2D crystal-structure planes that allow fast ionic mobility and ensure good reversibility during cycling. Recently, a new high capacity cathode material, a lithium manganese oxide with formula Li₄Mn₂O₅, was reported (Freire et al. 2016). This material has a very different, cubic-type crystal structure, but shows record charging capacity and promising cyclability. At the Institut NÉEL, we have been investigating its local structure to understand how Li+ ions can circulate so easily and reversibly in such a 3D atomic arrangement.

Our research was done in collaboration with this material’s discoverers: CRISMAT laboratory (Caen) and the French battery company SAFT. The new Li₄Mn₂O₅ material is prepared by high energy milling, yielding submicron size grains and a quite defective crystal structure at the nanoscale. On average, it has been found to be of the cubic rock-salt (NaCl) type, the Li and Mn occupying the same cation site and 1/6 of the oxygen sites being vacant, leading to additional disorder.

We used a combination of X-ray absorption near-edge spectroscopy (XANES) and pair distribution function (PDF) analysis of neutron and X-ray powder-diffraction data to reach a precise description of the atomic arrangement at the local scale. The measurements were carried out at the French Collaborative Research Group beamlines of the European Synchrotron Research Facility, and at the Institut Laue Langevin, Grenoble.

The X-ray spectroscopy allowed us to show that, despite the large number of vacancies on the O sites, the coordination of the Mn cation remains octahedral (that is 6 oxygens around every Mn atom). With this crucial information we could build a starting structural model which was used for a pair distribution function analysis. This technique allows one to obtain a histogram of the interatomic distances in a sample, disregarding its degree of ordering, and it can be used for liquid or amorphous as well as crystalline materials. It was the tool of choice to investigate, at the nm scale, the local structure of this highly disordered Li₄Mn₂O₅ material. For this investigation, we performed a joint fit to the neutron and X-ray total scattering data, both in direct and reciprocal space, by calculating a large box containing 21000 atoms while applying suitable constraints on distances and ion charges. (This used the Reverse Monte Carlo algorithm and the RMC-Profi le software.) Analysis of the final calculated atomic configuration that best fitted the data revealed that the Mn cation network is almost regular cubic, while most of the structure distortion is in the oxygen anion network.

Then by calculating the “bond-valence sums” for all points in voids inside the above structure, we could obtain a map of the 3D energy landscape (Fig. 1). This describes the regions available to the Li+ ions with minimal energy cost. Fig. 1 shows that the accessible volumes are connected in the three directions, so the Li+ ions can circulate within the structure, explaining the excellent electrochemical performance of Li₄Mn₂O₅.

This was the first time that this 3D energy landscape type of analysis was carried out for a disordered compound. We performed similar calculations on the well-known structures of the layered cathode materials having an ordered lamellar structure. The comparison shows how the 3D pathways in Li₄Mn₂O₅ can give Li+ ion mobility equivalent to that of the lamellar compounds.

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**FURTHER READING...**
“Local structure and lithium diffusion pathways in Li₄Mn₂O₅ high capacity cathode probed by total scattering and XANES”