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Transition metal alloy-modulated lithium manganese oxide nanosystem for energy storage in lithium-ion battery cathodes

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Abstract

This paper explores the synergistic and catalytic properties of a newly developed lithium ion battery (LIB) composite cathode of LiMn2O4 modified with bimetallic (Au–Fe) nanoparticle. Spinel phase LiMn2O4 was doped with bimetallic nanoparticles, LiMxMn2−xO4 (M = FeAu), with concomitant oxidation of the Mn3+ ions (responsible for LIB capacity loss) to Mn4+. This nano-composite architecture accommodates the structural transformation that occurs during Li+ ion charge and discharge. Ultra-low scan rate (0.01 mV s−1) cyclic voltammetry of the pure LiMn2O4 cathode material in 1 M LiPF6/electrolyte solution, showed two sets of redox peaks with a third observed at lower potentials for LiMxMn2−xO4. The FeAu incorporation increased the reaction rate upon reduction of LiMn2O4 as indicated by the enhanced reduction peak seen by cyclic voltammetry. Nyquist plots of the electrochemical impedance spectroscopy (EIS) results showed LiFeAuxMn2−xO4 having increased conductivity with lower resistance of charge. Xray diffraction studies showed the LiMxMn2−xO4 material retained well-developed octahedral structures bounded by (111) planes. The material crystallite size was ∼10 nm with clear lattice fringes having a separation value of 0.48 nm which concurrently improved the diffusion rate of Li+ . Solid-state NMR results showed the progressive increase in average nominal manganese oxidation state from +3.5 to +4 resulted in an increase in the super-transferred hyperfine field at the 7Li nucleus of the FeAu doped cathode material. The LiFeAuxMn2−xO4 material also showed improved cycleability, especially at high C rate. This improvement was due to the enhanced physical stability of LiMn2O4 and its improved electrical conductivity ascribed to the incorporated FeAu nanoparticles.