Electrochemical Characterization of Copper Phthalocyanine for Lithium-Based Batteries

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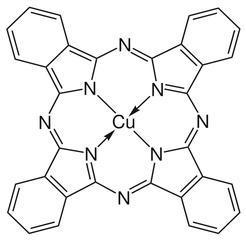
Abstract

Present an analytical formulation of the reversible voltage and electrode electrochemical kinetics at the interface between the active material, CuPc, and the electrolyte in a lithium-based cell.



Copper Phthalocyanine (CuPc)

Introduction

The phthalocyanine-based cathode active materials have been and still being investigated for the design/development of the higher energy density rechargeable lithium-based batteries. From the most recent research results, the electrochemical behavior of CuPc is observed to be more stable than FePc. This led us to develop the theoretical formulation for prediction of the reversible voltage and electrode electrochemical kinetics of the charge transfer process at the electrolyte-CuPc interface.

Developed Theoretical Formulation

The reversible process of charge transfer at the CuPc – electrolyte interface under the external open – circuit condition is represented as:

$$x\ g-moles\ of\ Li^{+}(in\ an\ electrolytic\ solution)+x\ g-moles\ of\ e^{-}(in\ an\ electronic\ conductor\ such\ as\ carbon)+1\ g-mole\ of\ host\ material, CuPc \rightleftarrows (x-g-moles\ of\ (Li^{+},e^{-})\ pairs\ in\ 1\ g-moles\ of\ CuPc)$$

The equilibrium condition of electrochemical reaction process for a set of temperature and pressure conditions can be presented as:

$$x\mu^{echem}_{Li^{+}(in\ electrolyte\ solution)}+x\mu^{echem}_{e^{-}(in\ e^{-}\ conductor)}=x\mu^{chem}_{Li(in\ CuPc)} \quad [1]$$

Using the thermodynamic information, equation [1] is transformed to:

$$E_{rev,T}=E_T^{\circ}+\left(\frac{RT}{F}\right)\left[\ln\left(\frac{\gamma_{Li^{+}}C_{Li^{+}}}{C^{\circ}_{Li^{+}}}\right)-\ln\left(\frac{\gamma_{Li}x}{x^{\circ}}\right)\right] \quad [2]$$

Where $\gamma_{Li^{+}}$ is the activity coefficient of lithium ions in the lithium-based cell electrolyte solution; x is the g-moles of lithium per g-mole of CuPc; E_T° is the standard-state electric potential at the cathode electrode-electrolyte interface at system temperature, with $C_{Li^{+}}=C^{\circ}_{Li^{+}}, x=x^{\circ}, \gamma_{Li^{+}}=\gamma^{\circ}_{Li^{+}}=1$, and $\gamma_{Li}=\gamma^{\circ}_{Li}=1$, the equation [2] provides the correlation for the prediction of $E_T^{\circ}=f(T)$. Equation [2] can be used to calculate $E_{rev,T}$; provided $\gamma_{Li^{+}}=f_c(T,C_{Li^{+}})$ and $\gamma_{Li}=f_x(T,x)$ are made available.

Also, x can be calculated by:

$$x=x_i+\left(\frac{M_{CuPc}}{m^t}\right)\left[\frac{\int_0^t|I^{tot}|\,dt}{F}\right] \quad [3]$$

Where $|I^{tot}|$ is the magnitude of total cathode current [A]; m^t is the total mass of CuPc in the cathode electrode [gms]

The overall reaction stoichiometric equation of the three phase (CuPc – carbon – electrolyte) is:

$$Li^{+}\ (from\ an\ electrolyte\ solution)+e^{-}(from\ an\ electron\ conducting\ solid\ C)+(Solid\ host\ material,\ CuPc)\underset{k_s^a}{\overset{k_s^c}{\rightleftarrows}}((Li^{+}\text{-}e^{-})\ pair\ in\ the\ solid\ host\ active\ material.\ CuPc) \quad [4]$$

The net reaction rate is represented by:

$$r=(r_a-r_c)=k_s^a\hat{a}_{Li}exp\left(\frac{\alpha_a-FE}{RT}\right)-k_s^c(x_{max}-x)\hat{a}_{Li^{+}}exp\left(\frac{-\alpha_cFE}{RT}\right) \quad [5]$$

where $\hat{a}_{Li}$ is activity of (Li^{+}-e^{-}) pairs in CuPc, α_a is the anodic direction charge transfer coefficient; x_{max} are the g-moles of theoretical or maximum effective active sites available for occupation by lithium via the lithium-ion intercalation process per g-mole of CuPc.

Based on equation [5], the net electrode-electrolyte interfacial charge transfer current per unit effective internal area is:

$$i_s=rF \quad [6]$$

Equation [5] and [6] have been coupled to obtain:

$$i_s=i_{s,eq}\left\{\left(\frac{\gamma_{Li}x}{\gamma_{Li,eq}x_{eq}}\right)exp\left(\frac{\alpha_aF(E-E_{eq})}{RT}\right)-\left(\frac{x_{max}-x}{x_{max}-x_{eq}}\right)exp\left[\frac{-\alpha_cF(E-E_{eq})}{RT}\right]\right\} \quad [7]$$

Total current at the cathode electrode-electrolyte interface, $|I^{tot}|=i_sA_s^{tot}$, is obtained using equation [7]:

$$|I_c^{tot}|=i_{s,eq}A_s^{tot}\left\{\left(\frac{x_{max}-x}{x_{max}-x_{eq}}\right)exp\left[\frac{-\alpha_cF(E-E_{eq})}{RT}\right]-\left(\frac{\gamma_{Li}x}{\gamma_{Li,eq}x_{eq}}\right)exp\left[\frac{\alpha_aF(E-E_{eq})}{RT}\right]\right\} \quad [8]$$

where A_s^{tot} = total interfacial area of the composite cathode electrode of a lithium-ion cell.

Equation [8] shows that the factor, $exp\left[\frac{\alpha_aF(E-E_{eq})}{RT}\right]$, dampens the effect of $\left(\frac{\gamma_{Li}x}{\gamma_{Li,eq}x_{eq}}\right)$.

Since under the assumption of $\left(\frac{\gamma_{Li,eq}}{\gamma_{Li}}\right)\approx 1, \alpha_a=(1-\beta), \alpha_c=\beta, (\alpha_a+\alpha_c)=1$, equation [8] leads to:

$$\left(\frac{\frac{x_{max}}{x}-1}{\frac{x_{max}}{x_{eq}}-1}\right)\geq exp\left[\frac{F}{RT}(E-E_{eq})\right] \quad [9]$$

For lithium insertion at very low $|I_c^{tot}|$, it is expected that $|(E-E_{eq})|\rightarrow 0$. For the assumption of $\left(\frac{\gamma_{Li}}{\gamma_{Li,eq}}\right)\approx 1$, the starting lithium content, $x_s, \frac{x_s}{x_{max}}\ll 1$, equation [8] can be rewritten as:

$$|I_c^{tot}|=i_{s,eq}A_s^{tot}\left[\left(\frac{x_{max}}{x_{max}-x_{eq}}\right)-\left(\frac{x_s}{x_{eq}}\right)\right] \quad [10]$$

Conclusions

a) Equation [2] shows the dependence of $E_{rev,T}$ on the lithium content of CuPc and lithium ion concentration in the electrolyte in contact with the cathode electrode active material at a given temperature.
b) The theoretical formula, Eq. [8], shows the dependence of the total current on various parameters such as $x, E, \alpha_a, \alpha_c, etc.$ at a given temperature.
c) Theoretical formulation can be employed in the design and performance analysis of a cathode electrode with the active material, CuPc.