

Improved Cycling Performance of Bismuth-Modified Amorphous Manganese Oxides as Cathodes for Rechargeable Lithium Batteries

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Manganese oxides in amorphous forms as cathode materials for rechargeable lithium and lithium-ion batteries have attracted increasing attention in recent years [1-4]. They exhibit very high intercalation capacities over a wide voltage range corresponding to more than one electron reduction of the Mn (IV) ions, i.e. a redox reaction involving both the $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples. However, for many amorphous manganese oxides synthesized by low temperature aqueous routes, unsatisfactory cycling performance becomes a limiting factor for them, as is the case for many crystalline manganese oxides and lithium manganese oxides as well.

The close to two electron transfer in the amorphous manganese oxides where Mn^{4+} is reduced to Mn^{2+} during the lithium intercalation process resembles what occurs in aqueous alkaline batteries where manganese oxides function as cathodes. Although difficulties exist when trying to make it rechargeable because of the poor reversibility of MnO_2 in alkaline batteries [5, 6], a breakthrough was achieved with MnO_2 modified by bismuth either chemically or physically [7, 8]. The bismuth-modified manganese oxide could be cycled hundreds of times with high discharge depths. Extensive research has been conducted and many suggestions have been given with regard to the role that the bismuth ions play in the modified MnO_2 in alkaline batteries.

Considering the resemblance between proton insertion and lithium intercalation, bismuth-modified manganese oxides might yield improved cycling performance for lithium intercalation as well. Despite the fact that bismuth-modified manganese oxides have accomplished significant success in alkaline batteries, related work is still scarce on their application in lithium or lithium ion batteries. Moreover, since confusion and controversy still exist as to the role of bismuth in manganese oxides despite the extensive work that has been done in aqueous alkaline batteries, investigation of the behavior of bismuth-modified manganese oxides as lithium intercalation hosts in non-aqueous systems might provide complementary or additional information with which to address and ascertain the role of bismuth in manganese oxides.

In the present work, bismuth-modified amorphous manganese oxides were synthesized and characterized as cathodes for rechargeable lithium batteries. They were galvanostatically tested as intercalation cathodes for rechargeable lithium batteries at 1 mA/cm^2 between 1.5 and 4.3 V. In sharp contrast to severe capacity fading of unmodified amorphous manganese oxide synthesized by

the same route, a stable cycling performance of the bismuth-modified amorphous manganese oxide was observed. After an initial drop from 185 to 145 mAh/g in around 10 cycles, the capacity of the bismuth-modified amorphous manganese oxide remains essentially unchanged for another 40 cycles. Based on results from X-ray diffraction and cyclic voltammetry characterization, it is suggested that the role of bismuth ions might be similar to the catalytic role proposed for them in bismuth-doped manganese dioxides for alkaline batteries. An electrochemically active and stable local structure evolves inside the bismuth-modified amorphous manganese oxide upon initial cycling, leading to the stabilized cycling performance for subsequent cycles.

References

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