Unveiling the Intricate Reaction Mechanism of Manganese Sesquioxide as Positive Electrode in Aqueous Zn-metal Battery

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Abstract

In the family of Zn/manganese oxide batteries with mild aqueous electrolytes, cubic α-Mn_2O_3 with bixbyite structure is rarely considered, because of the shortage of the tunnel and/or layered structure that are usually believed to be indispensable for the incorporation of Zn ions. In this work, a completely new charge storage mechanism is proposed, revealing that α-Mn_2O_3 is in fact a promising cathode material for aqueous zinc-ion batteries. Specifically, this involves an electrochemically induced irreversible phase transition from α-Mn_2O_3 to layered-typed L-Zn_xMnO_2 occurring upon the discharging during the initial cycles, which is accompanied by the dissolution of Mn^{2+} into the electrolyte, thus allowing the subsequent reversible de-/intercalation of Zn^{2+} in the latter structure. The repeated uptake/removal of H^+ in the cathode material and dissolution/deposition of Mn^{2+} on the cathode surface also contributes considerably to the overall charge storage. Based on this electrode mechanism, combined with fabricating hierarchically structured mesoporous α-Mn_2O_3 microrod array material, we this way obtained an unprecedented rate capability with 103 mAh g^{-1} at 5.0 A g^{-1} as well as an appealing stability of 2000 cycles with a capacity decay of only ca. 0.009% per-cycle.

Keywords: Aqueous zinc-ion battery, energy storage mechanism, hierarchical mesoporous structure, α-Mn_2O_3, cathode

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