Thermodynamic Investigation of Copper and Iron Oxides Used as Electrodes in Lithium Ion Batteries

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The developement of new electrodes is of great scientific and technological interest since environmentally friendly materials with higher storage capacities and improved energy densities are needed to meet property and perfomance requirements of future lithium ion batteries. The **CALPHAD** (Calculation of Phase Diagrams) method is an invaluable tool to support the search for high performance electrode materials, since electrochemistry and thermodynamics are closely related. Key data for metarials selection, such as plateau voltages, capacities and entropy of reaction can be calculated using consistent thermodynamic descriptions of multi-component systems developed by computational thermodynamics.

In this work copper and iron oxides which exhibit the conversion mechanism and therefore can store high amount of Faraday charge per formula unit compared with commercial intercalation electrodes, were investigated to better understand the converison mechanism.

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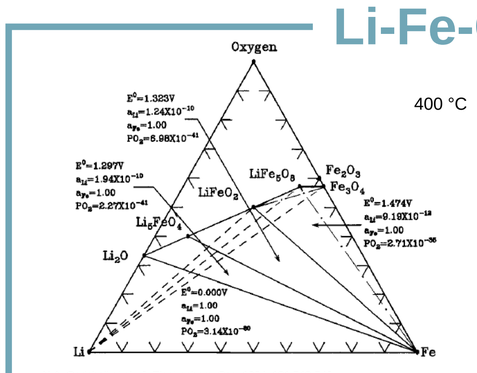
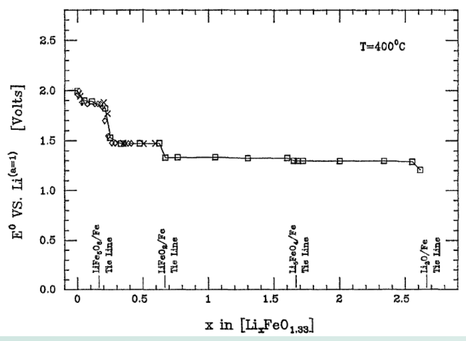
Critical Literature Review

Li-Fe-O System

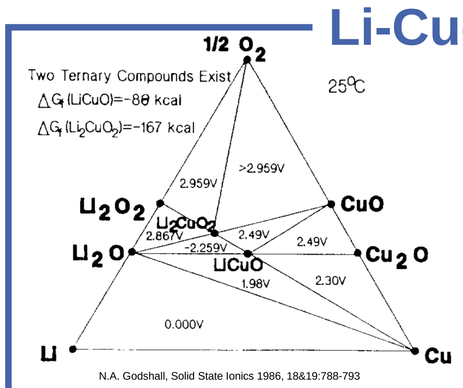


N.A. Godshall et al., J. Electrochem. Soc. 1984, 131:543-549

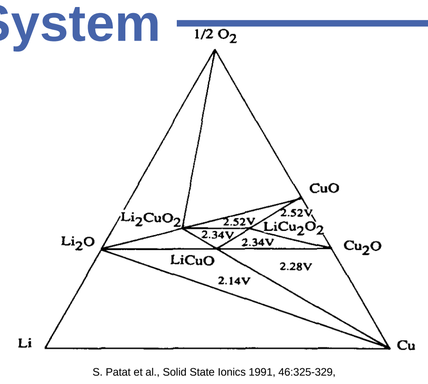


The Li-Fe-O system is well investigated. Data on thermochemical properties are available in the literature.

Li-Cu-O System



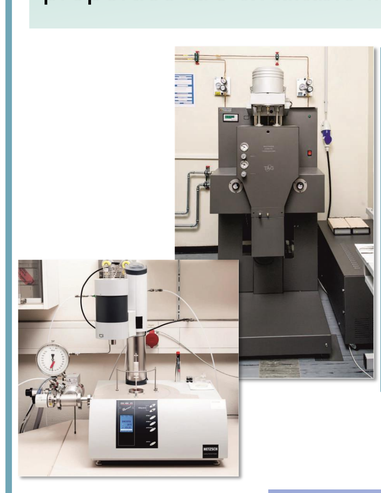
N.A. Godshall, Solid State Ionics 1986, 18&19:788-793



S. Patat et al., Solid State Ionics 1991, 46:325-329,

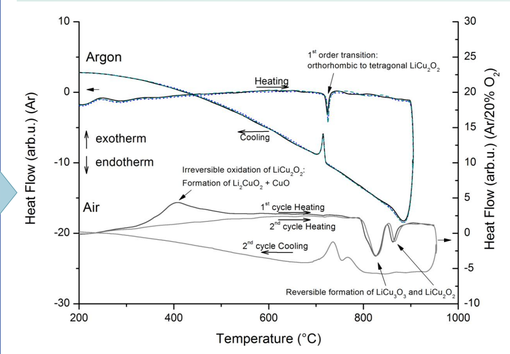
There is a lack of thermochemical data in the Li-Cu-O system in the literature. Experimental thermochemical investigations were performed to generate additional data.

Key Experiments on Key Compositions



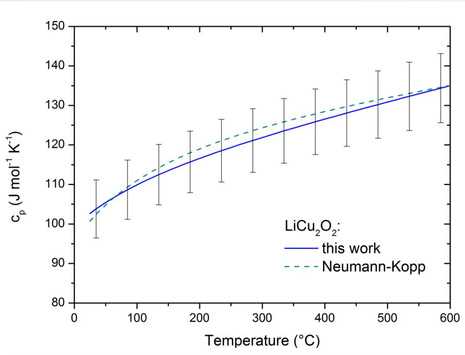
- Sample Synthesis (solid state method)
- Sample Characterization (XRD, ICP-OES)
- Simultaneous Thermal Analysis (DTA/TG)
- Differential Scanning Calorimetry (DSC)
- High Temperature Oxide Melt Drop Solution Calorimetry

For more thermochemical investigations on conversion type electrode materials see poster of N. Mayer et al. (Abstract Id. 1826, D3.3-P-TUE-P1-7)



Phase stabilities of $LiCu_2O_2$ in different atmospheres.

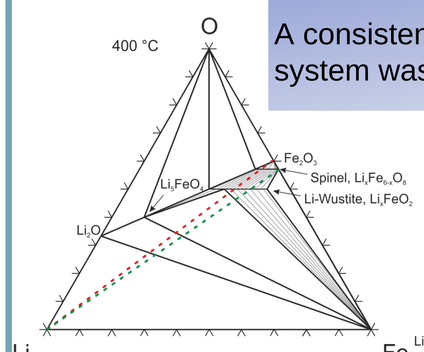
M. Lepple et al., J. Mat. Sci. 2013, 48:5818-5826

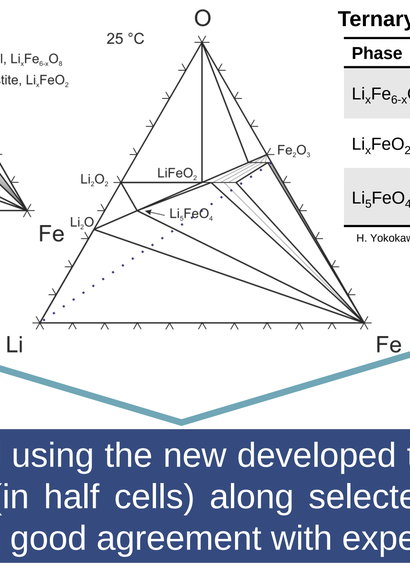


Heat capacity of $LiCu_2O_2$, the Neumann-Kopp rule is applicable.

M. Lepple et al., JPED 2014, 35: 650-657

Thermodynamic Modeling





A consistent thermodynamic description of the Li-Fe-O system was obtained based on literature data.

Ternary solid phases:

Phase	Model
$Li_xFe_{6-x}O_8$	(0 ≤ x ≤ 1), spinel structure, sublattice model
Li_xFeO_2	(0 ≤ x ≤ 1), rocksalt structure, sublattice model
Li_5FeO_4	Stoichiometric description by Yokokawa et al.

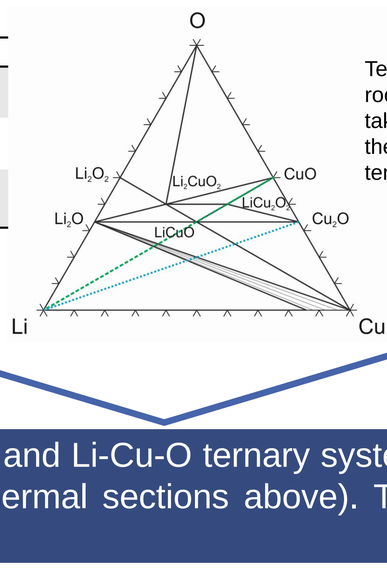
H. Yokokawa et al., J. Electrochem. Soc. ,1993, 140:3565-3577

A consistent thermodynamic description of the Li-Cu-O system valid at room temperature was obtained based on literature data and experimental results.

M. Lepple et al., J. Mat. Sci. 2013, 48:5818-5826

Ternary solid phases:

Phase	Model
LiCuO	Stoichiometric description
Li_2CuO_2	Stoichiometric description
$LiCu_2O_2$	Stoichiometric description

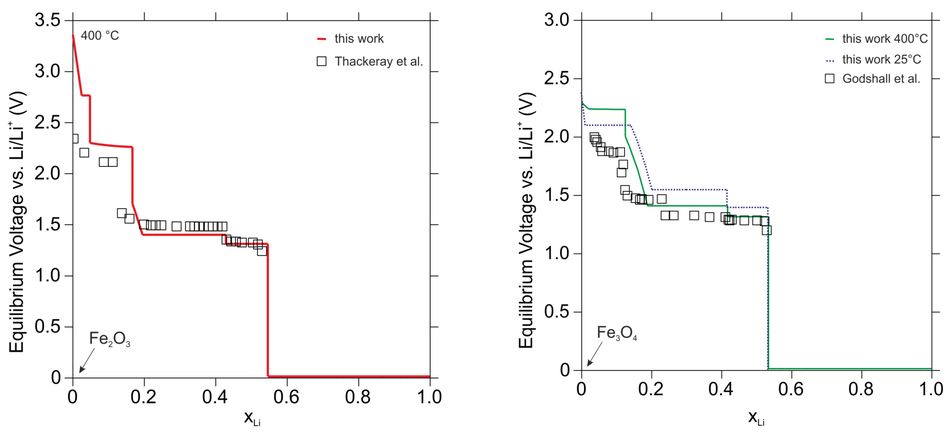


Ternary phases not stable at room temperature were not taken into account. Therefore, the system is only valid at temperatures around 25 °C.

Coulometric titration curves are calculated using the new developed thermodynamic descriptions of the Li-Fe-O and Li-Cu-O ternary systems. They give the equilibrium cell voltage at the electrode (in half cells) along selected composition paths (dotted lines in isothermal sections above). The titration curves calculated with the new descriptions are in good agreement with experimental literature data.

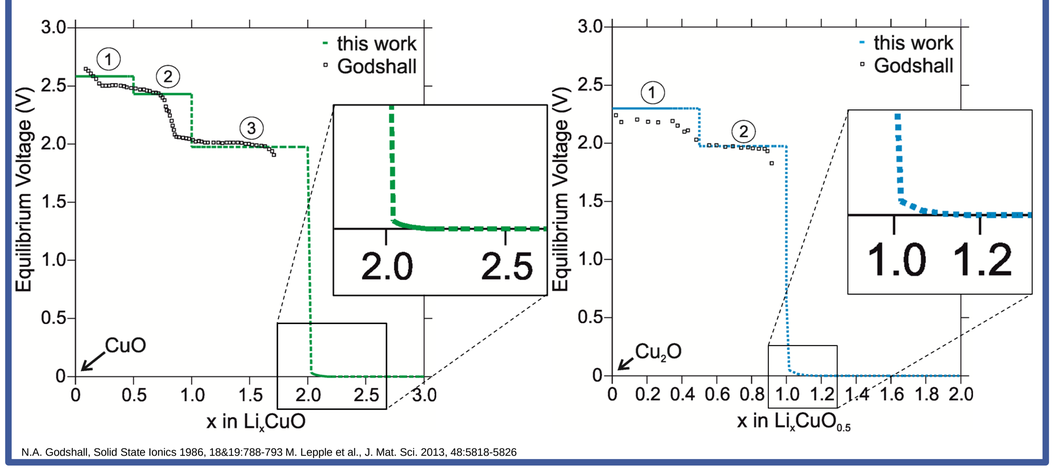
Prediction of Electrochemical Properties

Iron oxides:



M. M. Thackeray et al., J. Solid State Chem. 1984, 55: 280-286 N.A. Godshall et al., J. Electrochem. Soc. 1984, 131:543-549

Copper oxides:



N.A. Godshall, Solid State Ionics 1986, 18&19:788-793 M. Lepple et al., J. Mat. Sci. 2013, 48:5818-5826

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