

Bismuth Ferrites as Electrodes for Lithium batteries: An *in situ* XRD and XANES Investigation

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In this talk, we studied some Bi based ferrites as electrode materials for lithium batteries. The energy storage mechanisms based on Bismuth ferrites are further investigated by *in situ* XRD and XAS, which cover both structural and electronic transformations. All of these *in situ* experiments used an electrochemical cell feature, which allows for *in situ* studies while the batteries are cycled.

It was found that for bismuth oxides studied, Bi ions are mainly responsible for the charge transfer during the electrochemical cycling process. Large discharge capacity could be obtained.¹ For BiFeO₃, Fe ions are mainly responsible to maintain the structural integrity, while a Bi (III) to Bi (0) transformation was observed during the discharge and followed by Li-Bi alloy formation, which further increased the capacity. 5% Ce was successfully doped inside BiFeO₃ and as the consequence, the particle size were greatly decreased and contributed to an increase of electrochemical performance in both larger discharge capacity as well as higher discharge voltage. The *in situ* XRD patterns during the cycling process were collected and the perovskite structure was maintained even after the fully reduction of Bi (III) to Bi (0). Bi separation was clearly observed by *in situ* XRD, where the c axis lattice parameter is greatly decreased. However, a/b axis is not affected by Bi separation and thus two transportation mechanisms are observed. Namely, there are both electronic transportation and ionic transportation pathways, and one is along the c axis of the Hexagonal cell and the other is along the a/b plane.

For Bi₂Fe₄O₉, large discharge capacity is also observed, while for an orthorhombic unit cell, the discharge mechanism is different from that of hexagonal BiFeO₃. Bi₂Fe₄O₉ has an ordered alignment of FeO₆ octahedrons connected along the c axis. These FeO₆ octahedrons are connected in b axis direction by two Fe tetrahedrons (Fe₂O₇).² Bi ions aligned along c axis and formed 1 dimensional channel. During the discharge, Fe ions are first reduced to a valence state that is very close to that of Fe₃O₄. Then the electrochemical voltage decreased with the concomitant reduction of Bi ions. Bismuth ions are reduced to metallic Bi after fully discharged to 0.05V and further, Bi-Li alloy formation was observed, similar to those reported for BiFeO₃. Details of these investigations will be discussed in the presentation.

References:

- 1) Xia, H.; Yan, F.; Lai, M. O.; Lu, L.; Song, W. D. *Funct. Mater. Lett.* **2009**, 2, 163.
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