

# Characterization of Iron Phthalocyanine as the Cathode Active Material for Lithium-Ion Batteries

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## Abstract

The developed thermodynamic functions for the determination of Gibbs free energy, enthalpy, and entropy of formation of solid lithium-iron phthalocyanine ( $\text{Li}_x\text{FePc}$ ) from solid lithium and iron phthalocyanine as a function of  $x$ , defined as g-moles of the intercalated lithium per g-mole of iron phthalocyanine, at a fixed set of temperature and pressure conditions are presented. In addition, a proposed expression for the evaluation of lithium diffusion coefficient in solid iron phthalocyanine as a function of both  $x$  and temperature, and the experimental results from the ongoing research/development work on the lithium/iron phthalocyanine cells are included.

**Keywords:** Phthalocyanine; Thermodynamics; Diffusion coefficient; Cathode; Lithium; Cell; Battery

## Highlights

An empirical equation for the determination of the Gibbs free energy of the reaction of lithium insertion into iron phthalocyanine (FePc) as a function of lithium intercalation extent. Lithium ion diffusion coefficients in FePc determined at 80 and 100°C at full state of charge.

## Introduction

Currently, phthalocyanine-based materials are being investigated and characterized [1,2] to provide higher energy density rechargeable lithium-ion batteries. The charge capacities for the composite cathodes with FePc as the active material have been reported in the literature, for example, 1440 mAh.g<sup>-1</sup> FePc [3] and 2050 mAh.g<sup>-1</sup> FePc (which is equivalent to approximately 43.5 g moles of lithium per g-mole of FePc) with nano-graphene platelets (25% by mass) as the electronic conductor [4]. The experimental work of the reference [4] prompted us to further characterize FePc as a potential cathode active material for its application in the development of lithium-ion batteries to be employed for extended discharge periods. Also, the theoretical work [5] predicted that the overall performance of a lithium/di-lithium or iron phthalocyanine couple as an electric power generating cell is controlled by the lithium-ion diffusion in the cell cathode active material provided the lithium ion conductivity in the cell electrolyte and the cathode electronic conductivity are of the order of 1 mS.cm<sup>-1</sup> or greater. Transient lithium-ion concentration profiles in a spherical, active material particle of di-lithium or iron phthalocyanine depicted the lithium ion penetration toward the active material particle center. Theoretical work of the reference [5] implicitly suggested the control of the active material particle size for the optimum (i.e., maximum) utilization of a cathode active material during the cell discharge period as well as the provision of large electrolyte-cathode active material particle interfacial area per unit mass of the active material for achieving the smallest possible active material-electrolyte interfacial current per unit interfacial area to keep the cathode electrochemical reaction voltage loss at a minimum level for a desired amount of current per unit mass of the cathode active material. In a relatively recent theoretical work [6], it has been reported that the lithium/FePc cell reversible electric potential decreases as the number of g-moles of intercalated lithium per g-mole of FePc increases; in turn, suggesting that the absolute value of the available Gibbs free energy associated with (the lithium

intercalation into the iron phthalocyanine) process decreases as the lithium ions, with their electron partners, enter the active material of iron phthalocyanine in succession. The work of reference [6] also shows a change in crystal volume with a change in the number of intercalated lithium atoms in the active material FePc; e.g., 24% increase in the crystal volume corresponding to the intercalated storage capacity of 37 lithium atoms per molecule of iron phthalocyanine. The main objective of the work reported in this paper has been to characterize the active material, iron phthalocyanine, with regard to the thermodynamic and transport property data through experimental program. Such data are required to develop a mathematical model for the prediction of performance as well as for the design of a complete lithium-ion cell with its cathode active material of iron (or other metal, e.g., copper) phthalocyanine.

## Formulation of the thermodynamic functions and lithium-ion diffusion coefficient in iron phthalocyanine as the cathode active material:

In this section formulation for the determination of the thermodynamic functions: Gibbs free energy, enthalpy, and entropy of formation of the intercalated iron phthalocyanine,  $\text{Li}_x\text{FePc}$ , as a function of  $x$  is provided. Application of the literature-based formulation to experimentally determine the lithium ion diffusion coefficient in the cathode active material of iron phthalocyanine (FePc) as a function of  $x$ , using the alternating current (AC) impedance spectroscopic technique, is briefly discussed.

## Thermodynamic functions for the formation of lithium-iron phthalocyanine ( $\text{Li}_x\text{FePc}$ ):

The overall process of lithium insertion into the solid state cathode

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active material, FePc, is

$$xLi_{(s)} + FePc_{(s)} = Li_xFePc_{(s)} \quad (1)$$

For the occurrence of the overall reaction process, Equation (1), at the constant pressure and temperature conditions, the principles of the classical thermodynamics lead to

$$\Delta G_{f,x} = G_{Li_xFePc_{(s)}} - (G_{FePc_{(s)}} + xG_{Li_{(s)}}) = -F \int_0^x E_{rev} dx \quad (2)$$

$$\begin{aligned} \Delta H_{f,x} &= H_{Li_xFePc_{(s)}} - (H_{FePc_{(s)}} + xH_{Li_{(s)}}) \\ &= F \left[ -\int_0^x E_{rev} dx + T \int_0^x \left( \frac{\partial E_{rev}}{\partial T} \right)_x dx \right] \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta S_{f,x} &= S_{Li_xFePc_{(s)}} - (S_{FePc_{(s)}} + xS_{Li_{(s)}}) \\ &= \frac{\Delta H_{f,x} - \Delta G_{f,x}}{T} \\ &= F \int_0^x \left( \frac{\partial E_{rev}}{\partial T} \right)_x dx \end{aligned} \quad (4)$$

where  $\Delta G_{f,x}$ ,  $\Delta H_{f,x}$ , and  $\Delta S_{f,x}$  are the molar Gibbs free energy, enthalpy, and entropy of formation of  $Li_xFePc_{(s)}$ , respectively;  $G_{(s)}$ ,  $H_{(s)}$ ,  $S_{(s)}$  the chemical species Gibbs free energy, enthalpy, and entropy, respectively;  $E_{rev} = (Li_{(s)} / FePc_{(s)})$  cell reversible voltage at the cathode active material state of charge (SOC) represented by  $x$  (g-atoms of lithium in the intercalated state per g-mole of  $FePc_{(s)}$ );  $T$  = cell cathode temperature [K], and  $F$  = Faraday's constant = 96487 coulomb (C) per g-equivalent or g-atom of lithium. If, through experimental work, the variation of  $\left( \frac{\partial E_{rev}}{\partial T} \right)_x$  with change in  $x$  would be found negligibly small; then, Eq. (3) would be reduced to

$$\Delta H_{f,x} = F \left[ -\int_0^x E_{rev} dx + T \left( \frac{\partial E_{rev}}{\partial T} \right)_x x \right] \quad (5)$$

### Lithium ion diffusion coefficient determination:

In the experimental determination of lithium ion diffusion coefficient in graphite, it was shown and concluded [7] that the modified electrochemical impedance (M-EIS) method is relatively superior to the potential intermittent titration technique (PITT) and the conventional Warburg impedance method. This conclusion is based on the uncertainties involved in the estimation of the parameters such as the derivative of the cell open-circuit voltage with respect to the state of charge (SOC= $x$ ), initial lithium ion concentration, lithium ion concentration at the active material particle surface, molar volume of the lithiated electrode material, and the effective surface area per unit cell cathode mass required in the PITT and Warburg impedance methods to evaluate the lithium diffusion coefficient in a solid spherical graphite particle. In contrast, the M-EIS method only requires the values of the active material particle radius,  $R$ , and applied alternating current (AC) voltage angular frequency  $\omega$ ; thus, resulting in less uncertainty in comparison with the PITT and conventional Warburg impedance approaches for the lithium ion diffusion coefficient determination. The above given literature-based information led us to the selection of the M-EIS method for the determination of lithium ion diffusion coefficient in the cathode active material,  $Li_xFePc_{(s)}$ . For a SOC =  $x$  of the cathode active material,  $Li_xFePc_{(s)}$ , the Nyquist plot of  $Z_{im}$  versus  $Z_{re}$  [8] is experimentally obtained using the AC impedance spectroscopy. The slope of the plot in the diffusion controlled region,  $\left( \frac{-dZ_{im}}{dZ_{re}} \right)$ , is then employed to calculate the diffusion coefficient of (lithium ion-electron pair) in the cathode active material using the formula provided in ref. [7,9]. Effect of the double charge layer capacitance, in the solid-state diffusion controlled region, is assumed to be negligible because of much higher value of the diffusion time constant in a solid like graphite [10]

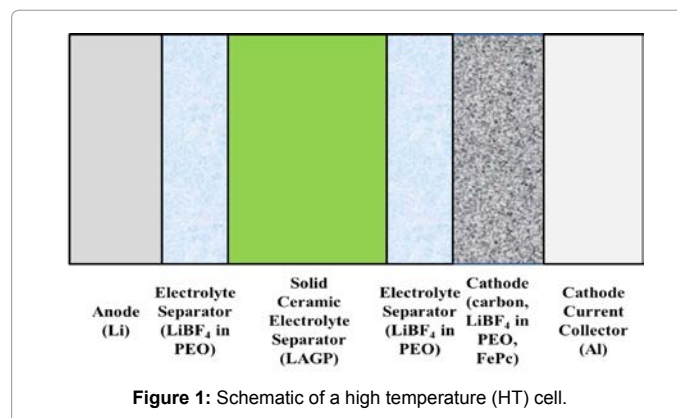
or  $Li_xFePc_{(s)}$  than the diffusion time constant for the double charge-layer capacitor region. Also, under the assumption of small variation in electric potential inside a nanoscale cathode active material particle, movement of a (lithium ion-electron) pair under the electric field effect is assumed to be negligibly small. Experimental program is in progress to determine the lithium ion diffusion coefficient in  $Li_xFePc_{(s)}$  as a function of both SOC,  $x$ , and temperature to develop a mathematical expression based on the empirical data for future design/performance analysis of a cell using  $Li_xFePc_{(s)}$  as the cathode active material. A proposed mathematical function, based on our knowledge of the fundamentals of transport phenomena, is

$$D(x, T) = D_0 x^n \exp[-E_d(x) / (RT)] \quad (6)$$

where  $D_0$  = pre-exponential factor,  $E_d(x)$  = lithium ion diffusion activation energy in the active material, which is perceived to be a function of  $x$ ,  $R$  = universal constant = 8.314 J mol<sup>-1</sup>K<sup>-1</sup>,  $T$  = absolute temperature of the cathode active material, K. The experimental data on the lithium ion diffusivity are to be used to determine  $D_0$ ,  $n$ , and  $E_d(x)$ .

### Experimental cells, instrumentation and procedure:

The HT cell consists of a lithium metal sheet as the anode, polyethylene oxide (PEO)-lithium tetra-fluoroborate ( $LiBF_4$ ) mixture (with atomic ratio of  $\left( \frac{O \text{ of PEO}}{Li \text{ of } LiBF_4} \right) = \frac{8}{1}$ ) as the electrolyte and separator between the cell anode and cathode. Dimensions of the cell anode, separator, and cathode are as follows: anode thickness of 149  $\mu$ m and cross-sectional area of 1.267 cm<sup>2</sup>, separator thickness of about 200  $\mu$ m and cross-sectional area of 1.979 cm<sup>2</sup>, cathode thickness of about 200  $\mu$ m and cross-sectional area of 1.603 cm<sup>2</sup>. Figure 1 shows the sketch of a typical high temperature (HT) cell employed to acquire the electrochemical experimental data. The HT cell cathode is composed of the active material, FePc ( $C_{32}FeN_8H_{16}$ ) particles, acetylene black powder or CNT (carbon nanotubes) as the electronic conductor, PEO (binder) and  $LiBF_4$  (electrolyte present in the spaces between the active material FePc particles) with percent (by wt) of 30, 30, 31.6, and 8.4%, respectively. The HT cell assembled in the cylindrical coin configuration was placed into a coin cell holder for its electrochemical behavior testing. A Maccor 3600 or a Gamry 3000 system was employed for testing high temperature as well as low temperature cells at constant currents. Gamry 3000 was used for the A.C. (alternating current) impedance spectroscopy at frequencies ranging from 10<sup>-4</sup> to 10<sup>5</sup> Hz at 5 mV amplitude. The HT cells were tested in a Tenny Jr environmental chamber in the range of temperature: 80 to 100°C. The cell temperatures were measured using Type T (copper-constantan)



thermocouples. The low temperature (LT) cells were tested at approx. 20°C (See the sketch of a low temperature cell in Figure 2).

## Results and Discussion

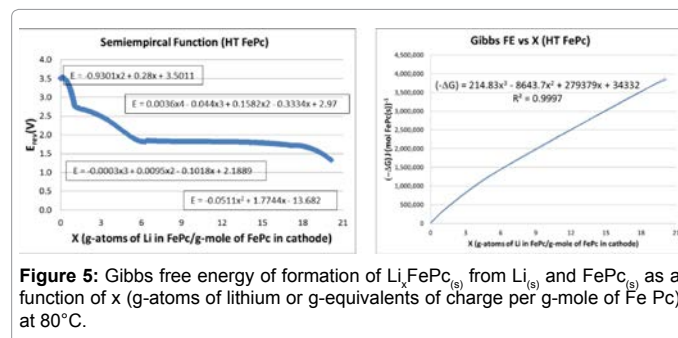
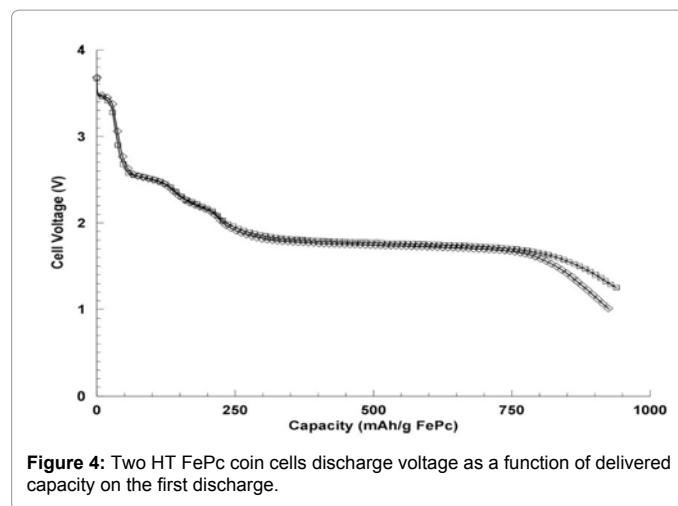
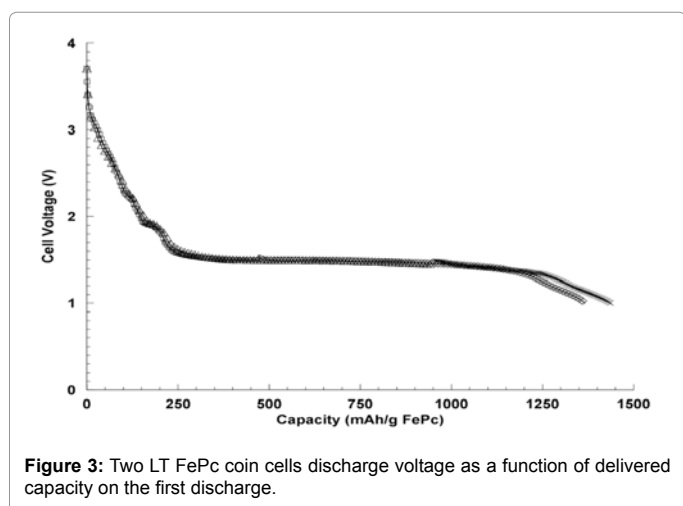
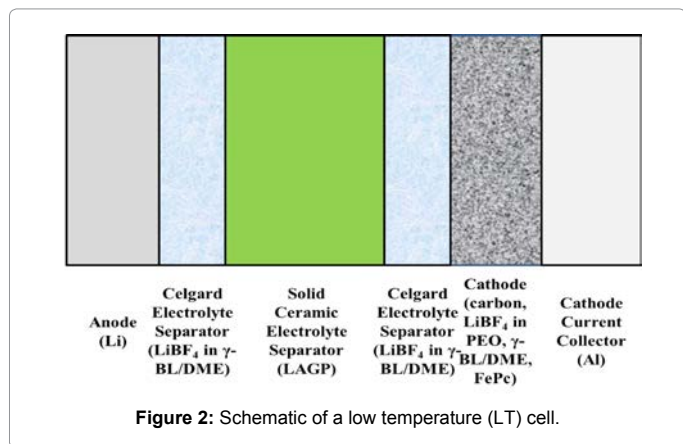
Figure 3 shows the cell voltage versus delivered capacity on the first discharge for two LT (20°C) coin cells. The LT cells were discharged at approximately  $C/100$  rate which is equivalent to about  $40 \mu A = 3.2 \times 10^{-5} A.cm^{-2}_{geom}$ . The experimental data in Figure 3 show that the low temperature cells can deliver charge storage capacity up to about  $1450 mAh.gm^{-1} FePc$  — 30.75 g-atoms of lithium or g-equivalents of charge per g-mole of FePc at a cut-off voltage of 1 volt. Figure 4 shows the cell discharge voltage as a function of delivered capacity on the first discharge for two HT cells at 80°C. The HT cells were discharged at approximately  $C/100$  rate which is equivalent to about  $40 \mu A = 2.5 \times 10^{-5} A.cm^{-2}_{geom}$  of cathode. These experimental data were employed to develop the correlation required to compute the Gibbs free energy of formation of  $Li_x FePc_{(s)}$ , ( $-\Delta G$ ), at 80°C. This correlation of ( $-\Delta G$ ) versus  $x$  (g-atoms of lithium or g-equivalents of charge per g-mole of FePc) is shown in Figure 5. Empirical mathematical functions of  $E_{rev}$  versus  $x$  were developed to fit the voltage versus  $x$  experimental data shown in Figure 4. These functions simulating the discharge behavior of the HT cell at 80°C are shown in Figure 5. Using these developed functions, the following expression for the Gibbs free energy of formation of  $Li_x FePc_{(s)}$ :

$$\begin{aligned}
 (-\Delta G) &= [G_{Li_x FePc_{(s)}} - (Li_{(s)} + FePc_{(s)})] \\
 &= F \int_0^x E_{rev} dx \\
 &= F \left[ \int_0^{x_1} E_{rev} dx + \int_{x_1}^{x_2} E_{rev} dx + \int_{x_2}^{x_3} E_{rev} dx + \int_{x_3}^{x_4} E_{rev} dx \right]
 \end{aligned}
 \tag{7}$$

as a function of  $x$  was developed and is shown in Figure 5 above. The correlation coefficient R value of 0.99985 is indicative of very high accuracy of the correlation-fit to the experimental data. The function ( $-\Delta G$ ) vs.  $x$  shown in Figure 5 matched the directly determined ( $-\Delta G$ ) from the experimental data.

Notice that ( $-\Delta G$ ) increases as  $x$  increases as expected.

Figure 6 shows the Nyquist plots of impedance of the  $Li/LiBF_4$  in PEO/LAGP/ $LiBF_4$  in PEO/ $FePc$  coin cell at 80°C and 100°C temperatures. LAGP (lithium aluminum germanium phosphate) was used for preventing the cell shorting during the cell charging period due to the formation of lithium dendrites at currents greater than  $C/100$  rate. The cell impedance in the diffusion controlled region is shown at each temperature at low frequencies; for example, at 0.001 Hz. The impedance data at low frequencies were employed to calculate lithium experimental diffusivity in the cathode active material,  $FePc_{(s)}$  using the formulation given in [7,9,10]. It is here noted that the lithium diffusion coefficients in the electrolytes used in the cells investigated in this study are greater than or equal to 100 times its diffusion coefficient in  $FePc_{(s)}$  cathode active material. The lithium diffusion coefficient,  $D$ , values derived from the impedance spectroscopic experimental data are  $D = 7.74 \times 10^{-12}$  and  $3.08 \times 10^{-11} cm^2 S^{-1}$  at 80 and 100°C, respectively; with diffusion activation energy,  $E_d = 75.7 kJ.mol^{-1}$  at  $x$  value of zero in the cathode active material.



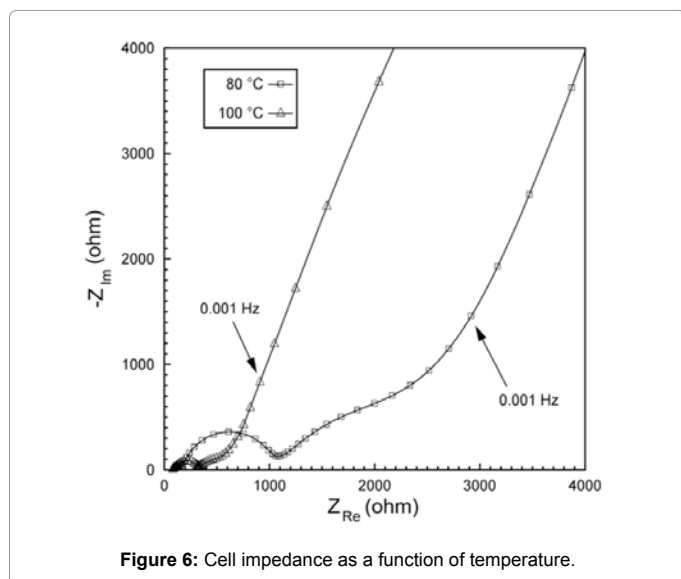


Figure 6: Cell impedance as a function of temperature.

Currently, the experimental work is in progress to assess the cyclical performance of low temperature (LT) coin cells. Preliminary results show that the LT FePc cells are capable of cycling at 20 equivalents or 943 mAh of charge per gram of FePc, cathode active material at a C/10 discharge rate. This experimental capacity of FePc<sub>(s)</sub> is much higher than that of LiMn<sub>2</sub>O<sub>4(s)</sub>, LiCoO<sub>2(s)</sub>, and LiNiO<sub>2(s)</sub>; with specific capacity of 126, 149, and 180 mAh/gm, respectively. The capacity of 943 mAh/gm of FePc<sub>(s)</sub> competes with those of Li<sub>(s)</sub>/S and Li<sub>(s)</sub>/O<sub>2(g)</sub> cells. Experimental work is in progress to enhance the charge reversible capacity and increase charge and discharge rates for optimum performance of the Li<sub>(s)</sub>/FePc<sub>(s)</sub> cells.

## Conclusions

Experimental data on the cell voltage versus capacity for a high temperature FePc cell at 80°C and a low temperature FePc cell at 20°C acquired at approx. 40i A (~  $\frac{C}{100}$  rate) were presented.

Empirical functions to simulate the cell voltage, E, versus x behavior during the various cell discharge stages were developed for a high temperature (i.e., 80°C) cell. In turn, such developed functions were used to develop an empirical equation for the determination of the Gibbs free energy of the reaction of lithium insertion into FePc<sub>(s)</sub>

as a function of x for a HT FePc operated at 80°C. The lithium/FePc cell impedance experimental data in the form of Nyquist plots were employed to evaluate the lithium diffusion coefficients in the cell cathode active material, FePc<sub>(s)</sub>. The experimentally determined diffusion coefficients for the lithium ion penetration into the cathode active material are:  $7.7 \times 10^{-12}$  and  $30 \times 10^{-12}$  cm<sup>2</sup>.s<sup>-1</sup> at 80°C and 100°C, respectively; with diffusion activation energy,

$E_d = 75.7$  kJ.mol<sup>-1</sup>. Current preliminary results show that the low temperature (LT) cells can reversibly cycle at 20 equivalents or 943 mAh.gm<sup>-1</sup> FePc at a C/10 discharge rate. This capacity is competitive with the experimental lithium<sub>(s)</sub>/sulfur<sub>(s)</sub> and lithium<sub>(s)</sub>/oxygen<sub>(g)</sub> cells.

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