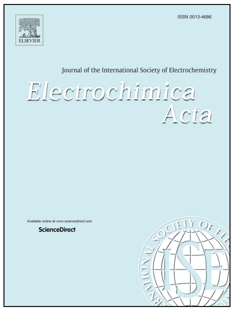

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ABSTRACT

Cubic spinel $LiMn_2O_4$ has been studied for the reversible extraction of Li^+ from natural brine after the application of suitable electrode potentials. In this work we report on the insertion/extraction of Li^+ from natural brine of Olaroz salt flat (Jujuy, Argentina) and aqueous LiCl solutions into/from $Li_{1-x}Mn_2O_4$ ($0 < x \leq 1$) to determine changes in the crystal structure and surface composition upon electrochemical polarization. In agreement with the behavior in organic electrolytes, we found that the insertion and extraction of Li^+ proceeds via a two stage process and that the crystal structure undergoes two cubic phase transitions as the lattice is expanded or contracted. Contrary to the behavior in organic solvents, no decomposition layer is formed on the electrode surface and the surface composition can be controlled with the electrode potential. We also found that sodium cations present in natural brine are not inserted into the crystal lattice in the potential window explored, however they are adsorbed on the oxide surface blocking Li^+ adsorption sites and decreasing the rate of Li^+ exchange.