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| Title | The dominant role of Mn2+ additive on the electrochemical reaction in ZnMn2O4 cathode for aqueous zinc-ion batteries. | | |
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| Abstract |  |
| Among zinc-ion battery (ZIB) cathodes, ZnMn2O4 (ZMO), with its high theoretical capacity and voltage, is an intriguing choice. In this study, we compared the electrochemical activity of a ZMO microrods cathode obtained through a simple co-precipitation process in the presence of a 0.1 ​M MnSO4 (MS) solution as a full-time electrolyte, as an additive in [zinc sulfate](https://www.sciencedirect.com/topics/engineering/zinc-sulphate) (ZMS) electrolyte (1 ​M ZnSO4 ​+ ​0.1 ​M MnSO4) and in its absence or a full-time zinc sulfate (ZS) electrolyte (1 ​M ZnSO4), respectively. Systematic investigations including ex situ X-ray diffraction (XRD), scanning electron microscopy (SEM), and [transmission electron microscopy](https://www.sciencedirect.com/topics/engineering/transmission-electron-microscopy) (TEM) studies revealed the reasons for the superior stability and high [reversibility](https://www.sciencedirect.com/topics/engineering/reversibility) of ZMO in the ZMS electrolyte medium. The exceptional performance was facilitated by the electrochemical equilibrium between Zn2+ and Mn2+ ions via a stable Zn2+ (de)insertion in the bulk, a reversible electro-deposition/dissolution of MnOx from the Mn2+ additive in the electrolyte onto(from) the surface of the cathode and the reversible Zn-insertion into the undissolved surface MnOx layer. This finding is significant as it is contrary to the conventional understanding that the addition of Mn2+ merely tends to prevent manganese dissolution thereby facilitating a stable cycle-life performance of the cathode in ZIBs. | |