Thermodynamic Modeling of the Li-Fe-O System

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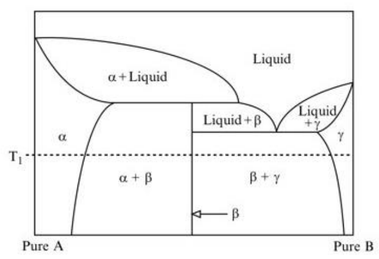
Introduction

1) Li_2O in metallurgical slag and flux system
- Na_2O-K_2O-CaO-MgO-Al_2O_3-SiO_2-FeO-Fe_2O_3-F
- Na_2O-K_2O-Li_2O-CaO-MgO-Al_2O_3-SiO_2-F
- To combine above system the Li_2O-FeO-Fe_2O_3 system should be optimized

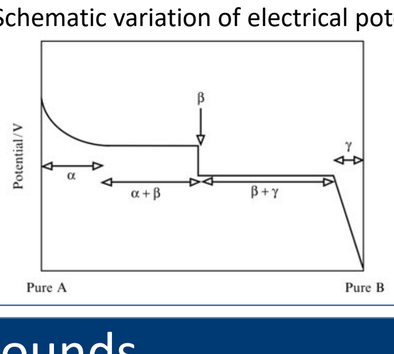
2) Battery cathode materials
- Understanding phase diagram is useful for electrical potential diagram

$$g_i = g_i^o + RT\ln a_i \qquad \Delta g_i = -nF(E^o - E)$$

Hypothetical binary phase diagram



Schematic variation of electrical potential



Model

- Cubic Spinel solution (Compound Energy Formalism)

$(Li^+, Fe^{2+}, Fe^{3+})^T[Li^+, Fe^{2+}, Fe^{3+}, Va]_2{}^O O_4$

$$G^m = \sum_i\sum_j Y_i^T Y_j^O G_{ij} - TS_C + G^E$$

$$S_C = -R\left(\sum_i Y_i^T \ln Y_i^T + 2\sum_j Y_j^T \ln Y_j^T\right) \qquad G^E = \sum_i\sum_j\sum_k Y_i^T Y_j^T Y_k^O L_{ij;k} + \sum_i\sum_j\sum_k Y_k^T Y_i^O Y_j^O L_{k;ij}$$

- Monoxide solution (Simple Random mixing Model)

$FeO - LiFeO_2(Fm3m) - Li_2O$

$$G^m = \sum_i X_i G_i + RT\sum_i X_i \ln X_i + \sum_i\sum_j X_i^m X_j^n \left(\frac{X_i}{X_i+X_j}\right)^m \left(\frac{X_j}{X_i+X_j}\right)^n q_{ij}^{mn}$$

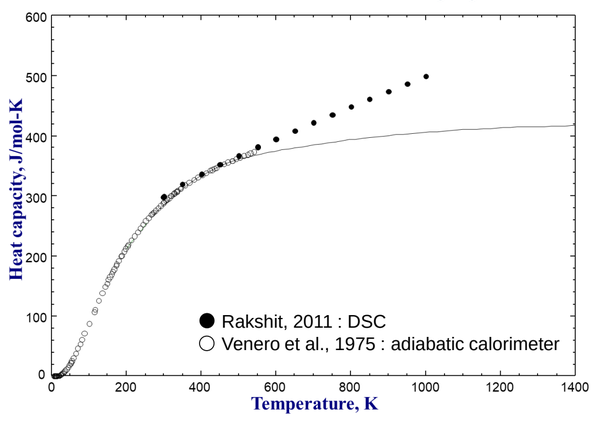
- Liquid solution (Modified Quasichemical Model)

$Li_2O - FeO - Fe_2O_3$

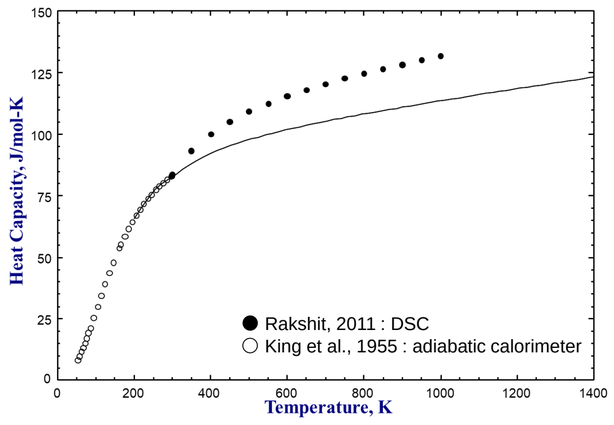
$$G^m = \left(n_i g_i^o + n_j g_j^o\right) - RT\Delta S^{config} + \left(\frac{n_{i-j}}{2}\right)\Delta g_{i-j} \qquad \Delta g_{i-j} = \Delta g_{i-j}^{00} + \sum g_{i-j}^{mn} x_{ii}^m x_{jj}^n$$

Thermodynamic data for solid compounds

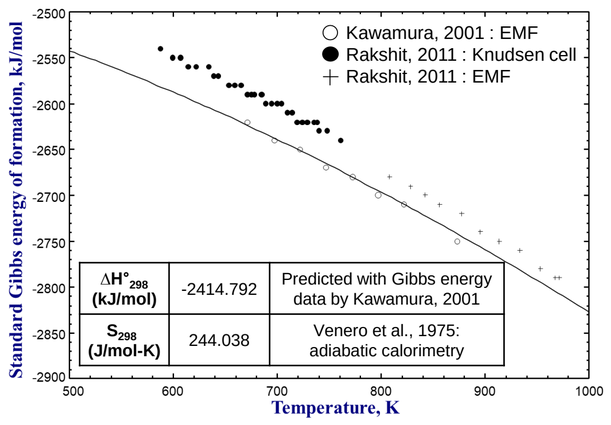
Heat capacity of $LiFe_5O_8$



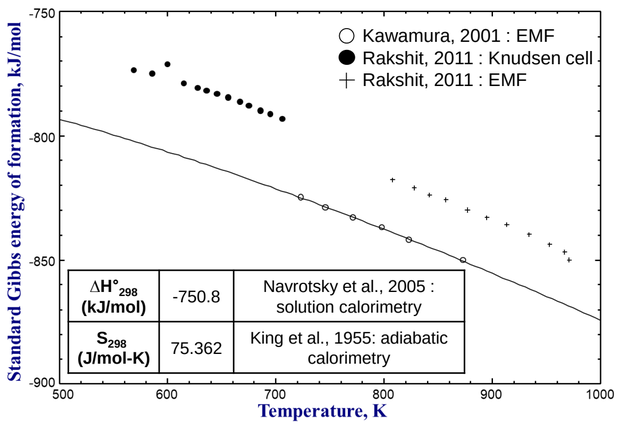
Heat capacity of $LiFeO_2$



Formation Gibbs energy of $LiFe_5O_8$



Formation Gibbs energy of $LiFeO_2$



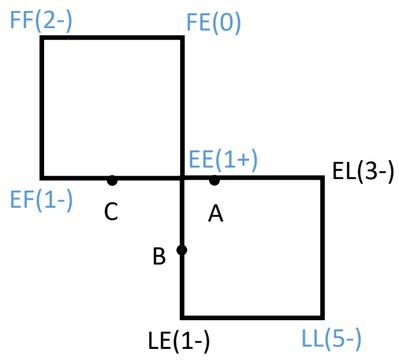
Compound	ΔH°_{298}(kJ/mol)	S_{298}(J/mol-K)	Cp(J/mol-K)
Li_5FeO_4	-1973.130	133.582	$2C_P(Li_2O) + C_P(LiFeO_2)$

Model Parameters

Cubic Spinel Solution End members;

$(Li^+, Fe^{2+}, Fe^{3+})^T[Li^+, Fe^{2+}, Fe^{3+}, Va]_2{}^O O_4$

Li^+:L , Fe^{2+}: F, Fe^{3+}: E, Va: V

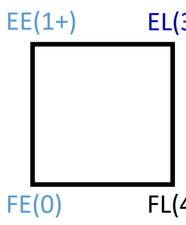


Blue are done, black need to be fixed

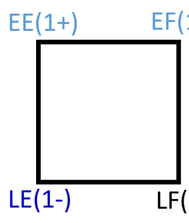
A; $(Fe^{3+})[Li^+_{0.25}Fe^{3+}_{0.75}]_2O^{2-}_4$ ➡ $0.5LiFe_5O_8$
B; $(Li^+_{0.5}Fe^{3+}_{0.5})[Fe^{3+}]_2O^{2-}_4$
C; $(Fe^{3+})[Fe^{2+}_{0.5}Fe^{3+}_{0.5}]_2O^{2-}_4$

$$0.5G_{LiFe_5O_8} = \frac{3}{4}G_{EE} + \frac{1}{4}G_{EL} + 2RT(0.75\ln 0.75 + 0.25\ln 0.25)$$
$$G_B = 0.5(G_{LiFe_5O_8} + 2I_{LE}) = 0.5G_{EE} + 0.5G_{LE}$$

$$G_{EL} = 2G_{LiFe_5O_8} - 3G_{EE} - 2RT(0.75\ln 0.75 + 0.25\ln 0.25)$$
$$G_{LE} = G_{LiFe_5O_8} + 2I_{LE} - G_{EE} - 2RT(0.5\ln 0.5 + 0.5\ln 0.5)$$



$\Delta EE: FL = G_{EE} + G_{FL} - G_{EL} - G_{FE}$



$\Delta EE: LF = G_{EE} + G_{LF} - G_{EF} - G_{LE}$

Cubic Spinel Solution;

$$G_{LiFe_5O_8} = G_{ordered\ LiFe_5O_8} + 300 - 3.0152T$$
$$I_{LE} = 9500 - 0.9913099T$$
$$\Delta EE: LF = 0$$
$$\Delta EE: FL = -9000$$

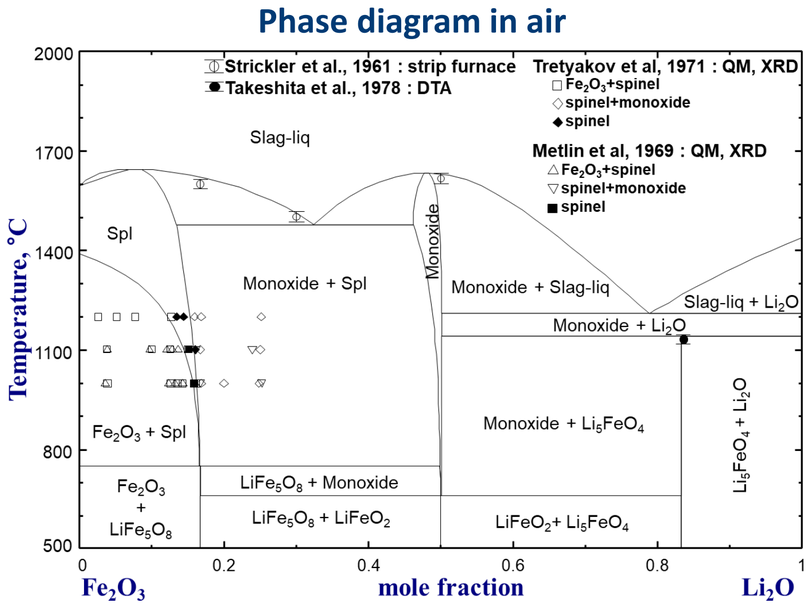
Liquid Solution;

$$\Delta g^{00}_{Fe^{3+}-Li^+} = -156900 + 33.42895T$$
$$g^{11}_{Fe^{3+}-Li^+} = -4184$$
$$g^{01(1)}_{Li-Fe^{2+}(Fe^{3+})} = 55647.2$$

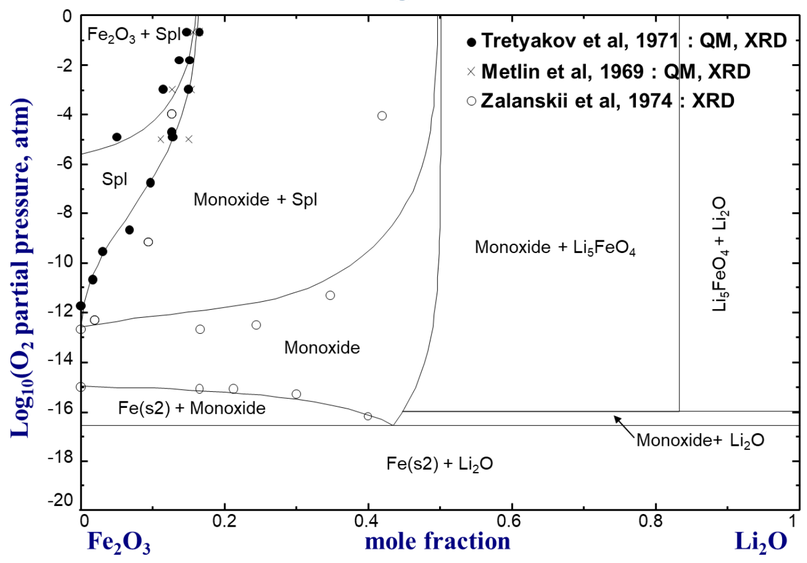
Monoxide Solution; ideal solution

Results & Discussion

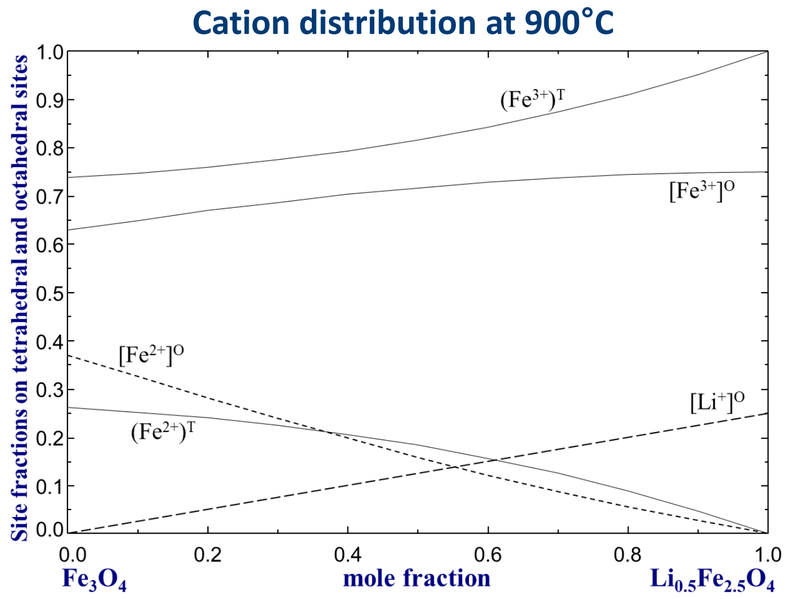
Phase diagram in air



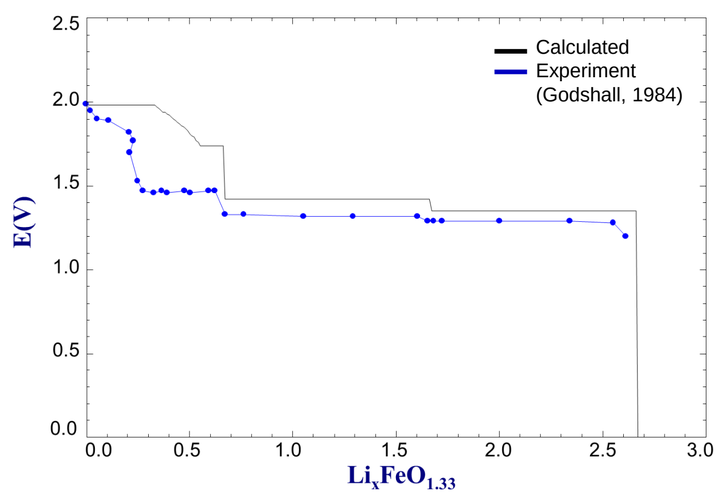
Phase diagram at 1000°C

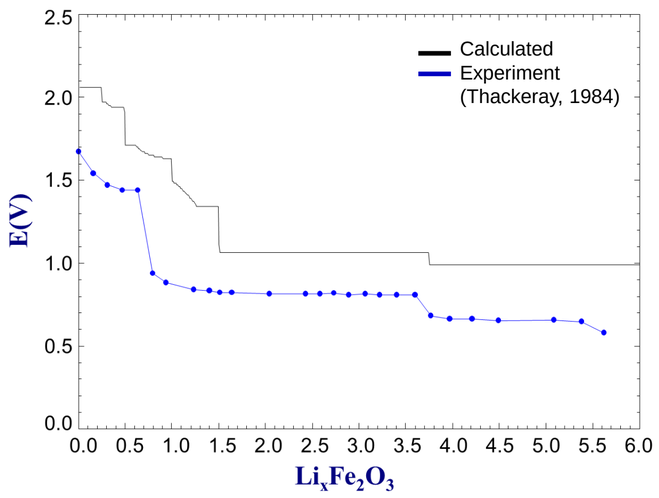


Cation distribution at 900°C



Application (Electrical potential diagram)





Summary

- The Li_2O-FeO-Fe_2O_3 system was optimized.
- Calculations from models are in a good agreement with thermodynamic property data and phase diagram data.

Future works

- Modeling other Li_2O-MOx system for Li battery cathode application
  - ✓ Li_2O-MnO-Mn_2O_3
  - ✓ Li_2O-CoO-Co_2O_3
  - ✓ Li_2O-NiO