5th European Symposium on Super Capacitors & Hybrid Solutions

April 23-25, 2015

$Na_XCo_{2/3}Mn_{2/9}Ni_{1/9}O_2$ AS CATHODE MATERIAL FOR HIGH ENERGY DENSITY SODIUM ION BATTERIES

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Abstract

The abundance and the low cost of sodium as well as its suitable redox potential ($E_{(Na+/Na)}$ = −2.71 V *vs.* SHE) has made the electrochemical energy storage community to return again to sodium ion batteries as possible replacements for lithium ones. Sodium ion batteries are considered good candidates for stationary electrical storage devices. Herein, we present $Na_xCo_{2/3}Mn_{2/9}Ni_{1/9}O_2$, which has been synthesized by a sol-gel route in air followed by a heat treatment at 800°C for 12 h. Its structure has been studied by X-Ray diffraction showing that the material crystallized in a P2-structure type (space group P63/mmc) (Figure 1). Indeed, the electrochemical study of the material has showed that the intercalation/ de-intercalation process of Na^+in this material is reversible and proceeds smoothly, thus proving that the coexistence of cobalt, manganese and nickel with this stochiometry offers a stabilized structure. $Na_xCo_{2/3}Mn_{2/9}Ni_{1/9}O_2$ provides a specific capacity of 110 $mAhg^{-1}$ when cycled between 2.0 and 4.2 V *vs.* Na^+/Na. The electrodes exhibited a good capacity retention, a capacity loss of only 11% after 90 cycles, and a coulombic efficiency exceeding 99.4%, as well as a reversible discharge capacity of 140 $mAhg^{-1}$ when cycled between 2.0 and 4.5 V (figure2). [1, 2]
The structural changes occurring during the (de)intercalation of Na^+through the material were studied using *operando in situ* X-ray powder diffraction (XRPD).
When the material is cycled up to 4.5 V a severe decrease in the specific capacity is noticed and this is accompanied by a fast deterioration of the performance of the material (figure 2). Cycling at this high voltage causes decomposition of the electrolyte. Therefore, understanding the chemical composition of the interface between the electrolyte and the material is crucial. In particular, elucidating its behavior during cycling, alongside with the oxidation states of the transition metals at this interface is mandatory to understand the impact of the latter on the resulting electrochemical properties at different voltages. In order to achieve that, HAXPES measurements were performed at different stages of charge and discharge for this compound. The electronic properties of $Na_xCo_{2/3}Mn_{2/9}Ni_{1/9}O_2$ were also investigated using magnetic measurements.
In-situ XRD, HAXPES and magnetic measurements have granted access to a deeper understanding of the (de)intercalation processes of sodium ions in our material.

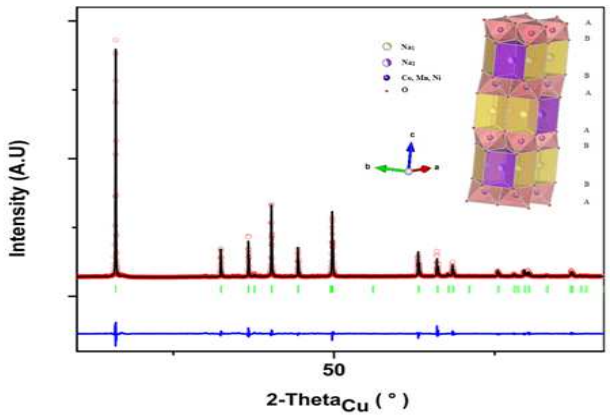

Figure1. Observed and calculated XRD patterns for the $Na_{2/3}Co_{2/3}Mn_{2/9}Ni_{1/9}O_2$ phase. Illustration of the P2 structure.

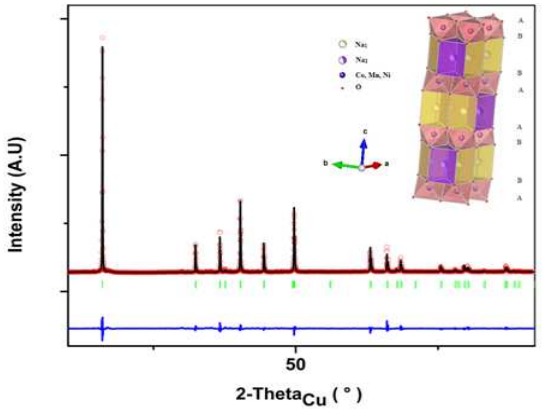

Figure2. Comparison of the specific discharge capacities upon galvanostatic cycling (10 cycles) at C/20 using two different upper cut-off voltages (4.2 V and 4.5 V *vs.* Na^+/Na)

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ACKNOWLEDGEMENT: The authors are grateful to the Swedish Research Council for the support of this work. S. Doubaji is grateful to CNRST (Morocco) for the scholarship (H003/005).