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Regulating the crystal structure of $LiMn_2O_4$ material by Zn doping

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The substitutional defect consisting of the aliovalent substitution of lithium ions by zinc ions in the tetrahedral sublattice of the $Li_{1-x}Zn_xMn_2O_4$ spinel changes the overall charge of the ionic compound. In order for the ionic compound to remain neutral, a charge compensation mechanism is required. There are different ways to do this, e.g. partial reduction of manganese occurs or ionic vacancies are created. Cooperative control of atomic composition and defect engineering allows for obtaining materials with extraordinary properties[1-3].

We adopted $Li_{0.9}Zn_{0.1}Mn_2O_4$ oxide as a model system to investigate the chemical strain induced by tetrahedrally located zinc ions insertion and its potential effect on the electrochemical performance. In the lithium manganese spinel $LiMn_2O_4$, the monovalent Li^+ cation occupies the tetrahedral A sites, and the octahedral B sites are occupied by a mixture of Mn^{4+} ions and the Jahn-Teller active Mn^{3+} ions. This cation distribution results in a cubic structure (*Fd*-3*m*). The number of Mn^{3+} ions in the octahedral sublattice is insufficient to generate the cooperative Jahn–Teller effect at ambient temperature and to deform the crystal structure.

The unique properties of the material studied in this work result from the relatively unique distribution of ions in two crystallographic positions. Reducing the number of lithium ions in the tetrahedral positions, as in $Li_{0.9}Zn_{0.1}Mn_2O_4$, allows the remaining tetrahedral sites to be filled with Zn^{2+} ions. As a consequence, the oxidation state of manganese in octahedral positions decreases, resulting in a Jahn–Teller distortion with tetragonal symmetry and $c/a' > 1$.

For the laboratory synthesis of multicomponent spinel oxide, we used a modified Pechini method. The method was based on mixing standard solutions of manganese and nickel nitrate with lithium carbonate and citric acid, and then the solution of trimetallic citrate complexes was transformed into a polymer gel by controlled heating and finally thermal decomposition of the polymer matrix to remove the organic component[4]. When the heating temperature reaches 673 K, oxidation and pyrolysis of the polymer matrix occur. We made several attempts, performing heat treatments at different temperatures, each time ending with rapid cooling of the sample in solid CO_2. The structure of the sample was investigated by the powder diffraction experiment performed at the I711 beamline in MAXLab (Lund, Sweden).

Knowledge of the structure design strategy via cationic distribution will facilitate the design of materials with new desirable properties, including high energy density and long cycle life cells, selective catalysts, and nonvolatile resistive random access memory devices.

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