

In-situ Spatial and Temporal Studies of Electrochemistry in Advanced High Temperature Batteries Under Operating Conditions

J. Rijssenbeek¹, Y. Gao¹, Z. Zhong², N. Jisrawi³, I. Ignatov⁴, M. Croft⁴

¹GE Global Research, One Research Circle, Niskayuna, NY 12309

²National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973,

³Department of Applied Physics, University of Sharjah, POB 27272, Sharjah, United Arab Emirates

⁴Dept. of Phys. and Astr., Rutgers Univ., 136 Frelinghuysen Road, Piscataway, NJ 08854

National interest mandates advanced battery development across a broad spectrum of applications/power-levels: from portable electronics, to transportation, to utilities. In-situ x-ray diffraction has proved to be valuable tool to probe basic electrochemistry. Typically these studies have used thin cells designed specifically for the x-ray experiments. A high-energy x-ray diffraction facility has been established at NSLS beamline X17B for precision lattice dilatation and crystalline phase mapping. This energy dispersive X-ray diffraction (EDXRD) facility provides an excellent platform for 4D-mapping (3D-spatial plus time/charge-state) measurements of the internal electrochemistry of full-sized commercial cells under real-world operating conditions.

We have performed in-situ studies on high-temperature sodium, metal (M) chloride cells (M=Fe and Ni) that are being considered for diverse transportation sector applications: from city electric vehicles, to delivery vehicles, to buses, to locomotives. The ~50 mm diagonal (see Fig. 1), steel encased cells operate at 300°C. Fig. 1 shows diffraction patterns across the cell's diagonal taken at various states-of-charge. Also shown are cross-sectional images of the cell, with the blue shading schematically highlighting those parts that have been charged (as determined by the loss of NaCl and appearance of MCl₂ diffraction peaks). It is clear that the reaction begins at the outside of the cathode (top and bottom of each strip in Fig. 1) nearest the beta"-alumina solid electrolyte. This data provides unprecedented rate information, and details on the width and propagation of the reaction front. Moreover, we are able to detect reactions involving additives present at the 1-5% level.

We have also monitored the passage of the reaction front at a fixed position in the cell. Fig. 2 shows portions of EDXRD spectra, scattered intensity vs. x-ray energy, at selected times (charge states) in the NaCl/M ⇒ Na/MCl₂ cell charge cycle. It should be noted an intermediate Na₆MCl₈ phase also appears in the charge sequence (M=Fe). In Fig. 3a, the integrated relative intensity of Bragg lines associated with each of these phases is plotted versus charge time (diffraction scan number). Fig. 3b shows the derivatives, dI/dN, of the spectral areas of the Bragg lines in Figure 3a and reveals the relative rate of change of the individual phases.

In the charge-time region 1 (Fig. 3), the data shows the appearance of the Na₆MCl₈ phase, with a simultaneous loss of NaCl. In region 2, the NaCl/Na₆MCl₈ phase ratio appears to stabilize. In region 3, the intermediate Na₆MCl₈ phase disappears, while the MCl₂ phase increases. In region 4, the NaCl phase disappears to form MCl₂. Finally, in region 5, the sodium-containing phases have disappeared completely to be replaced by the MCl₂ phase. Interestingly, the transient Na₆MCl₈ phase at the reaction front appears to form from newly generated MCl₂ and existing NaCl phase, and the further transformation of NaCl/M ⇒ Na/MCl₂ proceeds only after its disappearance.

In summary such EDXRD measurements show great promise in revealing local electrochemical kinetics in unprecedented levels of detail deep inside of commercial size cells under non-trivial operating conditions. Examples of similar measurements on Li-based commercial batteries will also be presented in the talk.

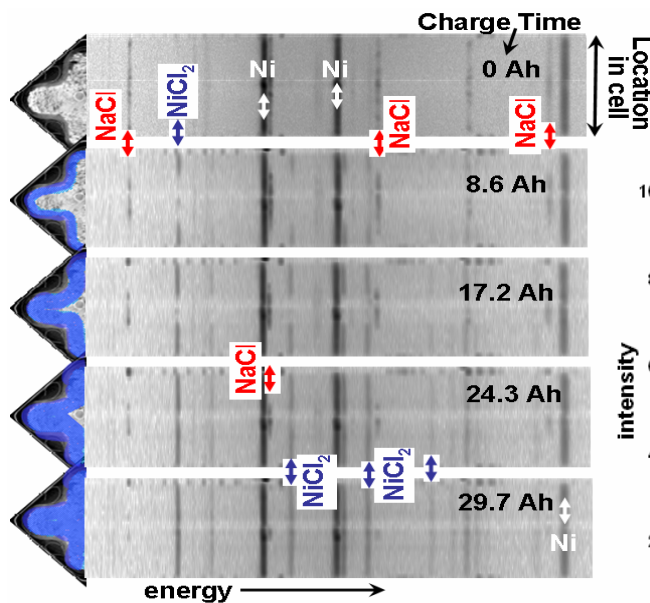


Fig 1(left). Cross-sectional x-ray diffraction patterns taken at various times during charging of a Na/MCl₂ ⇌ NaCl/M battery with

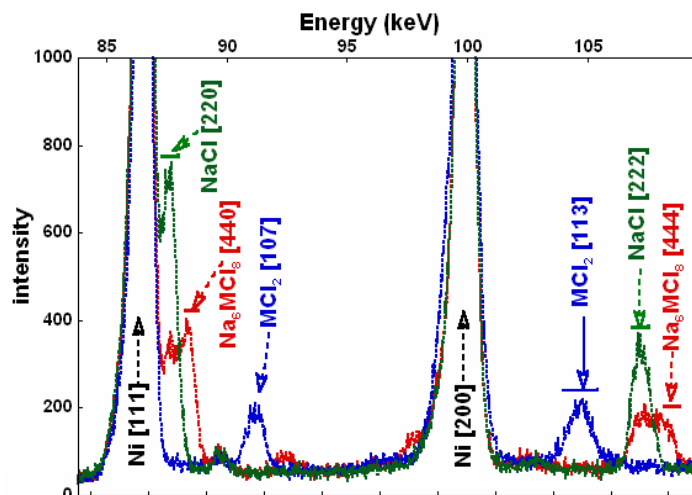


Fig.2 (above) Selected partial diffraction patterns at differing charge times showing specific Bragg lines, for the NaCl, MCl₂, and Na₆MCl₈ phases.

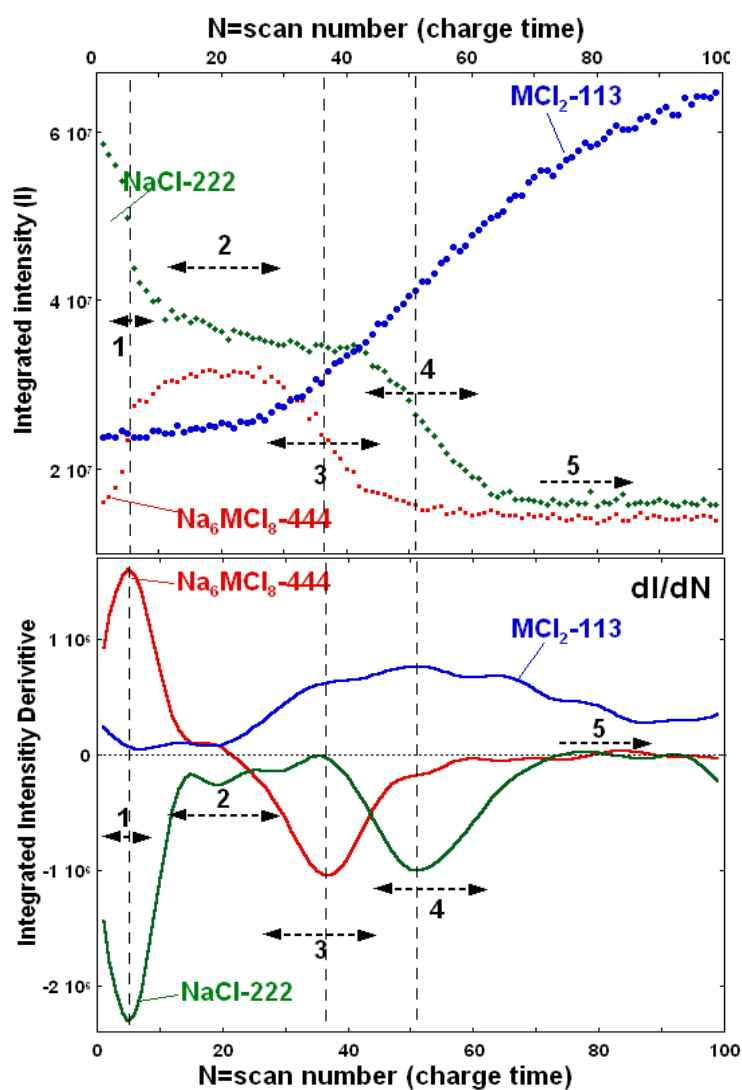


Fig. 3a. The charging time (diffraction scan number) variation of the integrated spectral intensities for regions chosen to reflect the relative phase abundances of the NaCl, MCl₂, and Na₆MCl₈ phases. The vertical lines and regions 1-5 identify regions of the electrochemical kinetics discussed in the talk.

Fig. 3b The smoothed derivative curves, dI/dN, of the intensity (I) curves from Fig. 3a.