Computational Thermodynamic Modeling of Mixed Polyanion Glasses for Lithium Ion Battery Cathode Materials

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We have used computational thermodynamic approach to model Lithium-bearing mixed polyanion (LBMP) as an effort to predict electrochemical properties of glass cathode materials. Individual LBMP have been modeled within the framework of the compound energy formalism (CEF) as implemented in the CALPHAD (CALculation of PHAse Diagram) approach [1, 2].

To model the baseline material Li/$FePO_4$ thermodynamic descriptions for the crystalline solid and liquid phases of constituent Fe_2O_3 and P_2O_5 have been taken from the Scientific Group Thermodata Europe (SGTE) Substance Database and used as reference states. Thermodynamic model parameters for $FePO_4$ and $Fe_4(P_2O_7)_3$ have been self-consistently evaluated to reproduce Fe_2O_3-P_2O_5 pseudo-binary phase diagram reported in the literatures. Afterward thermodynamic model parameters for the $FePO_4$-$LiFePO_4$ pseudo-binary system has been evaluated to represent experimentally determined phase equilibrium data [3, 4]. The model successfully reproduces the miscibility gap at low temperatures as shown in FIG. 1 by introducing positive interaction between $FePO_4$ and $LiFePO_4$.

From the developed thermodynamic database the open circuit voltage (OCV) of crystalline and glass Li/$FePO_4$ have been predicted by calculating chemical potential of Li (see FIG. 2). In order to model the Li_xFePO_4 glass phase, different ratios between the liquid and solid phases of $LiFePO_4$ and $FePO_4$ (L:S) have been used and ideal mixing between two end-members have been assumed. The glassy form is more sloping, and has a significantly lower potential.

Thermodynamic modeling of Li-Fe_2O_3-V_2O_5 has been carried out to incorporate additional polyanion species in the model for the glass cathode materials. From the completed thermodynamic modeling of Li/$FeVO_4$ which combined with the baseline system, the cell voltage of Li/$Fe_4(0.5P_2O_7{\cdot}0.5V_2O_7)_4$ has been benchmarked against experimental measurements. The ratio between the solid and liquid thermodynamic descriptions to describe the electrochemical behavior of the LBMP glass materials has been established and will be used for other polyanion species to be added in the baseline system.

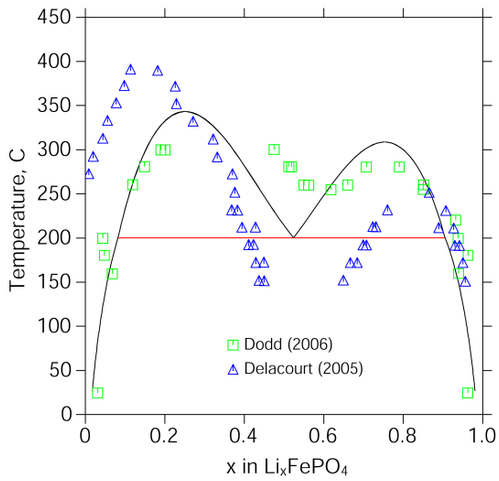

FIG. 1. Calculated $FePO_4$-$LiFePO_4$ phase diagram with experimental phase equilibrium data [3, 4].

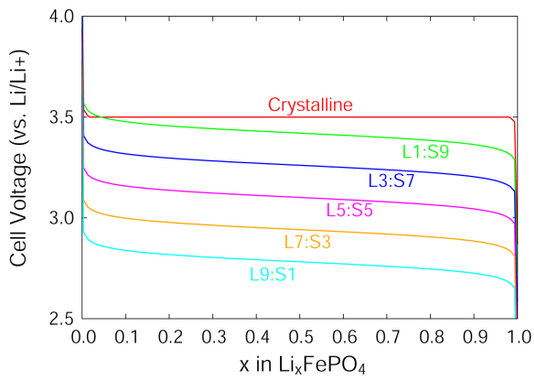

FIG. 2. Calculated cell circuit voltage of Li_xFePO_4 of crystalline and glass phases. Different ratios between the liquid and solid phases of $LiFePO_4$ and $FePO_4$ (L:S) have been used to model glass phase.

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References

[1] L. Kaufman, H. Bernstein, *Computer Calculation of Phase Diagram*, New York, Academic Press Inc., 1970.
[2] N. Saunders, A. P. Miodownik, *CALPHAD (Calculation of Phase Diagrams): A Comprehensive Guide*, Oxford, New York, Pergamon, 1998.
[3] J. L. Dodd, R. Yazami, B. Fultz, *Electrochem. Solid State Lett.*, 9(3): A151-A5, 2006.
[4] C. Delacourt, P. Poizot, J. M. Tarascon, C. Masquelier, *Nature Mater.*, 4(3): 254-60, 2005.