Modeling a CuCl(aq)/HCl(aq) Electrolyzer using Thermodynamics and Electrochemical Kinetics

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Abstract

Research efforts on the CuCl(aq)/HCl(aq) electrolyzer would greatly benefit from the ability to quantify the dissipative processes that undesirably increase the cell's applied potential, E_{cell} , which decreases its efficiency. To date, little is known about what impact further improvements to active surface area, extent of CuCl(aq) conversion and ohmic resistance would exactly have on the electrolyzer performance. To better understand how this electrolyzer can be improved, a model was developed to quantify and separate the effects of electrochemical kinetics, membrane transport and open circuit potential, E_{OCP} , on E_{cell} for a given current density. By employing data obtained from previous studies with electrochemical cells into the developed model, it was possible to calculate E_{cell} values that agreed with data collected from a lab scale electrolyzer using just one adjustable parameter, the Nernst diffusion layer at limiting current. The model was then used to identify the predicted E_{cell} contributions as a function of CuCl(aq) conversion, active electrode area and ohmic resistance. It was found that the extent of CuCl(aq) conversion can

1 dramatically impact the electrolyzer electrode kinetics and E_{OCP} . More importantly, as CuCl(aq)
2 conversion increased, the E_{cell} values needed consistently increased to keep the same current
3 density. Overall, E_{cell} could be most readily reduced by improving R_{ohm} , whereas improvements
4 to electrode kinetics have limited impacts.

6 **Keywords**

7 CuCl(aq)/HCl(aq) Electrolyzer, Electrochemical Kinetics, Thermodynamics, Current-Potential
8 Modeling, Conversion

10 **1. Introduction**

11 As the complexity of matching power production to power consumption increases, the pursuit of
12 a viable energy storage solution that is capable of storing both thermal and electric energy will
13 continue. One option for storing harnessed thermal and electric energy is the hybrid Cu-Cl
14 thermochemical cycle to efficiently produce hydrogen [1,2]. When compared to other
15 thermochemical cycles under development, previous research found that the four-step Cu-Cl
16 hybrid thermochemical cycle had significantly lower temperature requirements [1]. For example,
17 while the hybrid-sulfur thermochemical cycle required operating temperatures above 800 °C [3],
18 the four-step Cu-Cl hybrid thermochemical cycle only needed temperatures up to 550 °C [4].
19 Given that much of the energy needed for this cycle to split the water is obtained from thermal
20 energy, the electric energy needed to split water by the Cu-Cl cycle has been shown to be
21 considerably less than an acid or alkaline electrolyzers [5]. After including the efficiency loss
22 from electricity production, the overall efficiency this cycle can be between 30-50 %, whereas
23 conventional water electrolysis is between 18-24 % [6]. Additionally, many studies were carried

1 out with the purpose of evaluating different cost scenarios for the Cu-Cl cycle such as
2 incorporation with solar molten salt power plants [2], geothermal plants [7] and nuclear power
3 plants [8]. Despite the considerable research already performed, many fundamental questions
4 about the maximum electric energy required of the key electrolysis step for this cycle still exist.

6 Though research and development progress have made large strides in understanding this cycle
7 [1,4], many questions relating to each of the cycle's steps still remain. A recent focus on this
8 process in a number of research groups has centered around the hydrogen production step, the
9 CuCl(aq)/HCl(aq) electrolyzer [5,9–14]. These studies found that the faradaic efficiency was
10 greater than 90 % and applied potentials can be less than 0.7 V [10]. Though many aspects of the
11 electrolyzer have been improved in the last decade, the effects of operational parameters are still
12 being explored, and more importantly, the electrolyzer's key limiting factors have yet to be
13 established with kinetic and thermodynamic relations.

15 In this work we present a model based on equilibrium thermodynamics and electrochemical
16 kinetics to provide insight into trends expected of the open circuit potential values, membrane
17 transport limitations, and electrode overpotentials for the CuCl(aq)/HCl(aq) electrolyzer. The
18 advantage of this model over other models is that it uses fundamental thermodynamic, kinetic
19 and transport coefficients in non-equilibrium thermodynamic relations, making extrapolations
20 more reliable. The model parameters were obtained through experimental methods using single
21 cells where each coefficient can be isolated and conveniently quantified. As such, the parameters
22 used in the model presented here provide an easy path to extending the applicability of this
23 model into higher temperatures, pressures, concentrations, etc. With this model, for the first time,

E_{cell} trends and its contributions were defined to provide insights into key limiting factors and performance limitations of the electrolyzer as a whole. With some select approximations, the predicted applied electric potentials or E_{cell} values were in excellent agreement with data obtained from a lab-scale experimental CuCl(aq)/HCl(aq) electrolyzer using only one adjustable parameter, the Nernst diffusion layer at limiting current, δ_N . It is important to note that the electrolyzer was operated with a high flow rate to avoid the bulk reactant concentration from changing by more than a fraction of a percent from the bulk inlet concentration. This procedure was adopted to keep the bulk concentration within the cell as constant as possible between inlets and outlets. Afterwards, comparisons of the impact of different potential losses were presented for a series of case studies to refine future research efforts onto the key limiting processes. Particular focus was placed on the sensitivity of E_{cell} to changes to experimental parameters including ohmic resistance, R_{ohm} , the extent of CuCl(aq) conversion, ξ_{CuCl} , and the active electrode area.

2. Theory

2.1 Overview of CuCl(aq)/HCl(aq) electrolyzer

In the CuCl(aq)/HCl(aq) electrolyzer, the positive electrode, or the anode when the cell is operating in electrolytic mode, oxidizes aqueous Cu^I(aq) chloride complexes to Cu^{II}(aq) chloride complexes. A recent thermodynamic analysis of the speciation in the anode solution demonstrated that a number of Cu^I(aq) chloride complexes to Cu^{II}(aq) chloride complexes exist [10]. As such, the following half-reaction is what is expected at the positive electrode:

where in literature $\text{CuCl}(\text{aq})$ often refers to all CuCl_n^{1-n} , and $\text{CuCl}_2(\text{aq})$ refers to all $\text{CuCl}_n^{2-n}(\text{aq})$ species with n being an integer from 0 to 4 [14]. The concentration of a CuCl_n^{1-n} species for a particular value of n depends on available number of free chloride ions from the $\text{HCl}(\text{aq})$. At 7 mol L^{-1} $\text{HCl}(\text{aq})$, a desirable concentration in the electrolyzer, the concentration of $\text{CuCl}_3^{2-}(\text{aq})$ was orders of magnitudes higher than all other CuCl_n^{1-n} species [10]. When $\text{CuCl}_3^{2-}(\text{aq})$ had a concentration of 2 mol/kg, the next most abundant complex was $\text{CuCl}_2^-(\text{aq})$ with a concentration between 10^{-2} and 10^{-3} , while $\text{Cu}^+(\text{aq})$ was 10^{-11} mol/kg [10]. Furthermore, a 2 mol/kg change in the bulk $\text{HCl}(\text{aq})$ concentration did little to change this distribution of Cu^I complex concentrations [10]. Though the difference between $\text{CuCl}_n^{2-n}(\text{aq})$ species were less dramatic, $\text{CuCl}_3^{2-}(\text{aq})$ was one of the most abundant in concentration, suggesting the primary reaction occurring at the positive electrode was as follows [10]:

The half-reaction occurring at the negative electrode, or the cathode when the cell is operating in electrolytic mode, is the hydrogen reaction:

The two compartments where these reactions take place are separated by a proton conductive membrane, typically Nafion [9,11,13]. The species present and phases of interest can be

1 conveniently displayed in an electrochemical diagram [15] that uses a cross (×) to display three-
2 phase boundary at the cell negative electrode as shown in Figure 1:

3
4 Figure 1.

5
6 where the concentration of CuCl(aq) and CuCl₂(aq) species depends on the starting
7 concentrations for each species and CuCl(aq) conversion and, therefore, are not specified. A Pt/C
8 catalyst is the electrode material commonly used for this electrochemical cell [9–11,13]. Further
9 details on the type used here can be found in the experimental section.

10
11 To understand the electric power requirements needed to operate the electrolyzer, the cell
12 current, I_{cell} and E_{cell} must be determined. By Kirchoff's current law, the total current passing
13 through each of the cell's components connected in series must be equal. For convenience, the
14 electrolyzer will be sub-divided into three sections, the positive electrode, negative electrode and
15 the membrane. Though the total current, passing through each of these sections, are equal, the
16 potential drops at each of them should be different. As such, to model how these three sections
17 influence I_{cell} and E_{cell} , relations between I_{cell} and the potential contributions from each section
18 are needed. Here we will consider the following potential contributions to E_{cell} from the positive
19 electrode as the equilibrium potential contribution E_+ and the non-equilibrium contribution or
20 overpotential, η_+ . Similar contributions will be considered from the negative electrode as the
21 equilibrium potential term, E_- and the non-equilibrium term, η_- . The overpotentials have a clear
22 connection to the electrochemical affinity of the half-reactions, the driving force for the

electrochemical reaction [16]. Lastly, E_{IR} , or the potential drop from the ohmic resistance of the cell will be considered. These contributions can be summarized by the following relation:

$$E_{cell} = E_{-} - E_{+} + \eta_{-} - \eta_{+} - E_{IR} \quad (4)$$

where according to IUPAC conventions [17], η_{+} is positive due to its polarization in the anodic direction, η_{-} is negative due to its polarization in the cathodic direction and the equilibrium potentials, E_{+} and E_{-} are calculated as potentials of reduction reactions. In the following sections, relations collected from literature will be used to generate a model relating E_{cell} to I_{cell} for the CuCl(aq)/HCl(aq) electrolyzer.

2.2 Positive Electrode

The goal of this model was to simulate how E_{cell} changed with experimental parameters j_{cell} , ξ_{CuCl} and active electrode area. As such, the potential contributions of the positive electrode should be described in terms of the variables of interest. To start, the potential contribution of the positive electrode to E_{cell} was split into non-equilibrium and equilibrium parts.

The equilibrium potential contributions, E_{+} , of the CuCl(aq)/CuCl₂(aq) redox reaction occurring at the positive electrode was handled via Gibbs energy minimization as described in Ref. [10].

In short, the CuCl(aq) complexes considered were Cu⁺(aq), CuCl⁰(aq), CuCl₂⁻(aq) and CuCl₃²⁻(aq). The CuCl₂(aq) complexes included were Cu²⁺(aq), CuCl⁺(aq), CuCl₂⁰(aq) and CuCl₃⁻(aq) and CuCl₄²⁻(aq). Hydroxide and oxide complexes for both Cu^I and Cu^{II} redox states were included but not found to be significant [10]. Standard thermodynamic properties were obtained

from the HKF model used in the SUPCRT92 database [18] and the empirical b_γ of the background electrolyte HCl(aq) were used to calculate activity coefficients [10]. Using the results from Gibbs energy minimization, which used both standard thermodynamics values and activity coefficients, it was found that E_+ can be approximated by the following equation:

$$E_+ = E_{effective}^o + \frac{RT}{F} \ln \left[\frac{b_{CuCl_2(aq)}}{b_{CuCl(aq)}} \right] \quad (5)$$

where $E_{effective}^o = 0.656$ V, F is Faraday's constant equal to 96485 C mol^{-1} , $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is the molar gas constant, $T = 298 \text{ K}$ is the thermodynamic temperature and $b_{CuCl_2(aq)}$, $b_{CuCl(aq)}$ are the sum of the concentrations of Cu^{II} and Cu^{I} containing species respectively on the molal concentration scale. The term effective is used here because this value does not represent the standard Gibbs energy of reaction of a particular reaction. It is a purely empirical value that corresponds to the equilibrium potential when the total concentrations of CuCl(aq) and CuCl₂(aq) complexes are equal. This approximation makes it convenient to calculate the E_+ for ξ_{CuCl} from 0 to 0.99. However, due to the effects of complexation and activity coefficients, this approximation is only valid when the total concentration of all Cu(aq) is 2 mol L^{-1} and the concentration of HCl(aq) is 7 mol L^{-1} , the concentrations to be investigated here. As this is the equilibrium thermodynamic contribution, it is the same irrespective of the current passing through the cell and only depends on the bulk concentrations of CuCl(aq) and CuCl₂(aq), which can be directly related to ξ_{CuCl} and the initial concentrations in the following manner:

$$b_{\text{CuCl(aq)}} = b_{\text{CuCl(aq)initial}} - b_{\text{CuCl(aq)initial}} \times \xi_{\text{CuCl}} \quad (6)$$

$$b_{\text{CuCl}_2(\text{aq})} = b_{\text{CuCl}_2(\text{aq})\text{initial}} + b_{\text{CuCl}_2(\text{aq})\text{initial}} \times \xi_{\text{CuCl}} \quad (7)$$

here the subscript “initial” signifies the inlet concentration and ξ_{CuCl} is the ratio of $\text{CuCl}(\text{aq})$ converted over the initial concentration. Due to the high flow rates relative to the total current passing through the cell, further described in the experimental section, the experimental cell had essentially no change in the bulk concentrations between inlet and outlet. Therefore, we use ξ_{CuCl} , and by extension $b_{\text{CuCl}(\text{aq})}$ and $b_{\text{CuCl}_2(\text{aq})}$, to describe how the cell would operate if the constant bulk concentrations were changed to another set of concentrations. In a case where the electrolyzer does have a high enough residence time to change the bulk concentrations, each value of ξ_{CuCl} would correlate to different points within the cell between inlet and outlet. From another perspective, each input value of ξ_{CuCl} explores how the cell performance would be if the bulk concentration between inlet and outlet were still constant but not the initial 2 mol/L $\text{CuCl}(\text{aq})$ with trace amounts of $\text{CuCl}_2(\text{aq})$ used commonly in experimental systems.

The next contribution considered from the positive electrode was η_+ . This potential contribution is the driving force for the electrochemical reaction at the positive electrode. Unlike the equilibrium potential, this contribution is directly relatable to I_{cell} passing through the cell. While I_{cell} is what is measured, it is typically normalized to current density, j_{cell} , via the cell’s geometric area, A_{cell} with units of cm^2 geo, for comparability to other systems with different cell areas. According to the charge electroneutrality, I_{cell} can be related to the electrode current densities of the positive and negative electrodes, j_+ and j_- , provided that the area differences between A_{cell} and the active electrode areas are taken into account. The general relation between j_{cell} and j_+ can be described as follows:

$$j_{\text{cell}} = I_{\text{cell}} / A_{\text{cell}} = (A_+ / A_{\text{cell}}) j_+ \quad (8)$$

where A_+ with units of cm^2 , is the active area of the positive electrode, and using IUPAC conventions [17], the current density of the anodic polarization occurring at the positive electrode is positive. A similar relation can be obtained for j_- and will be presented in the following section. As the electrolyzer employs Pt/C catalyst, a conversion factor, $(A_{\text{active}}/g_{\text{pt}})$ with units of $\text{cm}^2 \text{ g}^{-1}$, is needed to convert the catalyst loading, m_{catalyst} with units of $\text{g cm}^{-2} \text{ geo}$, to obtain an active area of the electrode [19], which can be defined as follows:

$$A_+ = m_{\text{catalyst}} (A_{\text{active}}/g_{\text{catalyst}}) A_{\text{cell}} \quad (9)$$

Resulting in A_+ being the active area with units of cm^2 . Previous work provided estimates the conversion factor for Pt/C catalysts via data collected from capacitive current values due to adsorbed species such that $A_{\text{active}}/g_{\text{catalyst}} = 110 \text{ m}^2 \text{ g}^{-1}$ for platinum on an activated carbon support [19]. For the positive electrode, $m_{\text{catalyst}} = 0.1 \text{ mg Pt cm}^{-2} \text{ geo}$. Now with an estimate of the active surface area, only a relation between j_+ and η_+ is still needed.

Some models use a **simplified current** density – overpotential, $j_+ - \eta_+$, relation where the reverse reaction is neglected [20]. However, when the reverse reaction is found to have a significant impact, j_+ is relatable to η_+ , using the generalized Butler – Volmer (B-V) equation [15,21].

$$j_+ = (e^{\frac{(1-\alpha_{\text{C},+})\eta_+ F}{RT}} - e^{-\frac{\alpha_{\text{C},+}\eta_+ F}{RT}}) / \left(\frac{1}{j_{0,+}} + \frac{e^{\frac{(1-\alpha_{\text{C},+})\eta_+ F}{RT}}}{j_{\text{lim},a,+}} - \frac{e^{-\frac{\alpha_{\text{C},+}\eta_+ F}{RT}}}{j_{\text{lim},c,+}} \right) \quad (10)$$

where $j_{o,+}$ is the exchange current density of the positive electrode half-reaction, $\alpha_{c,+}$ is the transfer coefficient, $j_{lim,c,+}$ is the limiting current density of a cathodic polarization, $j_{lim,a,+}$ is the limiting current density of an anodic polarization. To use this relation, values for the electrochemical kinetic parameters of the anodic and cathodic directions need to be quantified. In addition to the electrochemical parameters, the presence of limiting current values dictates consideration of the boundary layer thickness [22].

In an earlier study, a rotating disc electrode (RDE) was used to collect the information needed to quantify $j_{o,+}$, $\alpha_{c,+}$, $j_{lim,c,+}$ and $j_{lim,a,+}$. It was found that $j_{o,+}$ values changed markedly between platinum (Pt) and glassy carbon (GC), in addition to changes in bulk aqueous concentrations of CuCl(aq) and CuCl₂(aq) [11]. As such, $j_{o,+}$ can be expressed in terms of kinetic values that depend on the catalyst materials and the bulk concentrations:

$$j_{o,+} = j_o^o (c_{CuCl}^{1-\alpha_{c,+}} c_{CuCl_2}^{\alpha_{c,+}}) \quad (11)$$

where j_o^o is the standard exchange current density, c_{CuCl} is the bulk concentration of CuCl(aq) with units mol cm⁻³ and c_{CuCl_2} is the bulk concentration of CuCl₂(aq) with units mol cm⁻³ [11].

Values for j_o^o and $\alpha_{c,+}$, were obtained previously for polycrystalline GC and Pt surfaces [11]. For Pt, $j_o^o = 12 \text{ A cm}^{-2}$ and $\alpha_{c,+} = 0.55$ [11]. Values for $j_{lim,c,+}$ and $j_{lim,a,+}$ were also obtained previously as a function of known bulk concentration and δ_N values. With this data, the diffusion coefficients could be obtained, as the relations between j_{lim} and $D_{cucl,cucl2}$ can be approximated as [15,22].

$$j_{lim,c,+} = FD_{CuCl_2}C_{CuCl_2}/\delta_N \quad (12)$$

$$j_{lim,a,+} = FD_{CuCl}C_{CuCl}/\delta_N \quad (13)$$

where $D_{CuCl_2} = 4.8 \pm 0.9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is the diffusion coefficient of the active $\text{CuCl}_2(\text{aq})$ species and $D_{CuCl} = 6.8 \pm 0.4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is the diffusion coefficient of the active $\text{CuCl}(\text{aq})$ species. Unlike the diffusion coefficients that can be determined from limiting ionic conductivity data [15], these represent the effective diffusion coefficient coming from the diffusion of multiple active complexes with varying concentrations such as $\text{CuCl}_2^-(\text{aq})$, $\text{CuCl}_3^{2-}(\text{aq})$, $\text{CuCl}_3^-(\text{aq})$ and $\text{CuCl}_4^{2-}(\text{aq})$. Now, j_{lim} values of the positive electrode can be simulated as a function of bulk concentrations and δ_N . Furthermore, j_+ can be quantified as a function of η_+ , ξ_{CuCl} , δ_N , and catalyst material. With the relations outlined in this section, the link between the positive electrode contributions, j_{cell} and E_{cell} can be quantified.

2.3 Negative Electrode

The approach to quantifying the potential contributions of the positive electrode was repeated for the negative electrode with some modifications. The equilibrium potential of the negative electrode was defined by the Nernst equation:

$$E_- = E^o - \frac{RT}{F} \ln \left[\frac{p_{H_2(g)}^{1/2}}{\gamma_{\pm} b_{H^+(aq)}} \right] \quad (14)$$

where $E^o = 0$ V is the standard electrode potential of the hydrogen reaction [23], $\gamma_{\pm} = 5.9$ is the mean activity coefficient of 7 mol L⁻¹ HCl(aq) [24] and $b_{H^+(aq)}$ is the concentration of H⁺(aq) on the molal scale. At 25 °C, E_- was calculated to be 0.099 V. This value with E_+ is equivalent to the open circuit potential, E_{OCP} , by the following relation [15]:

$$E_{OCP} = E_+ - E_- \quad (15)$$

Like the positive electrode, j_- can be related to j_{cell} , if the A_- and A_{cell} are specified. Equation 16 related j_- to j_{cell} :

$$j_{cell} = - (A_-/A_{cell}) j_- \quad (16)$$

where using IUPAC conventions [17], the current density of an electrode polarized in the cathodic direction is negative. Similar to A_+ , A_- can be determined using Equation 9. For the negative electrode, $m_{catalyst}$ was 0.4 mg Pt cm⁻² geo. Again, if j_- can be related to η_- , as in the case of the positive electrode, then the total potential contribution of the negative electrode can be quantified as a function of j_{cell} . It was found that the generalized B-V equation also matched experimental data for the H₂(g) evolution reaction in concentrated HCl(aq) [12]. As such, the j_- , η_- relation can be expressed as follows:

$$j_- = (e^{\frac{\alpha_{a,-}\eta_-F}{RT}} - e^{-\frac{\alpha_{c,-}\eta_-F}{RT}}) / (\frac{1}{j_{0,-}} + \frac{e^{\frac{\alpha_{a,-}\eta_-F}{RT}}}{j_{lim,a,-}} - \frac{e^{-\frac{\alpha_{c,-}\eta_-F}{RT}}}{j_{lim,c,-}}) \quad (17)$$

where $j_{o,-}$ is the exchange current density of the positive electrode half-reaction, $\alpha_{c,-}$ is the transfer coefficient of the cathodic polarization, $\alpha_{a,-}$ is the transfer coefficient of the anodic polarization, $j_{lim,c,-}$ is the limiting current density of a cathodic polarization, $j_{lim,a,-}$ is the limiting current density of the anodic polarization. Previously, it was found that $j_{o,-} = 1.3 \text{ mA cm}^{-2}$, and $\alpha_{a,-} = \alpha_{c,-} = 2$ for polycrystalline Pt in concentrated HCl(aq) saturated with $\text{H}_2(\text{g})$ at 1 bar [12]. Also, the $j_{lim,a,-}$ depended on δ_N but $j_{lim,c,-}$ was independent of δ_N and equal to -0.82 A cm^{-2} [12]. The $j_{lim,a,-}$ obtained via an RDE was used to estimate the values of $j_{lim,a,-}$ for changes in δ_N . When the rotation rate was 1600 RPM, using a $D_{\text{H}_2(\text{aq})}$ as $3.08 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, calculated using OLI Analyzer studio [25], it was found that $\delta_{N,RDE} = 1.98 \cdot 10^{-3} \text{ cm}$ when $j_{lim,RDE} = 1.5 \text{ mA cm}^{-2}$. Additionally, the $D_{\text{H}_2(\text{aq})}$ value obtained from OLI was comparable to an experimental value obtained in concentrated $\text{H}_2\text{SO}_4(\text{aq})$ [26]. As such, a simplified expression for $j_{lim,a,-}$ could be obtained as follows:

$$j_{lim,a,-} = \frac{nFD_{\text{H}_2(\text{aq})}c_{\text{H}_2(\text{aq})}}{\delta_N} = 2.97 \cdot 10^{-6} / \delta_N \quad (18)$$

Now the potential contributions of the negative electrode can be simulated as a function of j_{cell} .

Note that $2.97 \cdot 10^{-6}$ in Equation 18 has units of A cm^{-1} .

2.4 Membrane

As the membrane used here has no equilibrium potential contributions, only non-equilibrium processes were considered. The potential losses from the cell due to R_{ohm} , E_{IR} , was found to be largely due to the membrane [13], obtainable experimentally via Electrochemical Impedance Spectroscopy (EIS). Given the importance of the membrane to this potential loss, linear

irreversible (non-equilibrium) thermodynamics was used to determine E_{IR} , in our conditions of interest when the impact of the concentration gradient of $H^+(aq)$ species across the membrane are considered negligible [27]. Previous works, identified a relationship between $CuCl(aq)/HCl(aq)$ cell performance and linear non-equilibrium transport processes across the membrane [27]. These transport processes governed the energy dissipated due to ohmic resistance of the membrane for a given cell current [27]. The transport model equations can be summarized as follows [27]:

$$J_{Cu} = L_{11}\nabla\mu_{Cu} + L_{12}\nabla\mu_H + L_{13}\nabla\varphi \quad (19)$$

$$J_H = L_{21}\nabla\mu_{Cu} + L_{22}\nabla\mu_H + L_{23}\nabla\varphi \quad (20)$$

$$J_e = L_{31}\nabla\mu_{Cu} + L_{32}\nabla\mu_H + L_{33}\nabla\varphi \quad (21)$$

Where, in linear irreversible thermodynamics, J_i and X_k represent respectively the i -th flux and the k -th driving force, and L_{ik} is the phenomenological coefficient, relating the flux of type i to the force of type k . The fluxes of the membrane considered previously were aqueous copper species, J_{Cu} , protons, J_H , and electric charge from ionic conduction, J_e [27]. Similarly, the driving forces for transport across the membrane were the copper species chemical potential gradient, $\nabla\mu_{Cu}$, the proton chemical potential gradient $\nabla\mu_H$, and the electric potential gradient $\nabla\varphi$. With respect to the current-potential relationship, J_e and $\nabla\varphi$ could be described in terms of E and j by the following expressions, $E = \nabla\varphi l_{mem}/F$ and $j = J_e/F$ [27].

Using the phenomenological equation relating, J_e to $\nabla\phi$ with $\nabla\mu_{Cu} = 66.99 \text{ kJ cm}^{-1} \text{ mol}^{-1}$ and $\nabla\mu_H = 0$, the following relation can be obtained to connect j_{cell} , to E_{IR} [27]:

$$E_{IR} = l_{mem}(j_{cell}/F - L_{31}\nabla\mu_{Cu})/(L_{33} F) \quad (22)$$

where l_{mem} is the membrane thickness at $185 \text{ }\mu\text{m}$, L_{33} is the direct phenomenological coefficient between J_e and $\nabla\phi$, and L_{31} is the cross coefficient between $\nabla\mu_{Cu}$ and J_e [27]. If we assume the transport coefficient of copper species, t_{cu} , does not change significantly from the 0.15 reported previously [27], then L_{31} and L_{33} can be calculated for the electrolyzer with a measured R_{ohm} from a full cell [27].

$$L_{33} = l_{mem} / (F^2 R_{ohm} A_{mem}) \quad (23)$$

$$L_{31} = 0.15 L_{33} \quad (24)$$

where $A_{mem} = 5 \text{ cm}^2$ is the membrane area and $0.15 = t_{cu}$. Using Equations 22-24, E_{IR} contribution to E_{cell} can be readily calculated for different values of j_{cell} and R_{ohm} . Furthermore, the impact of $\nabla\mu_{Cu}$ on E_{IR} can be determined.

2.5 Model Description

The expressions above can be converted into a system of equations relating E_{cell} to the potential contributions, η_+ , E_+ , E_{IR} , η_- , E_- and j_{cell} . A visual summary of the potentials, current densities and model parameters for each of the three sections can be seen in Figure 2.

Figure 2.

For the system of equations, the first key relation is Equation 4 as it relates E_{cell} to its individual contributions. Here Equation 5 is used to determine E_+ with CuCl(aq) and $\text{CuCl}_2(\text{aq})$ as inputs, $E_- = 0.099 \text{ V}$ according to Equation 14, and E_{IR} is found from Equation 22 after values of R_{ohm} and j_{cell} are defined. Next, Equations 8 and 15 are used to relate Equation 10 to Equation 17 in the following manner to obtain η_+ and η_- .

$$j_{\text{cell}} = (A_+/A_{\text{cell}}) (e^{\frac{(1-\alpha_{c,+})\eta_+F}{RT}} - e^{-\frac{\alpha_{c,+}\eta_+F}{RT}}) / (\frac{1}{j_{0,+}} + \frac{e^{\frac{(1-\alpha_{c,+})\eta_+F}{RT}}}{j_{\text{lim},a,+}} - \frac{e^{-\frac{\alpha_{c,+}\eta_+F}{RT}}}{j_{\text{lim},c,+}}) \quad (25)$$

$$j_{\text{cell}} = (A_-/A_{\text{cell}}) (e^{\frac{\alpha_{a,-}\eta_-F}{RT}} - e^{-\frac{\alpha_{c,-}\eta_-F}{RT}}) / (\frac{1}{j_{0,-}} + \frac{e^{\frac{\alpha_{a,-}\eta_-F}{RT}}}{j_{\text{lim},a,-}} - \frac{e^{-\frac{\alpha_{c,-}\eta_-F}{RT}}}{j_{\text{lim},c,-}}) \quad (26)$$

Relations and values for j_{lim} 's, j_0 's and transfer coefficients can be collected from the above sections describing positive and negative electrodes. These equations require δ_N , c_{CuCl} , and c_{CuCl_2} as inputs.

Now that relations between the electrochemical reaction fluxes and forces that require electric potential are defined, simulations of E_{cell} values needed to supply j_{cell} values can be made for a wide range of changes to system parameters. Furthermore, the separation of potential contributions from one another, allow us to rank these contributions in order of significance. In addition to simulations, the equations summarized below can be numerically solved to determine

an adjustable parameter from experimentally measured $E_{\text{cell}}-j_{\text{cell}}$ data using the inverse method.

For example, no values of δ_N are readily available for the full cell but concentrations of $\text{CuCl}_2(\text{aq})$, $\text{CuCl}(\text{aq})$ and R_{ohm} can be measured. Before simulating $E_{\text{cell}}-j_{\text{cell}}$ relations with changes to test parameters, the model's system of equations will be used to determine a value for δ_N (a δ_N that matches all experimental data). After estimating the model parameter δ_N , the model can be used to simulate how changes to select variables alter E_{cell} and the potential contributions needed for a given j_{cell} . These simulations can provide insight into the key factors limiting the performance of the $\text{CuCl}(\text{aq})/\text{HCl}(\text{aq})$ electrolyzer.

3. Experimental

A lab scale electrolyzer with supporting systems developed and described previously was used to collect the polarization data to estimate the model parameter δ_N that match model calculations to the experimental data [9–11,13]. In short, carbon cloth electrodes used within the cell were coated, via airbrush, with a 20 % platinum, Pt, on Vulcan XC-72R in a Catalyst ink consisting of Nafion equivalent weight 1100 solution by a technique described previously [11]. Pt loadings were 4 mg Pt cm^{-2} geo on the cathode (negative electrode) and 1 mg Pt cm^{-2} geo on the anode (positive electrode). Each carbon cloth had a 5 cm^2 geometric surface area. The electrodes were used with hot-pressed Nafion 117 membrane that separated the anolyte and catholyte. Membrane preparation was carried out in a manner consistent with the procedures published previously and the exposed geometric surface area was 5 cm^2 [11]. The catholyte solution contained 7 mol L^{-1} $\text{HCl}(\text{aq})$ under an $\text{H}_2(\text{g})$ blanket at 1 bar. The anolyte solution contained $2 \text{ mol CuCl}(\text{aq})$ and $7 \text{ mol HCl}(\text{aq})$ per one liter of solution. A Gamry 3000 potentiostat was used to conduct the electrochemical measurements. Flow rate of the anolyte and catholyte were 220 ml min^{-1} . Cell

polarization measurements were made with a potential sweep rate of 10 mV s^{-1} . To obtain R_{ohm} , EIS measurements were made in the frequency range of 0.1 Hz to 100 kHz. The applied alternating current root mean square (RMS) perturbation was 5 mV about a constant 0.2 V applied potential. EIS data were collected at 5 points per decade. EIS data were collected from the full electrolytic cell to obtain R_{ohm} , for calculating L_{33} . E_{OCP} of the electrolytic cell during recirculation of the anolyte stream was found to be 0.235 V indicating the average concentration of $\text{c}_{\text{CuCl}_2(\text{aq})}$ was approximately $8 \mu\text{mol L}^{-1}$ and c_{CuCl} was 2 mol L^{-1} [10]. From the EIS data collected, it was found that the R_{ohm} was approximately 0.15Ω , which resulted in an L_{33} equal to $2.65 \cdot 10^{-10} \text{ mol}^2 \text{ m}^{-1} \text{ J}^{-1} \text{ s}^{-1}$ and an L_{31} equal to $0.40 \cdot 10^{-10} \text{ mol}^2 \text{ m}^{-1} \text{ J}^{-1} \text{ s}^{-1}$, which is slightly smaller but consistent with the $3.14 \cdot 10^{-10} \text{ mol}^2 \text{ m}^{-1} \text{ J}^{-1} \text{ s}^{-1}$ and $0.47 \cdot 10^{-10} \text{ mol}^2 \text{ m}^{-1} \text{ J}^{-1} \text{ s}^{-1}$ values previously obtained using a single conductivity cell [27]. Polarization data were collected to numerically determine the average δ_N values that the model was needed to match the experimental results. Polarization data less than 2 mA cm^{-2} were discarded due to fluctuations in the polarization response near E_{OCP} . These instabilities were likely due to small changes in the average $\text{CuCl}_2(\text{aq})$ concentrations, while the anolyte solution was recirculated.

4. Results and Discussion

With L_{33} estimated, 425 experimental polarization data points [10] collected between 0.275 V to 0.7 V were used to estimate the values of the adjustable parameter δ_N needed by the model to follow the experimentally measured behavior. The input parameters are presented in Table 1.

Table 1. Model inputs for numerically determining the adjustable parameter δ_N needed to match experimental $E_{\text{cell}}, j_{\text{cell}}$ data with Equations 4, 25 and 26.

Model Parameter	Value	Units
R_{ohm}	0.15	Ω
c_{CuCl}	0.002	mol cm^{-3}
c_{CuCl_2}	$8 \cdot 10^{-9}$	mol cm^{-3}
E_{OCP}	0.235	V
E_{cell}	See Figure 3	V
j_{cell}	See Figure 3	$\text{A cm}^{-2} \text{ geo}$

Using the experimental points collected, the average δ_N was calculated to be $1 \pm 0.5 \mu\text{m}$. This variation could be due to a number of reasons. The actual δ_N could be slightly different between the positive and negative electrodes, whereas the model treats them as the same. Additionally, with the carbon cloth and serpentine flow channel interface, any real δ_N is not uniform across each electrode surface. Still, when compared to the porous carbon cloth electrode thickness of 0.03 cm, it is reasonable to assume that any δ_N forming is within the carbon cloth.

The focus of this work is to use the system of equations presented in the earlier sections to determine the relative sensitivity of the E_{cell} needed for a given j_{cell} to different variables such as ξ_{CuCl} , electrode surface area and R_{ohm} for the $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolyzer. These analyses will provide insight into what cell design modifications would most impact the electrolyzer performance and ultimately the thermochemical cycle efficiency. For each case study, the system of equations was numerically solved to obtain a predicted E_{cell} for a given j_{cell} when changes were made to the input parameters. All cases were, unless otherwise stated, simulated with the following inputs: (1) starting anode concentrations are $2 \text{ mol L}^{-1} \text{ CuCl(aq)}$ and $8 \mu\text{mol L}^{-1}$ of

CuCl₂(aq), (2) the adjustable parameter $\delta_N = 0.001$ cm, (3) $R_{ohm} = 0.15 \Omega$, (4) $A_{active}/g_{catalyst} = 110$ m² g⁻¹ and (5) $\xi_{CuCl} = 0$. Though the experimental data were fit perfectly, with variations in δ_N values, all further model calculations will be performed assuming δ_N is a constant value. For these baseline conditions, the potential losses can be separated by contributions to better understand the influence of the factors that govern the E_{cell} . Figure 3 presents the baseline case model results.

Figure 3.

The baseline case with a fixed value of δ_N , is on average within 3 % of the experimental values. As seen from Figure 3, the two largest potential contributors are E_{OCP} and E_{IR} . One interesting observation was that despite the anode reaction having a larger j_o than the cathode reaction, the mass transfer limitations of the low CuCl₂(aq) caused η_+ to surpass η_- in magnitude. This phenomena can be readily understood considering the B-V equation results when j_{lim} of the reverse reaction is orders of magnitude smaller than j_o . For a 0.7 V magnitude of E_{cell} , the E_{OCP} contribution is 34 %, the E_{IR} contribution is 39 %, η_+ is 27 % and η_- is the lowest. This ranking of potential contributions when ξ_{CuCl} was low is quite comparable to the findings of an empirical model fitting for a CuCl(aq)/HCl(aq) electrolyzer with similar design [4]. However, our model indicates the primary contributions of η_+ are due to its concentration limitations from CuCl₂(aq) in the form of the $j_{lim,c,+}$, a limitation that should quickly disappear as ξ_{CuCl} increases. When compared to all other contributions, the effects of η_- appear to be minor under these conditions.

4.1 Extent of CuCl(aq) Conversion, ξ_{CuCl}

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4 1 Though most previous full cell studies focus on the starting concentrations, it is important to
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6 2 determine how E_{cell} changes for a given j_{cell} as the bulk $\text{CuCl}(\text{aq})$ is converted to $\text{CuCl}_2(\text{aq})$. E_{cell}
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8 3 simulations for $\xi_{\text{CuCl}} = 0, 0.25, 0.50, 0.75$ and 0.99 is displayed in Figure 4.
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19 7 As expected, the E_{cell} required driving the electrochemical reactions at a given rate increases in
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21 8 magnitude as ξ_{CuCl} increases. The large changes at 0 to 0.25 and 0.75 to 0.99 relative to changes
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23 9 within the 0.25 – 0.75 range can be explained by separating then comparing how the E_{cell}
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25 10 contributions changed with ξ_{CuCl} values. As the relations for η_- and E_{IR} are independent to
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27 11 changes in the $\text{CuCl}(\text{aq})$ and $\text{CuCl}_2(\text{aq})$ concentrations, they were the same for all values of ξ_{CuCl}
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29 12 and were neglected in the comparison. The significant increase in E_{cell} values can be attributed to
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31 13 the increases in the E_{OCP} . While E_{OCP} increased significantly in magnitude, some of these added
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33 14 potential demands were mitigated by the dramatic decrease of η_+ . Figure 5 presents the changes
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35 15 in E_{OCP} and η_+ as ξ_{CuCl} is increased.
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43 17 Figure 5.
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48 19 The trends of E_{OCP} and η_+ to changes in ξ_{CuCl} indicated that for most values, the E_{IR} and E_{OCP}
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50 20 were the two largest contributors to the E_{cell} . Figure 6 presents the contributions to E_{cell} for ξ_{CuCl}
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52 21 $= 0.50$.
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58 23 Figure 6.
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6 2 In the figure, it can be seen that the role of the electrochemical overpotential changes
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9 3 dramatically when ξ_{CuCl} is increased. In other words, the overall impact of E_{OCP} and E_{IR} quickly
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11 4 becomes dominant. In the figure, $|\eta_+|$ is barely visible, indicating no significant contribution.
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16 6 This presents an interesting issue about the impact of available surface area on the significance
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19 7 of the overpotential contributions to E_{cell} when ξ_{CuCl} is sufficiently far from the starting
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21 8 conditions.
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25 26 10 *4.2 Active Surface Area* 27

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29 11 A number of possibilities exist for the $110 \text{ m}^2 \text{ g}^{-1}$ Pt that was used as the baseline case to be
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31 12 changed. Previous studies found dramatic increases in performance, when the utilization of the
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33 13 catalyst was improved [11], albeit this was demonstrated at low ξ_{CuCl} . Decreases in the total
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35 14 available area could occur from inaccessible catalyst caused by common problems such as
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38 15 hydrogen bubbles forming on the surface, catalyst washout, and catalyst isolation during
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41 16 application. For comparison, the contributors to E_{cell} were recalculated assuming the anode and
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43 17 cathode's ratio of active area per gram of platinum was $1 \text{ m}^2 \text{ g}^{-1}$ Pt. Figure 7 presents the impact
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45 18 of active electrode area on the contributions of overpotential to total E_{cell} .
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55 22 As can be seen from Figure 7, the dramatic reduction in the active area, 100x, increased the
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58 23 combined overpotential contribution to a magnitude of about 130 mV from 40 mV, no longer
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negligible but still small relative to the E_{cell} magnitude of 960 mV. A similar response would be expected if the area were held constant but both j_o values were decreased 100x. Likewise, the effects are more pronounced at low ξ_{CuCl} when the anode reaction significantly impacts the total applied potential. This suggests that the role of the electrochemical reactions are minor at most ξ_{CuCl} values, provided no dramatic changes to the area and j_o occur. Furthermore, some flexibility in the catalyst material may be possible to optimize the added savings of not using Pt with small increases in the overall overpotential.

4.3 Impact of R_{ohm}

When considering the non-equilibrium processes, the previous case studies provide strong evidence that membrane transport has the significant influence on the performance of the electrolytic cells. As such, small changes in R_{ohm} , should have significant impacts on the E_{cell} . To demonstrate the impact, simulations were done for a series of R_{ohm} values up to a 10x increase in the magnitude with $R_{\text{ohm}} = 1.5 \Omega$.

Figure 8.

Despite that the changes to R_{ohm} were small relative to the 100x changes in active electrode area, the effect of R_{ohm} was dramatically larger on E_{cell} . Relative to changes in electrode surface area and j_o , small improvements in R_{ohm} would have the most notable impact on the cell's efficiency over the whole range of ξ_{CuCl} . Similarly, as E_{OCP} was the largest contributor in nearly all cases, decreasing the magnitude of E_{OCP} would be ideal but limited in feasibility other than altering the operating temperature or HCl(aq) concentration. Another interesting observation is the general

1 impact of the cross coefficient and concentration gradient of copper species on the E_{IR} . Though
2 copper permeation is not ideal for a wide range of reasons, the presence of the concentration
3 gradient, as seen in Equation 22, actually decreases the value of E_{IR} by a small constant value,
4 regardless of the j_{cell} and R_{ohm} value. For the concentration gradient and transport number used
5 here, the decrease in E_{IR} was only equal to 1.9 mV.

6 7 **5. Conclusions**

8 A model using principles of equilibrium thermodynamics as well as electrochemical kinetics was
9 formulated for the CuCl(aq)/HCl(aq) electrolyzer, which is a key component of the Cu-Cl
10 thermochemical cycle to efficiently produce hydrogen. Equations relating the positive and
11 negative electrode overpotentials to their respective reaction rates were used to represent the
12 impact of electrochemical kinetics on cell performance. Linear relations using phenomenological
13 coefficients were used to describe the impact of the potential losses due to the flux of charged
14 species across the membrane. It was found that the presence of a Cu(aq) gradient decreased E_{IR}
15 by a very small value, 1.9 mV. Gibbs energy minimization was used to estimate the anolyte
16 speciation to correctly determine E_{OCP} . Using these techniques, it was found that the developed
17 model could reliably predict values comparable to data obtained from a CuCl(aq)/HCl(aq)
18 electrolyzer at ambient conditions using only one adjustable model parameter, the Nernst
19 diffusion layer δ_N . Once the value of δ_N from the model was found to be compatible with the
20 current performance of the electrolytic cell, the influence of the experimental parameters on the
21 electrolyzer performance was investigated in detail.

Case studies of hypothetical modifications to key parameters of the electrolytic cell were carried out to determine the order of significance for the potential contributions to E_{cell} at 25 °C. The impact of variations in ξ_{CuCl} , R_{ohm} , and active electrode surface area on E_{cell} needed to obtain a given j_{cell} were quantified. It was found that for nearly all cases investigated, E_{OCP} and E_{IR} were the dominant contributors to E_{cell} . Though the anode kinetics contributed substantially at low extents of conversion, once significant amounts of $\text{CuCl}_2(\text{aq})$ were present, its contribution was dramatically diminished. Given the current state of the electrolytic cell defined here, it appears as though system modifications reducing E_{IR} and/or E_{OCP} could attain a significant improvement to the cycle's efficiency across a large range of ξ_{CuCl} . This can probably be done by increasing temperature assuming that the temperature effect on materials degradation can be mitigated.

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8. Figures

Figure 1. Electrochemical diagram of the CuCl(aq)/HCl(aq) electrolyzer.

Figure 2. Visual representation of the model for the positive electrode, negative electrode and membrane.

Figure 3. Experimental (grey squares) and $|E|$ contributions for the baseline case for a series j_{cell} values: (solid line = E_{cell} , dashed line = $-\eta_-$, dotted line = η_+ , dashed and dotted line = $-E_{\text{OCP}}$, small dashes line = $-E_{\text{IR}}$).

Figure 4. Simulated E_{cell} values for the baseline case with different ζ_{CuCl} and j_{cell} values: (solid line = 0, dotted line = 0.25, dashed line = 0.50, dashed with dots line = 0.75, small dashes line = 0.99).

Figure 5. Predicted E_{OCP} (Left) and η_+ vs. j_{cell} as ξ_{CuCl} is increased: (solid line = 0, dotted line = 0.25, dashed line = 0.5) (Right).

Figure 6. Simulated E_{cell} contributions at a given j_{cell} for $\xi_{\text{CuCl}} = 0.5$: (solid line = $|E_{\text{cell}}|$, dotted line = $|E_{\text{OCP}}|$, dashed with dots line = $|E_{\text{IR}}|$, dashed line = $|\eta_-|$, small dashes = $|\eta_+|$).

Figure 7. Simulated E_{cell} contributions at a given j_{cell} for $\zeta_{\text{CuCl}}=0.5$ when $A_{\text{active}}/m_{\text{catalyst}} = 1 \text{ m}^2 \text{ g}^{-1}$: (solid line = $|E_{\text{cell}}|$, dotted line = $|E_{\text{OCP}}|$, dashed with dots line = $|E_{\text{IR}}|$, dashed line = $|\eta_-|$, small dashes = $|\eta_+|$).

Figure 8. Simulated E_{cell} for a series j_{cell} and R_{ohm} values at $\zeta_{\text{CuCl}}=0.5$. (dashed with dots line = $1.5 \text{ } \Omega$, dashed line = $0.75 \text{ } \Omega$, dotted line = $0.3 \text{ } \Omega$, solid line = baseline case, $0.15 \text{ } \Omega$)