

## Rate-Law Application to Simulate Lithium-Based Cell Experimental Data

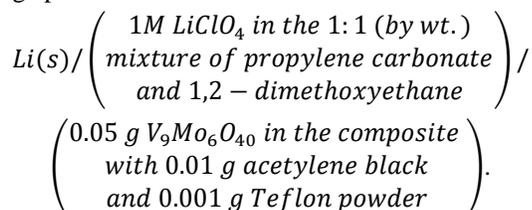
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| ARTICLE INFO  | ABSTRACT   |
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| Published Online:<br>24 December 2020   | A rate-law formulation, based on the concept of the overall activation energy barrier, has been developed [1] to simulate the experimental data of a lithium-based electrochemical cell/battery. This short paper illustrates the application of that formulation to simulate the experimental data acquired from the $Li(s)/V_9Mo_6O_{40}(s)$ cell during the discharge period. |
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| <b>KEYWORDS:</b> kinetics, semi-empirical, rate law, activation energy, lithium-ion battery |  |

### I. Introduction

Faced with the situation of nonavailability of relatively accurate values of the electrokinetics parameters, transport, and electrochemical thermodynamic properties required for the development of a theory-based comprehensive model to explain the performance behavior of an electrochemical power cell utilizing a novel cathode active material [2], a rate-law formulation was developed [1]. The concept of the overall activation energy barrier -accounting for the cell voltage losses due to the ionic and electronic transport as well as due to the charge transfer electrochemical kinetics at the electrode-electrolyte interfaces during the cell discharge or charge period- is the basis of the above-referenced formulation. In this relatively short paper, application of the formulation [1] is illustrated using the experimental data [3] acquired during the discharge period of the cell:



### II. Relevant Formulation

Equation (20) of reference [1] is re-expressed as

$$i_{gm} = F A_{f,0} (1 - r_x) \exp\left(\frac{-F|E_{ov}|}{RT}\right) \quad (1)$$

where  $i_{gm}$  is the gravimetric current density during the cell discharge period, amperes per gram of the active material in the cell cathode,  $A_{f,0}$  is the pre-exponential factor in g-moles of the forward reaction,

$Li(s) + Li_x V_9 Mo_6 O_{40}(s) \rightarrow Li_{x+1} V_9 Mo_6 O_{40}(s)$ , occurring per sec-gm of the active material,

$$r_x = \frac{x}{x_{sat}} = \frac{\left( \begin{array}{l} g\text{-atoms of lithium in the cathode} \\ \text{active material per } g\text{-mole of the} \\ \text{cathode active material} \end{array} \right)}{\left( \begin{array}{l} g\text{-atoms of lithium in the cathode active material} \\ \text{saturated with the intercalated lithium per} \\ g\text{-mole of the cathode active material} \end{array} \right)}, \text{ and}$$

$|E_{ov}| = |E_{open}(x) - E(x)|$  is the overall cell voltage loss due to the ionic and electronic species transport and electrochemical reaction charge transfer processes at the cell electrolyte-electrode interfaces.  $E_{open}(x)$  is the electrochemical cell open-circuit voltage and  $E(x)$  is the cell actual voltage at an  $x$  value when the cell is providing current at the level of  $i_{gm}$  to an external electric circuit.  $F$  is Faraday's constant, 96,487 coulombs per g-equivalent,  $R$  is the universal gas constant, 8.314  $Jmol^{-1}K^{-1}$ , and  $T$  is the cell temperature in degree Kelvin. A linear correlation of  $|E_{ov}|$  with  $r_x$  of the type:

$$|E_{ov}| = a + br_x \quad (2)$$

was used to simulate the cell discharge behavior. It is here noted that the  $x$  value during the cell discharge period at the cell current of  $i_{gm}$  can be calculated from:

$$x = \left[ \frac{\left( \int_0^t i_{gm} dt \right) M_{cath-act}}{F} \right] \quad (3)$$

where  $M_{cath-act}$  is the molecular weight of the active material in the cathode per g-mole of the active material (i.e., grams per g-mole), and  $t$  is the time in seconds during the cell discharge

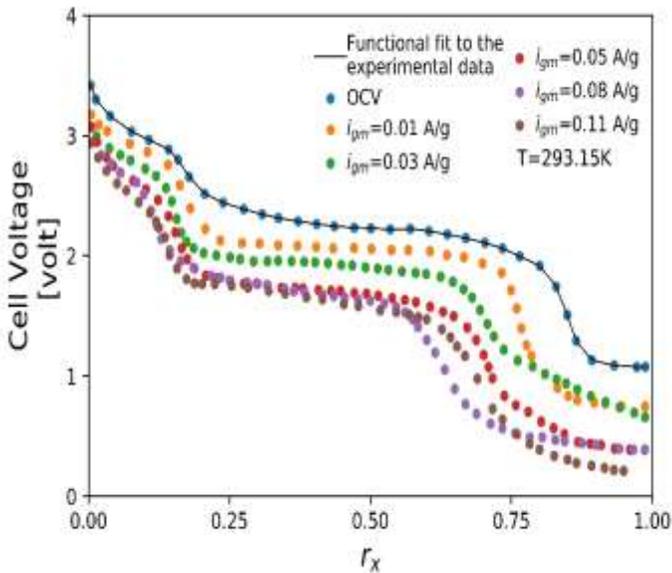
period. The electric power provided by an electrochemical cell can be calculated from:

$$\dot{P} = i_{gm}E(x), \text{ [watts per gram of the cathode active material]} \quad (4)$$

where  $E(x) = E_{OCV} - |E_{ov}|$ , volt. The set of equations given in this section were employed to simulate the experimental data [3] on the  $Li(s)/V_9Mo_6O_{40}(s)$  cell.

### III. Evaluation of $E_{OCV}$ , $|E_{OV}|$ , and $A_{f,0}$ , and Discussion

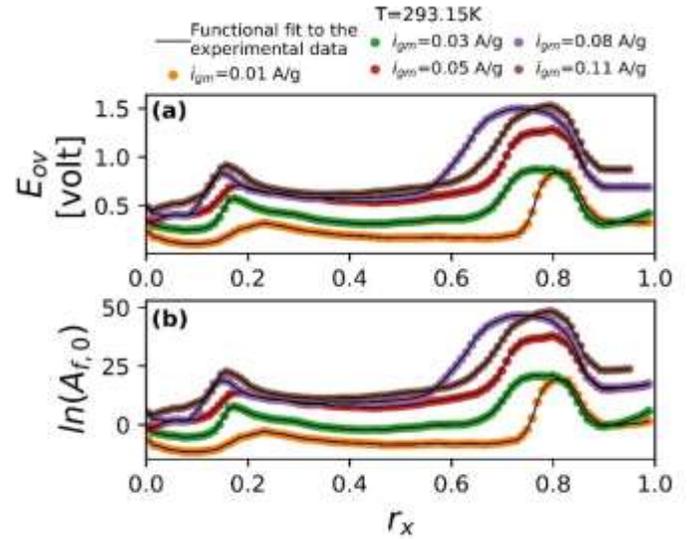
The open-circuit cell voltage,  $E_{OCV}$ , the overall voltage loss,  $|E_{ov}|$ , and the natural log of the pre-exponential factor in Eq. (1),  $\ln(A_{f,0})$ , were simulated using the cell experimental data presented in Figure 1 at each value of the cell gravimetric current density,  $i_{gm}$ . For tight simulation of the experimental data, a function of the type:  $(a + br_x)$  was fitted at each pair of two adjacent  $r_x$  values to calculate the values of  $E_{OCV}$ ,  $|E_{ov}|$ , and  $\ln(A_{f,0})$  as a function of  $r_x$ . The values of  $a$  and  $b$  at every  $r_x$  and  $i_{gm}$  can be found in the Supplementary Information located on the publisher’s website. Figure 1 shows the calculated data of the cell open-circuit voltage (solid line) as compared with the experimental data (solid circles) as a function of  $r_x$ . As expected, the calculated data are in perfect agreement with the experimental data.



**Figure 1.** Experimental cell voltage during the cell discharge period [3] versus  $r_x$ .

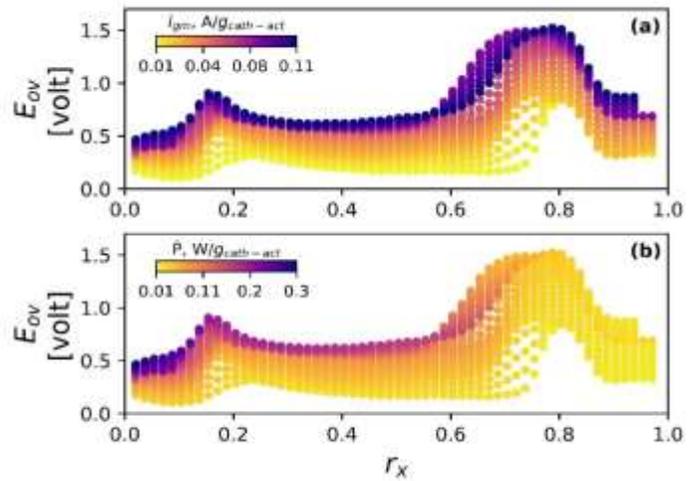
Figures 2a and 2b show the functional fit generated data for the overall cell voltage loss and the pre-exponential factor as a function of  $r_x$  at five  $i_{gm}$  values. Using the data in Figures 2a and 2b, one can calculate  $i_{gm}$  at any  $r_x$  value. Also, using the linear interpolation procedure, one can determine  $E_{ov}$  and  $A_{f,0}$  between any two adjacent current levels at an  $r_x$  value, and

then, inserting these values into Eq. (1), one can determine the  $i_{gm}$  value at that  $r_x$  between two current levels.



**Figure 2.** Comparison of the experimental and functional-fit calculated data. (a)  $E_{ov}$  and (b)  $\ln(A_{f,0})$  plotted versus  $r_x$ . Units of  $A_{f,0}$ :  $\left[\frac{mol}{g \cdot s}\right]$ .

Figure 3a shows the overall cell voltage loss over the  $r_x$  range of the experimental data depicted in Figure 1. The calculated values for  $i_{gm}$  in Figure 3a span from 0.01 to  $0.11 \frac{A}{g_{cath-act}}$ . Figure 3b is the representation of the calculated cell electric power,  $\dot{P}$ , over the same  $E_{ov}$  and  $r_x$  range.  $\dot{P}$  spans from 0.01 to  $0.30 \frac{W}{g_{cath-act}}$ . As expected, these plots follow similar trends. The average deviation associated with interpolation in Figure 3a, defined as the percent difference between the desired  $i_{gm}$  values being interpolated and the  $i_{gm}$  values calculated via the interpolated  $E_{ov}$  and  $A_{f,0}$  values, was determined to be 2.1%.



**Figure 3.** Plot of the functional-fit data. (a)  $i_{gm}$ , current, and (b)  $\dot{P}$ , electric power per gram of the active material in the cell cathode, plotted versus  $r_x$ .

**IV. Concluding Remarks**

Empirical linear-fit functions for  $E_{ov}$  and  $\ln(A_{f,0})$  were presented in the form of plots as a function of  $r_x$ . This plotted information can be employed to calculate  $i_{gm}$  from Eq. (1) at any  $r_x$  value as well as the cell electric power from Eq. (4). It is here suggested that the scheme presented in this paper may be used to simulate the laboratory-scale experimental cell loss data versus  $r_x$  or time during the discharge period of a cell incorporating a novel cathode active material for which accurate transport, electrode kinetics, and cell component thermodynamic property data may not be yet available. The approach briefly presented here may be used for the scaling of cells incorporating novel electrode active materials until more accurate values of the novel electrode properties become available for the development of more refined models to predict

the electrochemical behavior of the lithium-based cells/batteries.

**References**

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**Appendix**

- a. A sample calculation is performed here to more clearly illustrate the approach used in obtaining the data for Figures 3a and 3b. Say the desired  $i_{gm} = 0.04 \frac{A}{g_{cath-act}}$  between 0.03 and 0.05  $\frac{A}{g_{cath-act}}$  at  $r_x = 0.5$ . Using the linearly interpolated values of  $E_{ov}$  and  $A_{f,0}$  from Table 1 (corresponding to the desired  $i_{gm} = 0.04 \frac{A}{g_{cath-act}}$ ) in Eq. (1) results in:  $i_{gm,computed} = 0.0395 \left[ \frac{A}{g_{cath-act}} \right]$ . This differs from the desired value of  $0.04 \frac{A}{g_{cath-act}}$  by 1.15%. The power at  $r_x = 0.5$  and an  $i_{gm,computed} = 0.0395 \left[ \frac{A}{g_{cath-act}} \right]$  is then determined to be  $0.071 \frac{W}{g_{cath-act}}$  using Eq. (4) with  $E(x) = E_{OCV} - E_{ov} = 2.23 - 0.438 = 1.79 V$  and the value for  $E_{OCV}$  at  $r_x = 0.5$  obtained from the functional fit depicted in Figure 1

**Table 1.** Relevant parameters for the sample calculation presented here.

| $i_{gm} \left[ \frac{A}{g_{cath-act}} \right]$ | $E_{ov} = a + br_x$  | $\ln(A_{f,0}) = a_1 + b_1r_x$   | $A_{f,0} \left[ \frac{mol}{g \cdot s} \right]$ |
|--|--|---|--|
| 0.03   | $0.158 + 0.342(0.5)$<br>$= 0.329$  | $-9.14 + 15.55(0.5) = -1.36$  | 0.255  |
| 0.05   | $0.292 + 0.513(0.5)$<br>$= 0.548$  | $-3.14 + 22.30(0.5) = 8.01$   | $3.01 \times 10^3$                             |
| 0.04 (desired)                                 | $0.329 + \left( \frac{0.548-0.329}{0.05-0.03} \right) \times$<br>$(0.04 - 0.03)=0.438$ | $-1.36 + \left( \frac{8.01+1.36}{0.05-0.03} \right) \times (0.04 -$<br>$0.03)=3.32$ | 27.8   |