

PhD dissertation's abstract

„Theoretical studies of electronic structure and electrochemical properties in materials for ion batteries”

The doctoral thesis focuses on theoretical investigations of cathode systems in lithium-ion and sodium-ion batteries belonging to the family of layered transition metal oxides. The analysis of selected battery systems was performed based on electronic structure calculations using the Korringa-Kohn-Rostoker (KKR) method. Because real systems contain various types of defects (vacancies in Li/Na positions, oxygen vacancies, and disorder in the transition metal sites) that can significantly influence their electrochemical properties, it was necessary to account for these defects in the calculations. This was achieved by using the Coherent Potential Approximation (CPA) combined with the KKR method. The investigation of the electronic structure of the considered cathode materials served as a tool for interpreting the measurement results of the electrochemical parameters of ion batteries, especially the discharge curve, cathode chemical stability, and transport properties.

For layered cathode materials with structures similar to LiCoO_2 , the electronic structure of three systems was thoroughly examined: $\text{Li}_x\text{Ni}_{0.55}\text{Co}_{0.35}\text{Mn}_{0.1}\text{O}_{2-\delta}$, $\text{Li}_x\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_{2-\delta}$ and $\text{Li}_x\text{Ni}_{0.58}\text{Co}_{0.3}\text{Mn}_{0.1}\text{Cu}_{0.02}\text{O}_{2-\delta}$. KKR-CPA calculations of the relative Fermi level changes as a function of Li ion concentration in these systems accurately reproduced the monotonous shape and the range of variation of the OCV (Open Circuit Voltage) curve. The theoretical results concerning the nature of electrical conductivity and the sign of the thermoelectric power are in good agreement with experimental data. Partial DOS calculations suggested that the increased oxygen contribution near the Fermi energy is the source of the observed structural instability in the $\text{Li}_x\text{Ni}_{0.55}\text{Co}_{0.35}\text{Mn}_{0.1}\text{O}_{2-\delta}$ system for $x_{\text{Li}} < 0.35$. KKR-CPA calculations also explained the improvement in transport properties in the copper-doped system $\text{Li}_x\text{Ni}_{0.58}\text{Co}_{0.3}\text{Mn}_{0.1}\text{Cu}_{0.02}\text{O}_{2-\delta}$ compared to $\text{Li}_x\text{Ni}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_{2-\delta}$ due to the presence of a strong d-Cu state peak near the Fermi energy.

For sodium cathode materials, electronic structure calculations were conducted for the following systems: $\text{NaFe}_{0.3}\text{Co}_{0.7}\text{O}_2$, $\text{Na}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_2$ and $\text{Na}_{0.67}\text{Mg}_{1/3}\text{Mn}_{2/3}\text{O}_2$. The calculated relative change in Fermi energy for different phases, amounting to 0.18 eV for $x_{\text{Na}} = 0.75$ accurately reproduced the step-like changes in the charge-discharge curve during the O3-P3 structural transition in the $\text{NaFe}_{0.3}\text{Co}_{0.7}\text{O}_2$ system. KKR-CPA-DLM calculations of the electronic structure of the $\text{Na}_x\text{Fe}_{1-y}\text{Mn}_y\text{O}_2$ system in the paramagnetic state, particularly the analysis of the density of states around the Fermi energy, partially explained the increase in electrical conductivity with increasing Mn concentration. Furthermore, the calculated relative change in Fermi energy correlated well with the experimentally determined OCV curve. Comparative calculations using the KKR-LDA+U method with strong electronic correlations for ordered models of NaMnO_2 and $\text{NaMg}_{1/3}\text{Mn}_{2/3}\text{O}_2$, as well as KKR-CPA for models with chemical disorder in the $\text{Na}_{0.67}\text{Mg}_{1/3}\text{Mn}_{2/3}\text{O}_2$ system, showed that the addition of Mg increases the active oxygen contribution to the electronic structure, partially explaining the observed increase in electrical conductivity compared to the NaMnO_2 system.

In summary, this doctoral thesis provides a valuable theoretical tool that can be used in further research on cathode materials for ion batteries. Obtained results from this work can contribute to the development of more efficient, environmentally friendly, and safe batteries, which is of great importance for the advancement of electrochemical energy technologies.