

ESRF Beamtime report

ESRF Project: 26-01 1133

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**“Elucidating the origin of remarkable electrochemical cycling performance of Manganese spinel oxides towards  $\text{Mg}^{2+}$  via operando XANES/EXAFS study”**

**Objectives:**

The aim of this experiment was to investigate the origin of the high reversible capacity of  $\text{Mn}_3\text{O}_4$  vs.  $\text{Mg}^{2+}$ . Due to its size and polarity reversible, effective intercalation of  $\text{Mg}^{2+}$  ions into a host structure is seen as major challenge. In their recent study our collaborators have shown that high cycling capacity can be obtained in  $\text{Mn}_3\text{O}_4$  which is believed to be at least partially attributed to bulk faradaic insertion mechanism[1]. Furthermore they show that the choice of electrolyte plays a decisive role on the storage mechanism and total amount of capacity obtained. To elucidate the nature of storage mechanism we proposed to measure XANES and EXAFS of Mn K-edge under operando conditions to follow any changes of electronic and or local structure upon reaction vs  $\text{Mg}^{2+}$ .

**Results:**

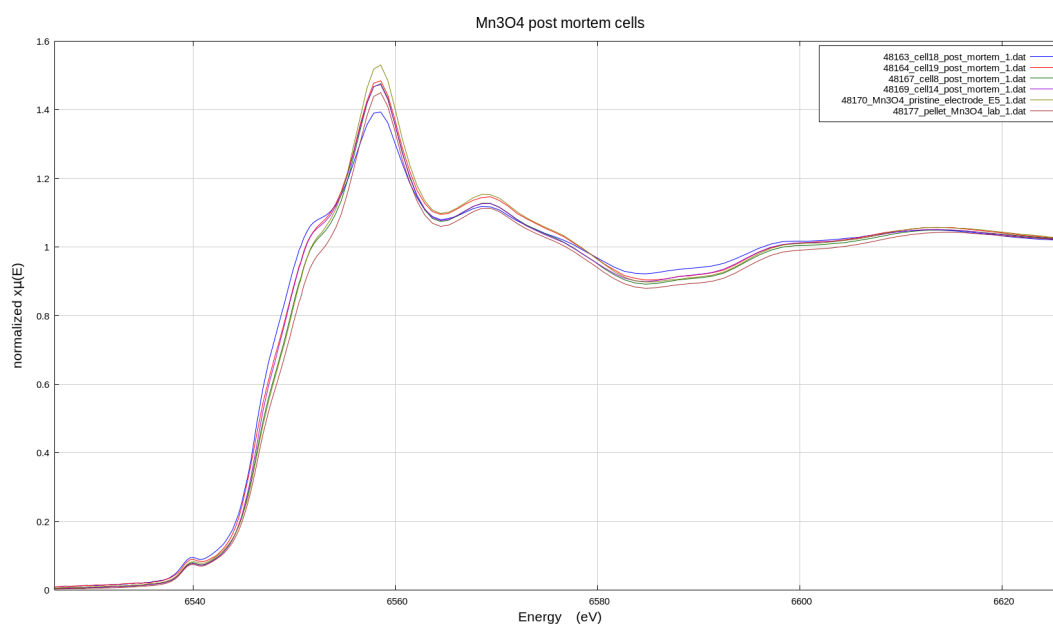
Coin cells with Kapton window for transmission mode setup were prefabricated and brought to ESRF containing different active material loadings and electrolyte solvents (THF, tetraglyme and diglyme).

As a first unexpected difficulty we discovered that the Mg counter electrodes contained traces of heavy elements (probably Zr) which at these low energies (Mn K-edge 7.5 keV) results in almost total absorption of the beam. We therefore had to switch to fluorescence mode which allowed us to acquire the acquisition of Mn k-edge XANES via front window but significantly compromises quality of data in the EXAFS region. As a further challenge the electrochemical cycling performance of the operando cells was far below of what had been previously obtained in home lab. We experienced a fast voltage drop in the cell when applying current. This can have several reasons. Leaking of window material leading to exposure of the electrolyte to ambient air resulting in fast degradation, expressed by decrease of open circuit potential. Also we found that the window in the coin cells results in a reduction of pressure which can result in loss of contact. The delay of several days between battery assembly and the cycling seems to have a negative effect on the cycling performance as well.

Despite of these difficulties we could show that for none of the  $\text{Mn}_3\text{O}_4$  samples a significant shift of the Mn edge was observed, see Illustration 1. This indicates that the entire capacity obtained was due to capacitive storage and or electrolyte decomposition (SEI formation, etc) . These results have to be considered with some care since total capacity obtained and reversibility were lower than the values achieved for optimized cells in home lab. Therefore we discharged two cells in standard coin cells without window and recovered the electrode film for postmortem XANES analysis, see illustration 1. Even for these cells which achieved better

capacity (100mAh/g) we did not observe any changes in the edge that would indicate reduction of Mn.

Additionally we carried out SAXS measurements of the Mn<sub>3</sub>O<sub>4</sub> electrodes before and after Mg insertion. Deviations are observed in the q region around 1 nm<sup>-1</sup>. To study this region of interest, SAXS in higher q range (higher energy) should be carried out.



*Illustration 1: XANES of Mn K-edge of various Mn<sub>3</sub>O<sub>4</sub> cells cycled vs Mg<sup>2+</sup> after complete discharge (EOD) compared to pristine electrode material*

#### Outlook:

Focus should be on optimizing the cells and thorough testing of operando cells to find optimum cycling conditions. The replacement of counter electrode material with pure mg or other material with similar x-ray transparency is needed for transmission setup. A operando SAXS-XANES setup at low and high q region would be of interest for this material system.

[1] L. Wang, K. Asheim, P. E. Vullum, A. M. Svensson, and F. Vullum-Bruer, "Sponge-like porous manganese(II,III) oxide as a highly efficient cathode material for rechargeable magnesium ion batteries," *Chem. Mater.*, vol. 28, no. 18, pp. 6459–6470, Sep. 2016.