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Structural analysis of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ materials synthesized by Pechini method

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Layered tri-transition metal oxides, specially $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC 333), have become a promising alternative to $LiCoO_2$ electrode material in the rechargeable Lithium-Ion Battery (LIB). The electrochemical performances of NMC 333 mainly depend on its crystallographic structural properties including lattice parameters, the unit-cell, c/a ratio, volume, crystallite size (D), dislocation density(δ), and lattice strain. This study aims to synthesize $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$, and $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ materials and study their structural properties. The Pechini method was used for powder synthesis in this study. The synthesized materials were characterized using X-ray diffraction (XRD). X-ray characterization confirmed the formation of only the single-phase layered hexagonal lattice (α-$NaFeO_2$-type) structure without any impurity phase for all these prepared materials. Interestingly, while confirming the formation of layered structures, a better splitting of the (006)/(102) and (108)/(110) peaks appeared for $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ than that of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ in the diffractograms. The lattice parameters, i.e. a, c, c/a, the unit-cell volume, the crystallite size (D), and dislocation density(δ) are 2.8641(Å), 14.2143(Å), 4.9629, 100.979(Å^3), 77.45 nm,1.666×10^{14} m^{-2}, for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. While they are 2.8675(Å), 14.2317(Å), 4.9630, 101.347(Å^3), 85.06 nm, 1.382×10^{14} m^{-2} for $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ and 2.869 (Å), 14.2421(Å), 4.9641, 101.528(Å^3), 128.38 nm, 0.606×10^{14} m^{-2} for $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$, respectively. It is also observed that the lattice parameters, the unit-cell volume, c/a, and the crystallite size are increased with the substitution of Li^+ by Na^+ and K^+. It may be due to the radii of Na^+ and K^+ are bigger than that of Li^+ and that will pave the way for increasing the interlayer space of the substituted materials with the substitution of bigger ions. The c/a ratio constitutes a direct indication of the cation mixing. $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ exhibit higher c/a values than $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, supporting the observation that the substituting bigger ions such as Na^+ and K^+ into $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ suppresses the cation mixing and forms a well-defined layered structure. The micro-strain calculated for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$, and $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ are 1.38×10^{-3}, 2.17×10^{-3} and 1.46×10^{-3}, respectively. This implies a slight difference in the crystallinity of the materials, as the micro-strain was slightly affected by substituting Na^+ and K^+. Crystallite size (D) was 77.45 nm, 85.06 nm, and 128.38 nm for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $Li_{0.96}Na_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $Li_{0.96}K_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$, respectively. It exhibits an increment of crystallite size, indicating a lowering of the dislocation density with the substitution of bigger ions. Altogether, this study reveals that substituting Li^+ with bigger ions of Na^+ and K^+ is improving the structural stability of NMC 333.

Keywords: NMC materials, Na doping, K doping, Li-ion battery, Pechini method

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