High Voltage Mg-doped Na$_{0.67}$Ni$_{0.3-x}$Mg$_x$Mn$_{0.7}$O$_2$ ($x = 0.05, 0.1$) Na-ion Cathodes with Enhanced Stability and Rate Capability

Gurpreet Singh, Nuria Tapia-Ruiz, Juan Miguel Lopez del Amo, Urmimala Maitra, James W. Somerville, A. Robert Armstrong, Jaione Martinez de Ibarlucea, Teófilo Rojo, Peter G. Bruce

1CICenergie, Parque Tecnológico de Álava, Albert Einstein 48, ED.CIC, 01510, Miñano, Spain
2Department of Materials, University of Oxford, Oxford OX1 3PH, United Kingdom
3School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, United Kingdom
4Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU, P.O. Box. 644, 48080, Bilbao, Spain

Chem. Mater., Just Accepted Manuscript
DOI: 10.1021/acs.chemmater.6b01935
Publication Date (Web): June 27, 2016
Copyright © 2016 American Chemical Society

Abstract

Magnesium substituted P2-structure Na$_{0.67}$Ni$_{0.3}$Mn$_{0.7}$O$_2$ materials have been prepared by a facile solid-state method and investigated as cathodes in sodium-ion batteries. The Mg-doped materials described here were characterised by X-ray diffraction (XRD), $^{23}$Na solid-state nuclear magnetic resonance (SS-NMR) and scanning electron microscopy (SEM). The electrochemical performance of the samples was tested in half cells vs. Na metal at room temperature. The Mg-doped materials operate at a high average voltage of ca. 3.3 V vs. Na/Na$^+$ delivering specific capacities of ~ 120 mAh g$^{-1}$ which remain stable up to 50 cycles. Mg doping stabilizes the structure in the high voltage region by suppressing the well-known P2-O2 phase transition observed in the pristine composition. Instead, an OP4 phase was observed during charging (during Na removal) of the Mg-doped materials. GITT measurements showed that the Na-ion mobility is improved by two orders of magnitude with respect to the parent P2 Na$_{0.67}$Ni$_{0.3}$Mn$_{0.7}$O$_2$. The fast Na-ion mobility may be the cause of the good observed rate performance.