Spray-drying synthesis of $Na_3V_2(PO_4)_2F_3$ as cathode material in hybrid-ion batteries

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In recent years, fluorophosphates with the NASICON (Na Super-Ionic Conductor) type structure have been studied as cathode electrode materials. These fluorophosphates exhibit rich chemistry, attractive lithium/sodium insertion properties and thus offer promising electrochemical properties. Among them, $Na_3V_2(PO_4)_2F_3$ deserves attention because of promising electrochemical properties and ease of fabrication [1]. This material was reported by Song et al. in hybrid-ion batteries [2] and sodium ion batteries [1,3].

Here, $Na_3V_2(PO_4)_2F_3$/C powder was synthesized for the first time by the spray-drying method. $Na_3V_2(PO_4)_2F_3$/C contains 15% of carbon nanotubes (CNTs) added in situ to increase the electronic conductivity and connection between particles. In this method a solution/suspension is sprayed by air creating fine droplets in drying chamber with hot air flow (100–300 °C). These droplets are instantly dried, making it possible to harvest a homogeneous composition powder while avoiding thermal degradation of the compound (oxidation).

Structural and microstructural characterizations were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Study of firing and heat treatment influence on the powder purity and particle morphology showed that powders dried at 180 °C and fired at 600 °C have the best properties.

Electrochemical measurements were carried out in hybrid-ion batteries, using a potentiostat (BT-LAB) in the range of 1.6-4.6 V and 2-4.6 V vs. Li^+/Li^0 at different cycling rates. Addition of CNTs increased the conductivity and as a result the capacity. $Na_3V_2(PO_4)_2F_3$/C samples cycled between 1.6-4.6 V vs. Li^+/Li° demonstrated specific capacities of 175 and 149 at C/15 and C/10-rate, respectively. These results are higher than the capacity of 147 $mAh.g^{-1}$ at 0.09C-rate reported by Song et al.[2].

Better cycling performance and capacity retention was observed when electrochemical cells were cycled between 2-4.6 V with capacities of 140, 128 and 102 $mAh.g^{-1}$ at C/15, C/10 and 1C-rate, respectively with 80% capacity retention over 300 cycles.

These preliminary results show that the spray-drying technique is suitable for obtaining complex powders with a very good homogeneity leading to very good electrochemical properties.

References:

[1] R. A. Shakoor, D. H. Seo, H. Kim, Y. U. Park, J. Kim, S. W. Kim, H. Gwon, S. Lee and K. Kang, J. Mater. Chem., 2012, 22, 20535.

[2] W. Song, X. Ji, J. Chen,Z. Wu,Y. Zhu, K. Ye, H. Hou, M. Jinga and C. E. Banks, Phys. Chem. Chem. Phys., 2015, 17,159.

[3] Bianchini, M., Brisset, N., Fauth, F., Weill, F., Elkaim, E., Suard, E., Masquelier, C., Croguennec, L., Na3V2(PO4)2F3 Revisited: A High Resolution Diffraction Study, Chem. Mater. 2014, 26, 4238−4247.