Surface studies of $Na_2Ti_3O_7$ electrodes for rechargeable sodium-ion batteries

M.A. Muñoz-Márquez[1,*], M. Zarrabeitia[1], E. Castillo-Martínez[1], A. Eguía[1], T. Rojo[1,2], M. Casas-Cabanas[1]

[1] CIC energiGUNE, Albert Einstein 48, 01510 Miñano, Spain
[2] Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU, P.O. Box 644, 48080 Bilbao, Spain.
[*] E-mail: mamunoz@cicenergigune.com

Nowadays, the Li-ion battery research is focused in the development of high energy and high voltage batteries to cover the needs of the portable electronics market and electric vehicle industry. However, in order to fulfil the continuously increasing energy demand, more efficient distribution grids and bulk energy storage systems have to be developed. For this, Na-ion batteries are becoming an attractive solution for stationary energy storage; where, despite the increase of weight from lithium to sodium, the total price is decreased by using aluminium current collector for anodes and being the sodium far more abundant and easier to obtain than lithium.

Recent works have shown that many lithium ion analogues are successful candidates able to operate as cathodes in sodium ion batteries [1]. Nevertheless when it comes to anodes, the lack of sodium insertion into graphite along with the fact that a material with a stable SEI layer has not been reported to date [2], much more deficiencies are encountered. So far hard carbons and Sn or Sb alloys have produced the most satisfactory results.

Recently, reversible reaction in $Na_2Ti_3O_7$ [3] has been reported at significantly lower voltage than any other oxide electrode for sodium-ion batteries. A reversible phase transition is found to occur between $Na_2Ti_3O_7$ and a $Na_{12}Ti_{10}O_{28}$-like $Na_4Ti_3O_7$ phase during the electrochemical reaction with a voltage of approximately 0.3 V. Two Na ions could be inserted into $Na_2Ti_3O_7$: 0.67 Na per Ti, leading to a specific capacity of 200 $mA \cdot h \cdot g^{-1}$. However, despite the optimum performance reported for this electrode material, no information has been gathered on the electrode surface properties as well as on the electrode/electrolyte interface. It has been found that the most powerful technique for probing the chemical nature of the electrochemical interface is X-ray photoelectron spectroscopy (XPS); other techniques such as surface X-ray diffraction (XRD) or Raman spectroscopy although very relevant are less versatile in this respect [4]. Since there is a lack of XPS studies performed on sodium titanates, we decided to focus on results from XPS in this case.

In this work we will present quasi in-situ X-ray photoelectron spectroscopy (XPS) results that show the formation upon electrochemical cycling of a passivating layer in $Na_2Ti_3O_7$ laminates casted on aluminium current collectors. The behaviour and composition of the electrode surface was studied along with its stability at different points of the electrochemical curve [Fig. 1].

The photoemission experiments were combined with low energy ion etching so a depth profile of the passivating layer and electrode sub-surface was obtained. Moreover, structural information of the electrode material under study was obtained using techniques such as XRD, which have enabled us to have a complete picture of the factors governing the electrode stability.

Despite the formation of a passivating layer, the measured cyclability of the electrode and its specific capacity can position the $Na_2Ti_3O_7$ as a cheap and competitive anode for Na-ion batteries which can certainly be further improved after optimization of different parameters of synthesis and laminate preparation.

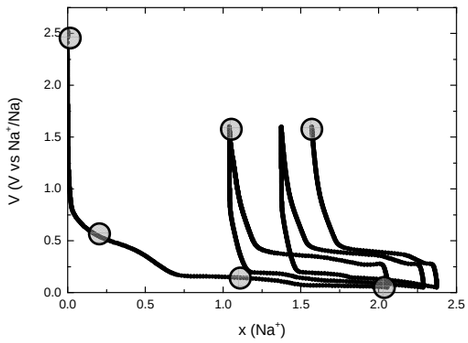

Fig. 1: Galvanostatic cycling of $Na_2Ti_3O_7$ vs. Na between 2.5-0 V at C/10 from the first to the third oxidation/reduction cycles using 1M $NaClO_4$ in EC:PC as electrolyte at room temperature. Spots indicate where the XPS measurements have been performed.

Acknowledgments

Financial support from the Gobierno Vasco/Eusko Jaurlaritza (ETORTEK CIC energiGUNE 10) is gratefully acknowledged.

References

[1] V. Palomares, P. Serras, I. Villaluenga, K. Hueso, J. Carretero-González, T. Rojo, *Energy Envirom. Sci.* **5**, 5884 (2012); S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.* **2**, 710 (2012).

[2] Komaba, T. Ishikawa, N. Yabuuchi, W. Murata, A. Ito, Y. Ohsawa, *Appl. Mat. Interf.* **3**, 4165 (2011).

[3] P. Senguttuvan, G. Rousse, V. Seznec, J.-M. Tarascon, M.R. Palacín, *Chem. Mater.* **23**, 4109 (2011).

[4] *Lithium-Ion Batteries: Solid-Electrolyte Interphase*, edited by P.B. Balbuena and Y.X. Wang. Imperial College Press, London (2004).