Theoretical study of disorder effects on electronic properties in Li_x(Co-Ni-Mn)O_2 battery system

M. Rybski[1], J. Tobola[1], S. Kaprzyk[1], J. Molenda[2]

AGH University of Science and Technology Mickiewicza 30, 30-059 Krakow, Poland
[1]Faculty of Physics and Applied Computer Science,
[2]Faculty of Energy and Fuels,
e-mail: rybski@fis.agh.edu.pl

Operation of Li-ion batteries is based on lithium intercalation into transition metals based oxides (or sulfides). This is always a process involving both ion and electron transfer, as follows $xLi^+ + xe^- + M_aX_b \longleftrightarrow Li_xM_aX_b$ (M-transition metal, X-O,S). The change of the electromotive force of the $Li/Li^+/Li_xMO_2$ battery cell corresponds to the variation of chemical potential of electrons and lithium ions in the cathode material. Since the variation of chemical potential of lithium ions is of the order of k_BT (c.a 25 meV at room temperature) and is much smaller than the change in chemical potential of electrons (being of the order of bandwidth) it is possible to investigate the performance of cathode materials on the basis of its electronic properties. Quite recently, the step-like vs. continuous-like character of the discharge curve have been interpreted in terms of close correlations between electronic structure and electrochemical properties in selected Na- and Li-ion cathode materials, respectively [1, 2, 3].

In this work, the results of electronic structure calculations of Li_x(Co-Ni-Mn)O_2 battery system are presented. Especially, the influence of chemical disorders, such as vacancy defects on Li and O sites, as well as Co/Ni/Mn alloying, on electronic density of states has been studied. Electronic structure calculations were performed with the use of the Korringa-Kohn-Rostoker method combined with the coherent potential approximation (KKR-CPA) [4, 5], which belonged to the well-established first principles technique allowing to account for chemical disorder effects in self-consistent way. The obtained results show that the Fermi level is strongly shifted not only due to Li deintercalation as well as the Co/Mn/Ni disorder, but also some extra electronic states apprear inside the energy gap when accounting for the KKR-CPA computations, the O vacancy defects.

[1] J. Molenda, D. Baster, M. Molenda, K. Swierczek, J.Tobola, Phys. Chem. Chem. Phys. **16**, 14845 (2014).
[2] A. Milewska, K. Swierczek , J. Tobola, F. Boudoire, Y.Hu, D.K. Bora, B.S. Mun, A. Braun, J. Molenda, Sol. St. Ionics, **263**, 110 (2014).
[3] J. Molenda, A. Milewska, W. Zajac, M.Rybski J.Tobola - to be submitted
[4] A. Bansil, S. Kaprzyk, P. E. Mijnarends, J. Tobola, Condens. Matter Mater. Phys. **60**, 13396 (1999)
[5] T. Stopa, S. Kaprzyk, J. Tobola, Phys. Condens.Matter, **16**, 4921 (2004).