

## ON THE ELECTROCHEMICAL BEHAVIOR OF IRON SUBSTITUTED $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ NANO COMPOSITES AS CATHODE MATERIALS FOR Na-ION BATTERIES.

Pedro Lavela, María J. Aragón, Gregorio Ortiz and José L. Tirado  
Laboratorio de Química Inorgánica, Universidad de Córdoba, 14071 Córdoba, Spain  
q72aralm@uco.es

Sodium is an abundant and non-toxic alkali element with outstanding electrochemistry that places sodium batteries as serious competitors of lithium batteries for large-scale stationary energy storage. Transition metal phosphates exhibiting a NASICON-type structure offer a rigid framework with interconnected vacant sites facilitating the insertion and fast diffusion of alkaline ions.<sup>1,2</sup>  $\text{Na}_3\text{V}_{2-x}\text{Fe}_x(\text{PO}_4)_3/\text{C}$  nanocomposites ( $0 \leq x \leq 0.5$ ) were synthesized by the sol-gel method. The carbon matrix notoriously improved the conducting properties of the raw material.

XRD patterns of these samples are characterized by narrow reflections corresponding to well-crystallized phases. On increasing the iron content, the cell volume increases due to the slightly higher radius of  $\text{Fe}^{3+}$ . Figure 1 shows  $\text{Na}_3\text{V}_{1.7}\text{Fe}_{0.3}(\text{PO}_4)_3$  particles with non-homogeneous shape and size in the nanometric range. Cyclic voltammetry showed two signals at ca. 3.5 and 4.0 V, which evidence a linear dependence of potential on the level of substitution. The appearance of the short plateau at ca. 4.0 V is closely related to the higher iron substitution levels. The evaluation of XPS and  $^{57}\text{Fe}$  Mössbauer spectra of charged and discharged electrodes allowed ascribing the 4.0 V plateau to the  $\text{V}^{4+}/\text{V}^{5+}$  redox reaction and the reversible insertion of extra sodium ions from octahedral M1 sites. Galvanostatic cycling showed capacity values as high as  $115 \text{ mA h g}^{-1}$  for samples with  $x = 0.1, 0.2, 0.3$  and exceptional cyclability (Figure 2).<sup>3</sup>

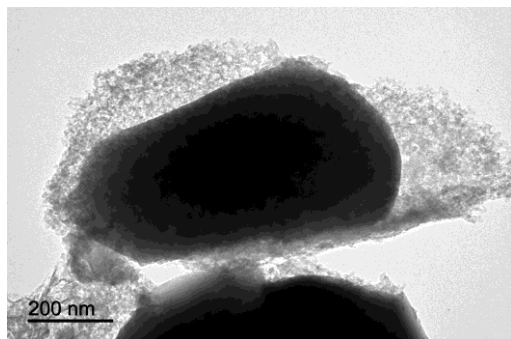


Figure 1: Transmission electron micrograph of  $\text{Na}_3\text{V}_{1.7}\text{Fe}_{0.3}(\text{PO}_4)_3$ .

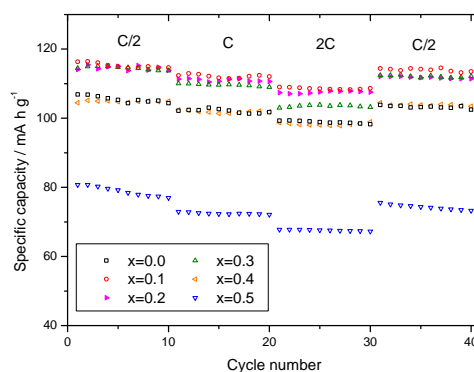


Figure 2: Capacity versus the number of cycles of sodium cells assembled with  $\text{Na}_3\text{V}_{2-x}\text{Fe}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 0.5$ ).

### Acknowledgements

The authors are grateful to Junta de Andalucía for financial support (Contract FQM-6017 and group FQM288) and MICINN (MAT2011- 22753).

<sup>1</sup> Aragón, M. J.; Vidal-Abarca, C.; P. Lavela; Tirado, J.L. *J. Power Sources*, **2014**, 252, 208.

<sup>2</sup> Aragón, M. J.; Vidal-Abarca, C.; P. Lavela; Tirado, J.L. *J. Mater. Chem. A*, **2013**, 1, 13963.

<sup>3</sup> Aragón, M. J.; Lavela, P.; Ortiz, G. F.; Tirado J. L. *J. Electrochem. Soc.*, **2015**, 162, A3077.