Enhanced capacity retention of MnO_2 cathode enabled by Bi doping

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Zn-ion batteries (ZIBs) are a promising future technology to complement Li-ion batteries as ZIBs consist of less expensive and non-toxic elements. One of the most promising cathode materials for ZIBs is MnO_2.[1] However, it is plagued by several surmountable shortcomings like the dissolution of active material due to corrosion, deterioration of the electrode's structure, and a reduction in capacity. A way to overcome these shortcomings is to introduce heteroatoms into the structure of the active material. [1,2]

In this work, we have synthesized Bi-doped MnO_2 by hydrothermal synthesis method. Bi-doping was fixed at concentrations – 0, 0.5, 1, 2.5, 5 and 10 mol%. Afterwards, a slurry was obtained by mixing Bi-MnO_2 powders with carbon black Vulcan and PVDF solution in NMP to form cathode materials on carbon paper. In a similar fashion cathodes with purchased MnO_2 active materials were formed for reference. The samples were analysed with an X-ray diffractometer, Raman spectrometer, and scanning electron microscope with energy-dispersive X-ray spectroscopy (EDX). Also, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and impedance measurements were performed.

The as-prepared samples consisted of α- and δ- MnO_2 mixture. Samples with high Bi doping showed also additional BiOCl phase. As seen from the electrochemical measurement results in Figure 1, synthesized material cathodes had higher specific capacity than a cathode constructed from purchased MnO_2. Also, improved capacity retention was seen for samples with larger Bi-doping. After electrochemical measurements, all the samples showed only δ-MnO_2 phase and EDX results revealed homogenous Bi atom scattering for samples with Bi doping.

In conclusion, Bi doping enhances capacity retention by promoting α-MnO_2 phase formation that is more electrochemically active. As the Bi^{3+} ion is two times larger than the Mn^{4+} ion, the Bi promotes 2x2 tunnel structure formation by occupying inter-lattice space inside the tunnels. In addition, Bi doping improves the electrical conductivity of MnO_2.

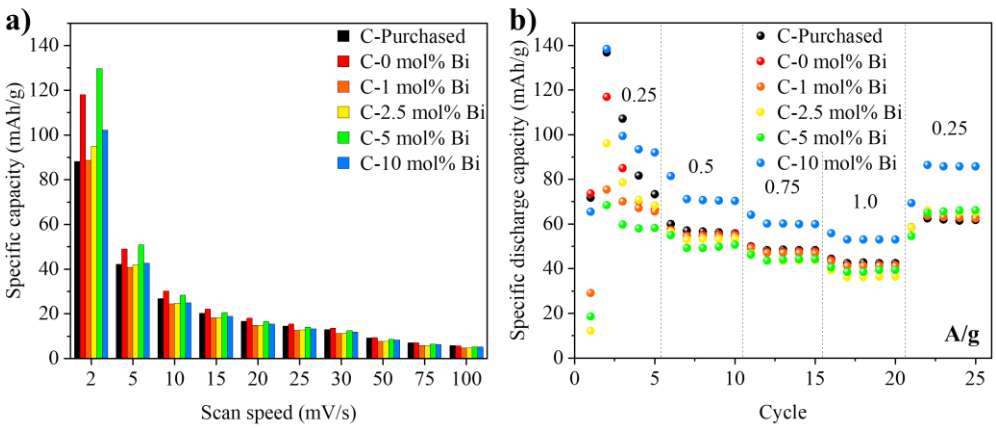

Figure 1: a) Specific capacities from CV measurements at various scan speeds and b) discharge capacities from GCD measurements at various current densities of purchased, undoped and Bi-doped MnO2 samples.

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References
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