

Report for ESRF Experiment 25-01 987 – Understanding the chemical origin of large capacitance in MnOx electrodes

Introduction

One of the more active research lines in the field of energy storage is the search for green and clean energy storage devices. In this sense, supercapacitors (also known as ultracapacitors or electric double layer capacitors) are electrochemical capacitors that can achieve a higher energy density than conventional capacitors and a better power performance than batteries [1].

An ample collection of different electrode materials and electrolytes are being scrutinized to improve both efficiency and cost of SCs. The electrode materials mainly determine the electrochemical performance of SCs. In redox-based electrochemical capacitors (also known as pseudocapacitors), transition metal oxides [2-4] are used for reversible redox reactions at the surface of active materials. These metal oxides such as RuO_2 , NiO , CoO , MnO_2 , Ni(OH)_2 and Co(OH)_2 are usually considered the best candidates for electrode materials in SCs owing to their large capacitance and fast redox kinetics. The behavior of these oxides as electrode for supercapacitor depends strongly of the oxidation state. Understanding the changes in the oxidation states for the different transition metal oxide during the charge/discharge cycles which give rise to this electrochemical behaviour would help to design an optimum electrode for SCs.

In-situ XAS is a powerful technique to analyse the electrochemical reactions produce in a supercapacitor electrodes. In addition, XAS technique can be used under reaction conditions. The in-situ measurements have been widely applied to many heterogeneous catalysts, which are operating under the reaction environments. The supercapacitor electrodes can also be studied by in-situ XAS measurements during the charging and discharging processes. This type of measurements could allow to establish the relation between the oxidation states of the electrode and its electrochemical response. Spline beamline has an experimental set-up design to perform dynamical cycling measurements. We have tried to follow the changes in the oxidation states of Mn during the charge/discharge cycles of MnOx electrodes.

Experimental

The electrochemical cell used for the in-situ XAS measurements is shown in Fig. 1. The cell is made of teflon, with a Kapton film as window for the X-ray. The cell has

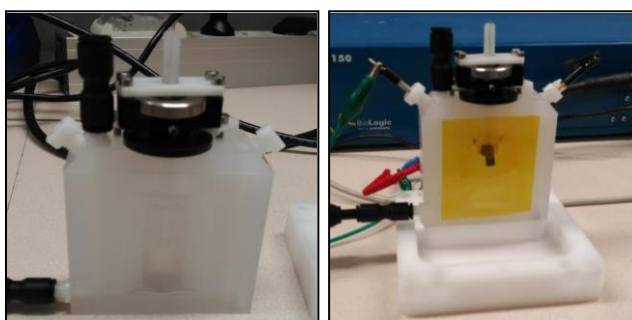


Fig. 1 (a) Image of the cell used to realize in-situ XAS measurements

two orifices to introduce the anode and the reference electrode. The active material is graphene foam coated with manganese oxide synthesized by sol-gel. We have also used a Pt mesh as anode and an Ag/AgCl reference electrode. Electrochemical experiments have been carried out in a 1M Na₂SO₄ solution. We carried out X-ray absorption (XAS) spectroscopy experiments at the Mn K-edge (6.539 keV) in fluorescence mode at room temperature.

Results

During the beamtime we made several efforts to acquire XAS spectra during the charge/discharge processes. In a first step, the cell was placed in the beam path and the measurement condition was optimized without introducing the electrolyte. We took a spectrum under this conditions as reference. In a second step we introduced the electrolyte and tried to take the same XAS spectrum. However, no signal was detected by the fluorescence detector when introducing the electrolyte. In order to understand why the signal disappeared, we tried to measure several spectra after introducing a few ml of water between the sample and the Kapton windows. We do not detect any signal in any case. It seems that the energy of the Mn K- edge is too low to measure XAS in a liquid environment.

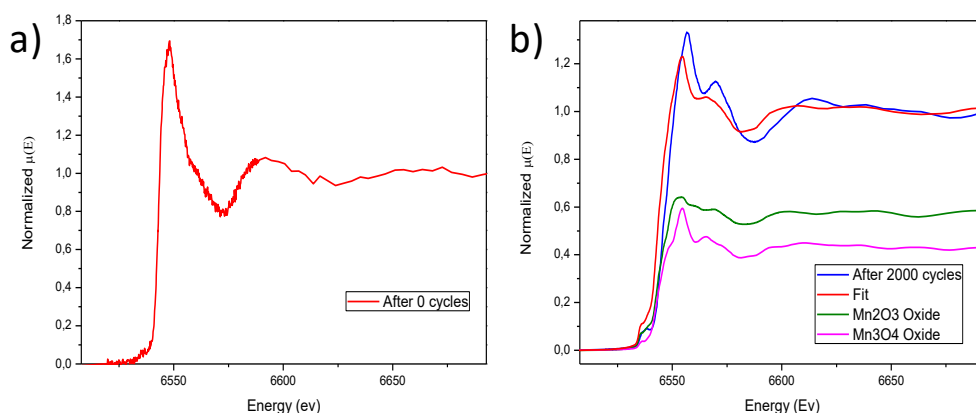


Fig. 2 (a) XAS spectra of manganese electrode before cycling. (b) Evolution of XAS spectra of manganese electrode after 2000 cycles.

Once we discard the possibility of making in-operando experiments, we cycle the samples ex-situ, stopping the cycling at different stages of the charge/discharge process for each sample. The measurement of the spectra after different cycles should give rise to similar information than in the in-operando experiment. As it can be seen in figure 2, the shape of the XAS spectra is different for the different samples. The electrodes evolve from an amorphous stage (fig 2 .a.) to a different stage (fig 2 .b.) in which the pre-edge could be fitted as a combination of different manganese oxides.

We measured 6 samples after different charge/discharge process in order to establish the relation between the electrochemical behaviour of the electrode and the Mn oxide state. We are now analysing the results using Athena software.

References

- [1] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, *Nature Mater* 4, 366–377.
- [2] R. R. Salunkhe, J. Lin, V. Malgras, S. X. Dou, J. H. Kim, Y. Yamauchi, *Nano Energy* 11, 211-218 (2015).
- [3] M. Zhi, C. Xiang, J. Li, M. Lia, and N. Wu, *Nanoscale* 5, 72–88 (2013).
- [4] T. M. Dinh, A. Achour, S. Vizireanu, G. Dinescu, L. Nistor, K. Armstrong, D. Guay and D. Pech, *Nano Energy* 10, 288-294 (2014).