

In-situ Neutron Diffraction Studies of Li Batteries

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***In-situ* neutron diffraction studies of Li batteries**

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In-situ neutron diffraction (ND) is a versatile experimental technique which can be used to probe structural transformations of electrodes in Li batteries as a function of charge and discharge. Moreover, both the cathode and anode can be analysed simultaneously providing detailed insight into the atomic and molecular scale structural mechanism of battery performance.

Both the sensitivity of neutrons to Li and the penetration depth of neutrons, relative to X-rays, permit a time-resolved structural study of Li in crystalline phases *via* refinements of Li occupancies and positions. Despite the advantages of neutrons for this purpose, relatively few studies [1-4] have successfully used *in-situ* ND to study Li batteries. A major hurdle in the widespread use of this technique for Li battery analysis is the high levels of unwanted neutron scattering arising from the hydrogen-containing liquid electrolyte and non-crystalline separator. Therefore, specialised cells are often constructed, which in turn do not resemble real-world batteries and can not be directly correlated to normal conditions of use. Thus there is a need to design and test cells that provide both sufficient structural information and which can be correlated to commercial batteries.

Neutrons interact weakly with matter, giving rise to their strong penetration and capacity for bulk sample measurement, and limiting scattering events from the sample. Therefore, to undertake *in-situ* ND an instrument is required that provides high flux. We present work investigating Li batteries using the WOMBAT diffractometer at the OPAL research reactor in Australia. WOMBAT has a relatively high incident flux and features an area detector spanning a large angular range, meeting the requirements for the *in-situ* analysis of battery materials.

Highlights of battery research using WOMBAT will be presented, including a Li ion battery based on the original technology developed by Sony [5]. ND data collected from this as-purchased battery reveal variation in the lattice parameters of the LiCoO₂ cathode and graphitic anode as a function of charge / discharge or Li insertion and extraction (Figure 1). Notably, we observed the presence of other phases at these electrodes undergoing changes in their lattice parameters, indicating that these phases are active in the Li insertion and extraction processes. Furthermore, the phases comprising the electrodes undergo a series of phase transitions with electrochemical cycling making analysis of these data challenging. Information gained from these data required careful application of the Rietveld method at specific charge states, followed by tracking individual component reflections with electrochemical cycling, and finally sequential Rietveld refinement of the multi-phase system.

Multi-phase Rietveld refinements using ND data of whole batteries can be made significantly easier by reducing the background which is predominantly caused by hydrogen in the sample. For example, switching components of the battery, such as replacing the plastic casing with vanadium cans, reduces hydrogen content. The result is

the design, construction and testing of AA or cylindrical batteries (Figure 2). Key features of these batteries include replacement of hydrogen-containing electrolytes with deuterated electrolytes and the use of non-standard separators. The construction was undertaken with a desire to resemble a real-world battery rather than a one-off experiment. This design has been shown to have similar electrochemical behaviour and good ND characteristics, the results of which will be presented.

The overall goal of this work is too provide a method where electrochemists can bring novel electrodes showing good electrochemical properties to WOMBAT and undertake *in-situ* ND experiments to determine the structural processes occurring with electrochemical cycling. Thereby, providing a real-time understanding of critical structural processes, from which further research can be tailored or developed. The results presented are intended to highlight the insight one can achieve by marrying ND with electrochemistry.

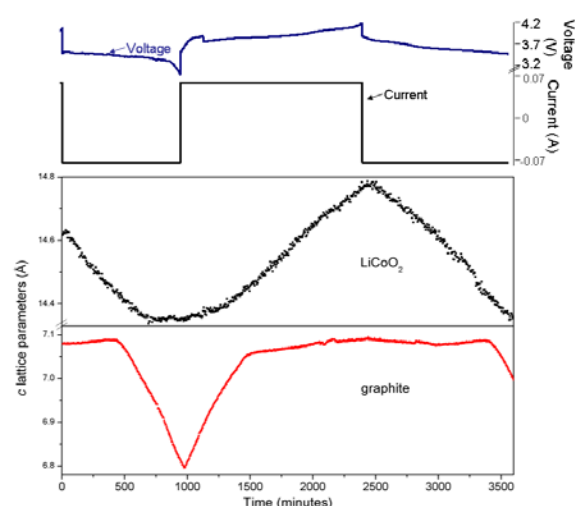


Figure 1. Variation in the *c* lattice parameter as determined by Rietveld refinements using *in-situ* ND data of a layered-type LiCoO₂ (cathode) and graphite (anode) with electrochemical cycling (top).

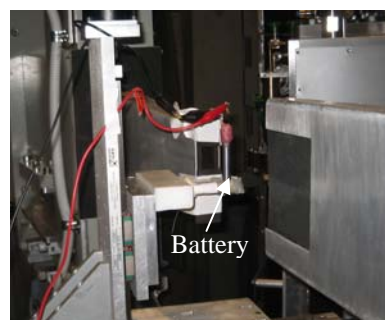


Figure 2. An image of a constructed *in-situ* ND electrochemical cell on the WOMBAT diffractometer.

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