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Carbon Bismuth Oxyfluoride Nanocomposites as Cathode Material for Lithium Battery

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Reversible conversion reactions for Li-ion batteries have first been introduced in metal oxide [1,2] and metal nitride [3,4,5]. The basic principle of such reaction is the reduction of the active material into metal and Li_2O or Li_3N and the reformation of a metal oxide or nitride during the following oxidation. As opposed to intercalation reactions, the conversion reactions enable large specific capacities as all redox states are utilized during the reduction process. Those sytems, to be used as negative electrodes in Li-ion batteries due to their low voltage, have all shown good or even excellent cycling stability.

More recently it has been demonstrated that reversible conversion reaction were also possible at the positive side of the batteries using metal fluorides as active material [6,7]. Owing to their higher ionicity the reduction of the metal fluoride into LiF and the corresponding metal occurs at much higher voltage than in oxide or nitride. To cope with the high electronic resistivity of the fluoride, metal fluoride carbon nanocomposite prepared by high-energy milling were utilized. A specific capacity as high as 600mAh/g has thus been extracted at 70°C from a FeF_3/C nanocomposite cycled between 4.5V and 1.5V [7].

We will present our work on more complex compounds where both the oxygen and fluorine ions coexist. Such systems are of interest since they could combine the high voltage of the metal fluorine with the better electronic conductivity of the metal oxide. The two oxyfluorides we have looked at are $BiO_{0.5}F_2$ and BiOF, prepared in house by aqueous synthesis from Bi_2O_3 and NH_4F. Like in the case of the FeF_3/C [7] and BiF_3/C [8], nanocomposites made of a fine dispersion of active material nanoparticles (<30nm) into a highly conductive carbon matrix were first prepared by high-energy milling in order to enable the electroactivity of the material.

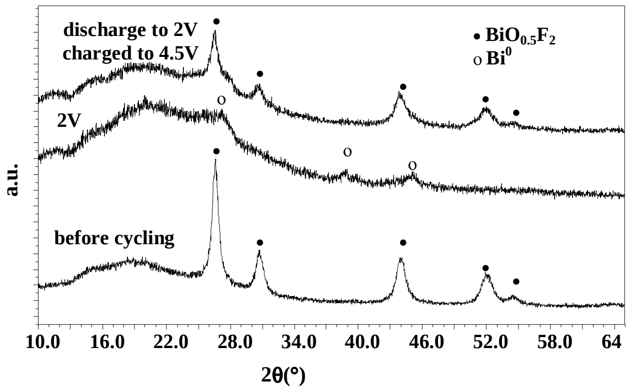

figure 1: Ex-situ XRD of the $BiO_{0.5}F_2$ /C nanocomposite prior to cycling, discharged to 2V and at 4.5V after one discharge down to 2V

Our results clearly demonstrate that reversible conversion reactions with the lithium are taking place at 24°C in the bismuth oxyfluorides. The chemical reactions involved can be written as:

$$BiO_{0.5}F_2 + 3Li \leftrightarrow Bi^0 + 0.5Li_2O + LiF$$
$$BiOF + 3Li \leftrightarrow Bi^0 + Li_2O + LiF$$

Like in bismuth oxide and fluoride the initial structure is completely broken down to the bismuth metal, lithium fluoride and lithium oxide during the reduction, and reformed during the following oxidation.

When cycled with a current of 7.58mA/g the specific capacity during the first discharge down to 1.5V of both the $BiO_{0.5}F_3$/C and BiOF/C are close to 270 mAh/(g of composite). The long term cycling stability was found to be poor. The basis for this behavior will be discussed.

Results of physical characterizations by means of potentiostatic and galvanostatic electrochemical methods, in-situ and ex-situ XRD as well as transmission electron microscopy will be presented to define the mechanisms involved. The correlation between the electrode voltage and the conversion reactions involving the fluorine anions on hand and the oxygen anions on the other will be discussed. A comparison with the results obtained on Bi_2O_3/C and BiF_3/C nanocomposites cycled under similar conditions will be carried out.

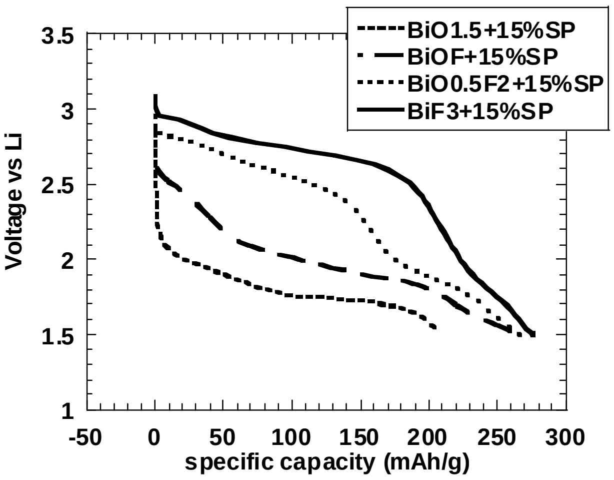

figure 2: Comparison of the voltage profile during the first discharge down to 1.5V of the BiF_3/C, $BiO_{0.5}F_3$/C, BiOF/C and Bi_2O_3/C nanocomposites

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