Thermodynamic Aspects of Copper Oxides and Iron Oxides Used as Conversion Electrodes for Lithium Ion Batteries

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Electrodes based on materials in the 3d transition metal oxide system Cu-Fe-O which apply the conversion mechanism for the electrochemical storage of energy are promising for next-generation lithium ion batteries as they exhibit a high theoretical specific capacity and charge density compared to the commonly used and well-established intercalation-type electrodes. Besides electrochemical investigations, thermodynamic studies can be used to get a better insight in the conversion mechanism, which is not well understood yet, since electrochemistry and thermodynamics are closely related via the Nernst equation. Therefore, evaluated thermodynamic descriptions of multi component systems containing the Gibbs free energy functions of all phases can be used to calculate equilibrium cell potentials and plateau capacities resulting from phase transformations during charge/discharge.

To create a consistent thermodynamic dataset of the quaternary Li-Cu-Fe-O system, the Li-M-O (M = Cu, Fe) sub-systems were addressed and are modeled using evaluated literature data. To generate additional experimental data to describe the temperature dependence of the ternary phases in the Li-M-O systems, differential thermal analysis and calorimetry were performed on key compounds. The oxide samples were prepared using solid-state reaction method from the oxides. The heat capacities for these compounds were measured in the temperature range from -40 °C to 200 °C and the phase stabilities under air and argon were determined. The standard enthalpies of formation of the oxides were also measured using high temperature drop solution calorimetry at 700 °C. Additionally, electrochemical measurements with different C-rates as well as open circuit voltage measurements were conducted using M-O compounds as the anode starting materials.

The results of the work are discussed in order to better understand the reaction mechanism and thermodynamics of conversion electrodes.

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