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Overall Semi-Empirical Rate-Law Formulation of a Lithium-Based Cell or Battery

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ABSTRACT

The concept of the overall activation energy barrier to the occurrence of catalyzed chemical reactions involving the chemical species mass transport and intrinsic chemical reaction kinetics has been employed to develop the formulation presented in this paper. In an electrochemical cell, for example, $Li_{(s)}/electrolyte/Li_xCuPc_{(s)}$, the overall cell activation energy barrier to the cell performance at a given temperature is expressed in terms of the difference between the cell open-circuit voltage and actual voltage as a function of the cell cathode active material lithium content, x, defined as g-atoms of lithium per g-mole of cell cathode active material. This voltage difference is assumed to account for the resultant sum of the energy barriers associated with the electrochemical reaction polarization at the cell electrode-electrolyte interfaces, lithium ion transport through the cell electrolyte, and lithium transport in the interstitial channels in a cell lithium-intercalating cathode active material, for example; solid copper phthalocyanine, $CuPc_{(s)}$.

To observe the trends of the cell current during the cell discharge and charge, computations were performed using the assumed values of some parameters involved in the presented formulation. The computed data are shown in the form of dimensionless quantities representing the cell discharge and/or charge currents as a function of lithium content in a cell, such as: $Li_{(s)}/electrolyte/Li_xCuPc_{(s)}$ for some assumed parametric values. However, it is strongly recommended for the determination of various parameters involved in the formulation through a carefully designed experimental program for obtaining a practical cell performance model.

KEYWORDS: kinetics, semi-empirical, rate law, activation energy, lithium-ion battery

I. INTRODUCTION

A team of engineers and scientists has been actively involved in the theoretical modeling and experimental activities to investigate and develop lithium-based cells or batteries since 2013 [1–6]. In this presentation, an overall semi-empirical rate-law formulation is presented for the performance evaluation of a given lithium-based cell, such as lithium/electrolyte/lithium-intercalating active material; e.g., copper phthalocyanine ($CuPc_{(s)}$).

During the discharge period of a cell of the type mentioned above, lithium ions are generated at the lithium foil/electrolyte interface and transferred across it into the cell electrolyte medium. The cell lithium foil, acting as the cell anode, provides electrons to an external electrical circuit used to control the current flow. Lithium ions migrate from the anode, through the cell electrolyte, to the cell cathode/electrolyte interface where the charge transfer at the three-phase contact points (electrolyte-cathode active material-carbon based conductor, e.g., graphene flakes) takes place. Then, not-completely discharged lithium ions diffuse through the narrow channels of the cell cathode active material such as copper phthalocyanine (in the solid-state, channel size range of 3-5Å) for their storage and accumulation. All these processes of electrochemical reactions and charge transfer across the cell electrode-electrolyte interfaces, lithium ion transport through the cell electrolyte and the not-completely discharged lithium ion transport in the cathode active material involve relative energy barriers to their occurrences depending on the cell current per unit mass of the cathode active material (e.g. $CuPc_{(s)}$) at a cell operational temperature condition. The overall resultant effect of all these process energy barriers is lowering of the cell voltage relative to the external open-circuit voltage or the cell emf at an x value (defined as the moles of the intercalated lithium into the cathode active material per mole of the cathode active material; (e.g. $CuPc_{(s)}$). That is: the overall cell operational energy barrier at a cell discharge current is: $E_{ov} = |E_{open}(x) - E(x)|$, [volt] at an x-value; where $E_{open}(x)$ is the cell open circuit electric potential and $E(x)$ is the cell actual electric potential at an x-

value during the cell discharge period at a desired cell current. It is here mentioned that all the cell processes, briefly explained above, also take place in the opposite direction during the cell charging period. The concept of the overall energy barrier to the occurrence of cell discharge or charge is similar to that used in the analysis of catalyzed chemical reactions involving the chemical species mass transport and intrinsic chemical reaction kinetics [7].

To stress the development of the formulation presented in this paper, it is stated that the theory-based comprehensive model for the accurate performance evaluation of the lithium-based cells utilizing the new cathode active materials, currently under investigation, requires accurate values of the electro-kinetics parameters, transport, and chemical-electrochemical thermodynamic properties. Determination of accurate values of such properties under the cell varied operational conditions is a very labor-intensive and difficult task; if not impossible. Faced with this situation, it was decided to develop an overall semi-empirical model for the performance analysis/design of a lithium-based cell.

II. MODEL FORMULATION

Figure 1 below is a simple sketch of the lithium-based cell being modelled.

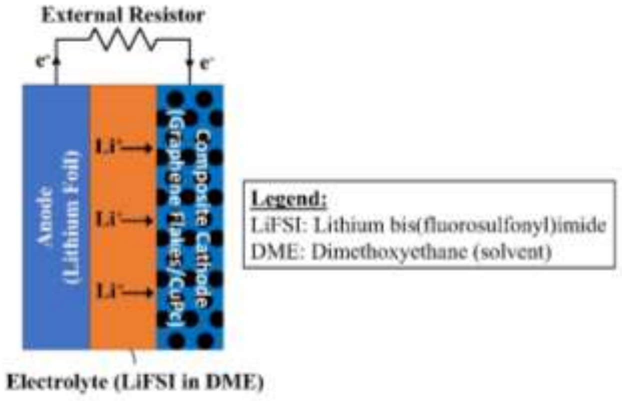

Figure 1. Simple sketch of a lithium-based cell.

The overall cell operational process involving the reactants $Li_{(s)}$ and $CuPc_{(s)}$ during the cell discharge period is represented by:

$$Li_{(s)} + Li_x CuPc_{(s)} \xrightarrow{k_f} Li_{x+1}CuPc_{(s)} \tag{1}$$

The rate of reaction (1) is given by:

$$\begin{aligned} r_f &= k_f a_{Li_{(s)}} a_{Li_x CuPc_{(s)}} \\ &= \frac{\text{g-moles of the net reaction (1) taking place in the forward direction}}{\text{time} \cdot \text{gram of the } CuPc_{(s)} \text{ material in the composite cathode}} \\ &= \frac{\text{g-atoms of lithium consumed}}{\text{time} \cdot \text{gram of the } CuPc_{(s)} \text{ material}} \\ &= \frac{\text{g-moles of } Li_{x+1}CuPc_{(s)} \text{ generated}}{\text{time} \cdot \text{gram of the } CuPc_{(s)} \text{ material}} \end{aligned} \tag{2}$$

where $a_{Li_{(s)}}$, $a_{Li_x CuPc_{(s)}}$, and $a_{Li_{x+1}CuPc_{(s)}}$ are the activities of the species $Li_{(s)}$, $Li_xCuPc_{(s)}$, and $Li_{x+1}CuPc_{(s)}$ in the solid-state. The activity of a species in its pure state is generally taken as equal to one. Therefore, $a_{Li_{(s)}} = a_{CuPc_{(s)}} = 1$. The reaction rate-related activity, for example, $a_{Li_x CuPc_{(s)}}$, is expressed as

$$a_{Li_x CuPc_{(s)}} = \left(1 - \frac{x}{x_{sat}}\right) \tag{3}$$

where x = (g-atoms of lithium in the cathode active material $CuPc_{(s)}$)/(1g-mole of the cathode active material $CuPc_{(s)}$) and x_{sat} = (g-atoms of lithium in the cathode active material saturated with the intercalated lithium)/(1g-mole of the cathode active material $CuPc_{(s)}$). x_{sat} is here defined as the g-atoms of lithium present in the cathode active material per g-mole of $CuPc_{(s)}$ when the cell voltage precipitously drops to a predefined cell cutoff voltage during the cell discharge period. k_f is the rate coefficient for the reaction, Eq. (1), mole/(time · gram of $CuPc$). Rewriting Eq. (2) as

$$r_f = k_f \left(1 - \frac{x}{x_{sat}}\right) \tag{4}$$

gives the rate of reaction, Eq. (1), per gram of $CuPc(s)$ during the cell discharge period for $0 \le x \le x_{sat}$. The reaction rate coefficient k_f at a cell temperature, T [K], and x (lithium content of the cathode active material) = (x gram-atoms of lithium per g-mole of $CuPc_{(s)}$) is given as $k_f = A_{f,0} \exp\left[\frac{-\alpha |E_{ov}| F}{RT}\right]$. The total or overall cell voltage loss, $|E_{ov}|$, associated with the Gibbs free energy loss due to the species transport and electrochemical reaction charge transfer processes at the cell electrolyte-electrode interfaces is given by

$$|E_{ov}(x)| = |E_{open}(x) - E(x)| \tag{5}$$

where $E_{open}(x)$ is the cell open-circuit voltage and $E(x)$ is the cell actual voltage at the x-value when the cell is providing electric current, I [amp], and power, $P = IE(x)$ [Js^{-1}]. The correlation between $|E_{ov}(x)|$ and x should be determined through the cell experimental data. A proposed correlation is:

$$|E_{ov}(x)| = a + bx \tag{6}$$

At a cell current I-value, if $|E_{ov}(x)|$ vs. $\frac{x}{x_{sat}}$ experimental data are available, then values of 'a' and 'b' should be determined from the $|E_{ov}(x)|$ absolute value using Eq. (6). Note that the x-value during the cell discharge period at the cell current of I is given by

$$x = \frac{\left[\left(\int_{t=0}^{t=t} I dt\right) / F\right]}{\dfrac{m_{cath-active\ material\ in\ the\ cathode}}{M_{CuPc}}} = \left[\frac{\left(\int_0^t I dt\right) M_{CuPc}}{F m_{cath-active\ material\ in\ the\ cathode}}\right] \tag{7}$$

where F is one gram-equivalent of charge or 96,487 coulombs of charge per gram-atom of lithium intercalating into the cathode active material $CuPc(s)$, M_{CuPc} is the molecular weight of *CuPc* [grams per gram-mole of *CuPc*], and *m*(*cath-active material in the cathode*) is the mass of *CuPc*(*s*) in grams in the cell composite cathode. Then, k_f can be expressed as:

$$k_f = A_{f,0}\exp\left[\frac{-\alpha F}{RT}(a+bx)\right] \tag{8}$$

Rewriting Eq. (8) now as

$$\begin{aligned} k_f &= A_{f,0}\exp\left[\frac{-(\alpha a)F}{RT}\right]\exp\left[\frac{-(\alpha b)xF}{RT}\right] \\ &= A_{f,0}\exp\left[\frac{-\alpha_1 F}{RT}\right]\exp\left[\frac{-\alpha_2 xF}{RT}\right] \end{aligned} \tag{9}$$

where, with units of volts, $\alpha_1 = \alpha a$ and $\alpha_2 = \alpha b$. The overall operational process during the cell charging period is represented by:

$$Li_xCuPc_{(s)} \xrightarrow[k_b]{} Li_{(s)} + Li_{x-1}CuPc_{(s)} \tag{10}$$

The rate of the reaction, Eq. (10), is given by:

$$r_b = k_b\left(\frac{x}{x_{sat}}\right) \tag{11}$$

where

$$\begin{aligned} k_b &= A_{b,0}\exp\left[\frac{-(\beta a)F}{RT}\right]\exp\left[\frac{-(\beta b)xF}{RT}\right] \\ &= A_{b,0}\exp\left[\frac{-\beta_1 F}{RT}\right]\exp\left[\frac{-\beta_2 xF}{RT}\right] \end{aligned} \tag{12}$$

where, with units of volts, $\beta_1 = \beta a$ and $\beta_2 = \beta b$. Inserting k_f and k_b from Eqs. (9) and (12) into Eq. (4) and (11), respectively:

$$r_f = A_{f,0}\exp\left[\frac{-\alpha_1 F}{RT}\right]\exp\left[\frac{-\alpha_2 xF}{RT}\right]\left(\frac{x_{sat}-x}{x_{sat}}\right) \tag{13a}$$

$$r_b = A_{b,0}\exp\left[\frac{-\beta_1 F}{RT}\right]\exp\left[\frac{-\beta_2 xF}{RT}\right]\left(\frac{x}{x_{sat}}\right) \tag{13b}$$

The current density during the cell discharge period at a time, t [sec], per gram of *CuPc*(*s*) is given by:

$$i_{gm} = r_f F \tag{14}$$

The total cell current is:

$$I_f = i_{gm} m_{cath-active} \tag{15}$$

$$I_f = r_f F m_{cath-active} \tag{16}$$

Inserting r_f from Eq. (13a) into Eq. (16),

$$I_f = A_{f,0}\exp\left[\frac{-F}{RT}(\alpha_1 + \alpha_2 x)\right]\left(\frac{x_{sat}-x}{x_{sat}}\right) m_{cath-active}F \tag{17}$$

which is valid for $0 \le x \le x_{sat}$ with $\alpha_1 = \alpha a$ and $\alpha_2 = \alpha b$. The current associated with the cell discharge, I_f, is related to the cathode active material-electrolyte interfacial current density, i_s $\left[\frac{\text{amp}}{cm_s^2 \text{ of the active material-electrolyte interface}}\right]$, as follows,

$$I_f = i_{gm} m_{cath-active} = i_s a_{eff} m_{cath-active} \tag{18}$$

where a_{eff} is the effective electrolyte-cathode active material interfacial area for the charge transfer across the electrolyte-cathode active material interface per gram of the cathode active material, $\left[\frac{cm_s^2}{gram}\right]$.

Rewriting Eq. (17) as:

$$I_f = \left(A_{f,0} m_{cath-active} F\right)\exp\left[\frac{-F\alpha}{RT}(a+bx)\right]\left(\frac{x_{sat}-x}{x_{sat}}\right) \tag{19}$$

and rearranging Eq. (19) yields a dimensionless current expression:

$$\frac{I_f}{\left(A_{f,0} m_{cath-active} F\right)} = \exp\left[\frac{-F\alpha}{RT}(a+bx)\right]\left(\frac{x_{sat}-x}{x_{sat}}\right) \tag{20}$$

Taking the natural logarithm of both sides of Eq. (20),

$$\begin{aligned} \ln\left[\frac{I_f}{\left(A_{f,0} m_{cath-active} F\right)}\right] &= \left[\frac{-F\alpha}{RT}(a+bx)\right] + \\ &\quad \ln\left(\frac{x_{sat}-x}{x_{sat}}\right) \end{aligned} \tag{21}$$

During the period of cell charge, the cell cathode active material is depleted of lithium as given by the reaction in Eq. (10). The reaction rate law equation for this process is expressed as

$$I_b = \left(A_{b,0} m_{cath-active} F\right)\exp\left[\frac{-F\beta(a+bx)}{RT}\right]\left(\frac{x}{x_{sat}}\right) \tag{22}$$

Or,

$$\frac{I_b}{\left(A_{b,0} m_{cath-active} F\right)} = \exp\left[\frac{-F\beta(a+bx)}{RT}\right]\left(\frac{x}{x_{sat}}\right) \tag{23}$$

Rewriting Eq. (23) as

$$\ln\left[\frac{I_b}{\left(A_{b,0} m_{cath-active} F\right)}\right] = \left[\frac{-F\beta(a+bx)}{RT}\right] + \ln\left(\frac{x}{x_{sat}}\right) \tag{24}$$

III. EXAMPLE CALCULATED DATA AND DISCUSSION

Equation (24) was subtracted from Eq. (21) and the resultant expression rearranged as shown below.

$$\begin{aligned} Y_{comp} &= \ln\left[\left(\frac{I_f}{I_b}\right)\left(\frac{A_{b,0}}{A_{f,0}}\right)\right] \\ &= \left[\frac{(\beta-\alpha)(a+bx)F}{RT} + \ln\left(\frac{1}{r_x} - 1\right)\right] \end{aligned} \tag{25}$$

where $r_x = \frac{x}{x_{sat}}$.

Equation (25) is indicative of the comparison of the cell discharge current, I_f, with the cell charge current, I_b, at a fixed cell operational temperature. This equation can also be viewed as the comparison of the forward with the backward reaction in Eq. (1) during the cell discharge period.

To observe the effect of $r_x = \frac{x}{x_{sat}}$ on the forward reaction rate or the cell current I_f, Eq. (21) was rearranged as shown below.

$$Y = \ln\left[\frac{y_{f,reciprocal}}{\exp\left[\frac{F\alpha a}{RT}\right]}\right] = \gamma - \delta \qquad (26)$$

where

$$y_{f,reciprocal} = \frac{m_{cath-active} A_{f,0} F}{I_f} \qquad (27)$$

and

$$\gamma = \left(\frac{\alpha b F}{RT}\right) x \qquad (28a)$$

$$\delta = \ln\left(1 - \frac{x}{x_{sat}}\right) \qquad (28b)$$

In the absence of actual required cell performance parametric data; parameter $\beta = \alpha$ was assumed in Eq. (25) and Y_{comp} calculated as a function of $r_x = \frac{x}{x_{sat}}$. Figure 2 is the representation of such a calculated data set. The plot shows a decrease in Y_{comp} with an increase in r_x. The plot nature can be interpreted as a decrease in the occurrence of the cell overall reaction process as the cell cathode active material channels are filled during the cell discharge period. Steep decreases in the values of the dependent variable Y_{comp} are observed in the r_x ranges: 0.01 to 0.10 and 0.90 to 0.99.

Using the assumed parametric values, α = 0.5, b = 0.25 *volt*, and x_{sat} = 4.0; the dependent quantity Y in Eq. (26) was computed as a function of r_x at 298.15 and 373.15K. The normalized calculated data as: $Y_{norm} = \left[\frac{Y(r_x)}{Y(r_x = 0.99)}\right]$ plotted vs. r_x is shown in Figure 3 for r_x ranging from 0 to 0.99. The Y_{norm} vs. r_x plot is an indirect representation of the decrease in the cell forward current, I_f, or increase in $y_{(f,reciprocal)}$ in Eq. (26). That is, Y_{norm} increases with an increase in r_x in an almost linear fashion in the r_x range: 0.00 to 0.90. A similar trend is observed at 373.15K. Furthermore, Y_{norm} values are close to each other at any r_x for these two temperatures. Beyond $r_x \cong 0.90$, the slope of Y_{norm} vs. r_x increases as the cathode active material becomes saturated.

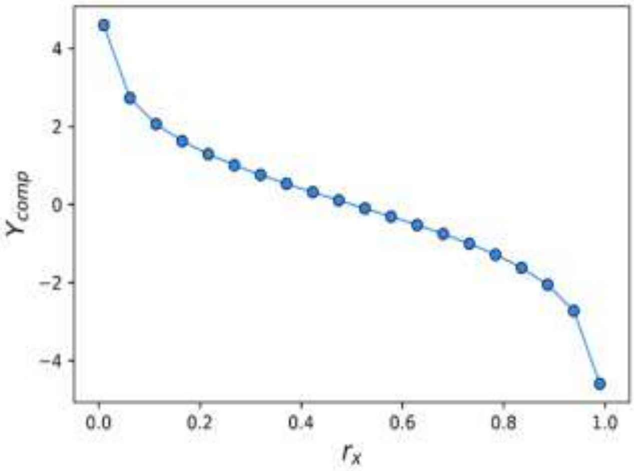

Figure 2. Plot of Y_{comp} vs. r_x

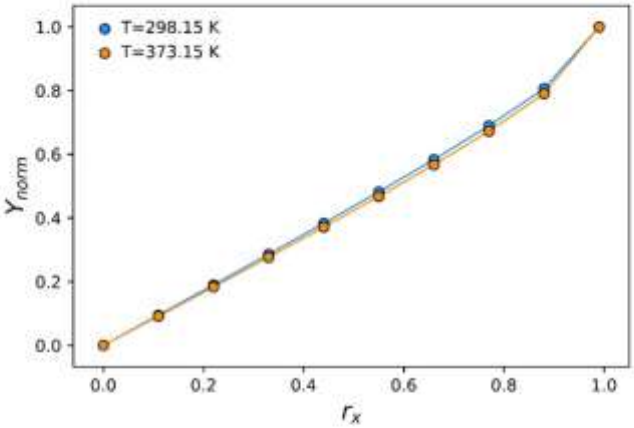

Figure 3. Plot of Y_{norm} vs. r_x

IV. CONCLUDING REMARKS

The formulation presented in this paper for the performance evaluation of a lithium-based cell or battery was developed using the concept of the overall activation energy barrier to the occurrence of a catalyzed chemical reaction involving the chemical species mass transport and intrinsic chemical/electrochemical reaction kinetics. Application of the formulated model was briefly illustrated in the form of plots: Y_{comp} vs. r_x and Y_{norm} vs. r_x in Figures 2 and 3, respectively. Insight gained from these plots supports some of our experimentally acquired data on a lithium-based cell with copper phthalocyanine as the cell cathode active material. It is, however, strongly recommended for the acquisition of values of the various parameters shown in the model equations through a carefully designed experimental program for acquiring a robust practical model for the performance evaluation of a lithium-based cell/battery as mentioned in the model formulation.

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