Thermodynamics and Efficiency of a CuCl(aq)/HCl(aq) Electrolyzer

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Abstract

The high ionic strength and complex speciation of the anolyte solution within the CuCl(aq)/HCl(aq) electrolytic cell have impeded predictions of the energy requirements for the cell's electrolytic reaction at 25 °C and 1 bar. After collecting experimental open circuit potential (OCP) data and comparing the values obtained with predictions from prospective thermodynamic models, an approach to predict thermodynamic values and the overall efficiency was formulated. The compositions of the experimental measurements ranged from 2-2.5 mol of CuCl(aq) with 8-9 mol of HCl(aq) per kilogram of water in anolyte solution and 8-9 mol of HCl(aq) per kilogram of water in catholyte solution. From the OCP data, it was found that

activity coefficient and speciation effects were critical in predicting the Gibbs energy, entropy and thermodynamic (intrinsic maximum) efficiency of the electrolytic cell. At equilibrium, all thermodynamic functions of the anolyte redox reactions were the same after activity coefficients and speciation effects were taken into account. The electrochemical reactions' Gibbs energy and entropy were found to be 9700 J/mol and 2.18 J/(mol K) at 25 °C and 1 bar, which indicated that the reactions required a small amount of electrical and thermal energy to proceed. With thermodynamic values for the electrolytic reaction and experimental data from a CuCl(aq)/HCl(aq) electrolytic cell, the voltage, current, thermodynamic and overall efficiency were calculated. The overall efficiency ranged from 15 to 95 % depending on the current density.

Keywords

Copper-chlorine (Cu-Cl) hybrid thermochemical cycle; CuCl(aq)/HCl(aq) electrolytic cell; decomposition potential; voltage, current, thermodynamic and overall efficiencies

1. Introduction

Growing concerns about the consequences of powering economies primarily from fossil fuels has spurred international interest in developing infrastructures able to support an inexpensive energy carrier to supplement fossil fuels. One of the energy carriers most researched is hydrogen gas. Considerable investments have already been made in developing hydrogen infrastructure technologies for storage, transportation and consumption. However, one of the major challenges to using hydrogen gas as an energy carrier is the lack of cost effective hydrogen production technologies powered with renewable resources. Of the technologies proposed to solve this

dilemma, the copper-chlorine (Cu-Cl) hybrid thermochemical cycle has been one of the most promising [1] among cycles studied in the U.S. and Canada.

The U.S. Nuclear Hydrogen Initiative identified seven hydrogen-producing thermochemical cycles for development on the basis of abundance of materials, simplicity, chemical viability, thermodynamic feasibility, control and safety [2–5]. More recently, the Hydrogen and Fuel Cell Program of the U.S. Department of Energy narrowed this list further to five thermochemical cycles. Of the cycles selected, two were two-step cycles (metal oxide and nanostructured hercynite) and three others were hybrid cycles (Cu-Cl, sulfur, and sulfur ammonia) [1]. Among the cycles examined, the Cu-Cl hybrid cycle holds a distinct advantage as it requires a maximum temperature less than 600 °C [6–8]. Given the cycle's inherent advantages, many studies have investigated possible designs of the Cu-Cl cycle with favorable efficiencies [9–11]. As such, successful development of the Cu-Cl cycle has the potential to bolster hydrogen production development.

Determining the theoretical efficiency for each of the cycle's components is a key milestone in assessing the practicality of the Cu-Cl hybrid cycle. Previous studies have undertaken aspects this task by performing energy and exergy analyses with standard thermodynamic properties, as one can do for a water electrolyzer, for a range of components including the electrolytic cell [9,10,12]. However, for cycle components with aqueous chemicals, such as the CuCl(aq)/HCl(aq) electrolytic cell, these standard thermodynamic values represent conditions when the concentrations of all species are 1 mol/kg with properties of an infinitely dilute solution, which is a hypothetical state that does not exist in reality. While for some electrochemical systems, such as a water electrolyzer or hydrogen/oxygen fuel cell, the use of standard thermodynamic properties is a suitable approach. However, for the CuCl(aq)/HCl(aq)

electrolyzer, this is not the case. In the CuCl(aq)/HCl(aq) electrolytic cell, large deviations occur from the standard thermodynamic values due to (1) significant intermolecular interactions between aqueous species, (2) the association of forming complexes and (3) concentrations greater or less than 1 mol/kg. These factors considerably alter the thermodynamics of all the electrochemical reactions vs. the standard state thermodynamics in both the electrolyzer anolyte and catholyte. As such, one of the major obstacles stymieing the development process of the CuCl(aq)/HCl(aq) electrolytic cell is insufficient experimental and theoretical studies of these effects on reaction thermodynamics and, therefore, efficiency of an electrolytic cell. One of the goals in this work is to thermodynamically analyze the CuCl(aq)/HCl(aq) electrolytic cell at 25 °C and 1 bar then confirm this analysis by a number of electrochemical measurements.

Previous experimental studies on the CuCl(aq)/HCl(aq) electrolytic cell have established common cell designs and operating conditions [2–5,8,13–17]. These electrolytic cells employed a proton conductive polymer electrolyte to separate the anolyte from catholyte solution. A general diagram for the CuCl(aq)/HCl(aq) cell is presented in Figure 1. In the previous studies the anolyte solutions contained CuCl(aq) species in a concentrated HCl(aq) solution, while catholyte solutions have varied between pure water and concentrated HCl(aq) solutions. The reported molar concentrations of CuCl(aq) within the anolyte have ranged from 0.1 to 2 mol/L depending on HCl(aq) concentration due to limited solubility of CuCl(s) in HCl(aq) . HCl(aq) concentrations within the anolyte and catholyte have varied from 1 to 14 mol/kg. Of the cell's two electrodes, the largest source of uncertainty in the reaction(s) thermodynamics was at the anode due to the complexity of CuCl(aq) and $\text{CuCl}_2\text{(aq)}$ speciation in high ionic strength conditions. Note that “speciation” in this work refers to the chemical forms (ions, complexes, ion pairs, and solid phases) in which an element can occur as well as to the quantitative distribution

of chemical forms. Therefore, this study collected experimental data of the anode equilibrium potential to provide insight into the effect of activity coefficients and speciation of the anolyte on the electrolytic cell's thermodynamic characteristics, including Gibbs energy, enthalpy and entropy of the cell's reactions. Theoretical predictions of the thermodynamic characteristics and the anode equilibrium potential were correctly calculated for the first time and compared to the experimentally obtained data to determine the accuracy of the predictions. Once a theoretical model was verified with experimental data, the electrolytic cell's solution speciation, enthalpy, entropy, decomposition potential (Gibbs energy) and thermodynamic efficiency were quantified. Furthermore, a laboratory scale electrolyzer system was used to determine values of the current and voltage efficiency with standard cell components. Values for each of the three efficiencies enabled estimations of the overall efficiency of the $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolytic cell for the first time.

2. Thermodynamic Model of the Electrolytic Cell

2.1 Standard Thermodynamic Properties

In order to conduct a thermodynamic analysis of the anolyte solution, standard thermodynamic properties of all possible species in all phases are needed. The solids considered for possible precipitation were the copper containing Cu(s) , CuO(s) , $\text{Cu}_2\text{O(s)}$ and CuCl(s) . Thermodynamic properties of CuCl(s) (nantokite) were adopted from Ref. [18] and [19]. Heat capacity equations for the remaining copper containing solids Cu(s) , CuO(s) , $\text{Cu}_2\text{O(s)}$, were obtainable from Ref. [20]. Thermochemical properties of the solids considered are tabulated in Appendix Table A.1. For the aqueous phase, the Helgeson-Kirkham-Flowers (HKF) model [21,22] was used to

calculate the standard partial molal properties of ions and neutral species. Here, CuCl(aq) refers to the sum of Cu(I) species in solution, whereas $\text{CuCl}^0(\text{aq})$ refers to a neutral species containing a Cu^+ cation and a Cl^- anion. This convention is used throughout the text for all aqueous species. The standard partial molal thermodynamic properties of $\text{Cu}^+(\text{aq})$ and its hydroxides $\text{CuOH}^0(\text{aq})$, $\text{Cu(OH)}_2^-(\text{aq})$, used in the solution equilibrium calculations were from Ref. [23]. For copper(II) chloride complexes [$\text{CuCl}^+(\text{aq})$, $\text{CuCl}_2^0(\text{aq})$, $\text{CuCl}_3^-(\text{aq})$, $\text{CuCl}_4^{2-}(\text{aq})$] as well as copper(II) oxide and hydroxides, the standard thermodynamic property values were taken from the SUPCRT92 database [24–27].

With respect to CuCl(aq) speciation, three competing models were considered from the papers of Balashov et al., (2011) [8], Brugger et al., (2007) [28] and Sverjensky et al., (1997) [27]. For the sake of brevity, references to the Balashov et al., (2011), Brugger et al., (2007) and Sverjensky et al., (1997) CuCl(aq) speciation model values will be referred to as Speciation 1, 2 and 3, respectively. The standard partial molal properties and HKF parameters for aqueous species used in all Gibbs energy minimization calculations are given in Table A.2 of the Appendix. Table A.3 provides the thermodynamic properties for CuCl(aq) species for Speciation 1, 2 and 3. The HKF equations used to calculate the standard thermodynamic properties are readily available in previous publications [21,22,25]. With this collection of the standard thermodynamic properties, calculations predicting anolyte speciation over a wide range of operating temperatures and pressures are possible. However, in this paper we will focus on thermodynamic calculations and experimental measurements at temperature of 25 °C and pressure of 1 bar.

2.2 Activity Coefficients

The high ionic strength of solutions used within CuCl(aq)/HCl(aq) electrolytic cell indicated that activity coefficients must be considered for reliable thermodynamic calculations. Due to the complex nature of aqueous non-ideality at high ionic strengths, the first approximation of the activity coefficients for aqueous species were estimated from mean activity coefficients of HCl(aq), $\gamma_{\pm}$, taken from experimental measurements at the ionic strengths of the anolyte and catholyte. From previously determined $\gamma_{\pm}$ values of concentrated HCl(aq) solutions [29], the empirical parameter within the third approximation of the Debye-Hückel equation can be used to approximate the activity coefficients of individual ions within the anolyte and catholyte. Table A.4 in the Appendix is a collection of the experimentally obtained mean activity coefficients for the range of the ionic strengths and three temperatures around 25 °C.

In this study, the mean activity coefficient values at temperatures between 20-30 °C are approximated by the third approximation of Debye-Hückel as proposed in Ref. [26]:

$$\log_{10}\gamma_{\pm} = -\frac{A_{DH}|z_c z_a| \sqrt{I_m}}{1 + \dot{a} B_{DH} \sqrt{I_m}} + b_{\gamma} I_m - \log_{10} \left(1 + \frac{b_t}{55.51} \right) \quad (1)$$

Here 55.51 is the number of mole of water in one kilogram of water; z_a and z_c are charges for the anion and cation; A_{DH} and B_{DH} stand for temperature and pressure dependent Debye-Hückel solvent parameters [30], $\dot{a}$ denotes the average ionic radius ($\dot{a} = 4.5 \text{ \AA}$ is accepted), and I_m is the stoichiometric ionic strength of the solution on the molal concentration scale. The third term in the right-hand side of the equation designates the mole fraction to molality conversion factor,

where $b_t = \sum b_i$ refers to the sum of molalities for all of the solute species. The ionic strength on the molal scale is calculated as follows:

$$I_m = 0.5 \sum z_i^2 b_i \quad (2)$$

where z_i and b_i represent the charge and molality of the i -th ion, respectively. The b_γ is an empirical extended-term parameter for the “supporting” electrolyte, where generally b_γ is a function of temperature and pressure. The b_γ term can be used to approximate the activity coefficient values of ions in Gibbs energy minimization calculations. As HCl(aq) is the dominating electrolyte in both the anolyte and catholyte, experimental data of $\gamma_\pm$ for HCl(aq) solutions can be used to estimate b_γ as shown in Table A.4. The activity coefficient of neutral species γ_n ($z_n = 0$) can be determined using the Setchenow equation for the molal scale in the same manner as previously used [21]:

$$\log_{10}(\gamma_n) = I_m b_n - \log_{10} \left(1 + \frac{b_t}{55.51} \right) \quad (3)$$

where b_n stands for the Setchenow coefficient of a neutral species in an electrolyte which is generally a function of temperature, pressure, and the identity of the dominating electrolyte. The Setchenow coefficient for HCl⁰(aq) is adopted from findings in previous investigations [31] and resulted in a constant value of $b_n = 0.21$ for the temperature of 20 – 30 °C [8]. Both b_n and b_γ were empirical parameters used to approximate the ionic and neutral species activity coefficients

when determining the speciation and Gibbs energy of reactions for the CuCl(aq)/HCl(aq) electrolytic cell.

2.3 Gibbs Energy Minimization and Speciation Calculations

Phase equilibrium calculations were performed using the Gibbs energy minimization approach.

The Gibbs energy minimization has become an increasingly popular method for calculating equilibrium conditions in complex multicomponent and multiphase systems [32–35]. Briefly, the Gibbs energy function, G , for a multiphase/multicomponent system can be described by a sum of the chemical potentials as follows:

$$G = \sum_p \sum_k \mu_k^p n_k^p \quad (4)$$

where μ_k^a is the chemical potential of a species (k) in phase (p) with a molar amount of n_k^p [36].

By definition, the chemical potential is a function of temperature, pressure and species activity.

Thermodynamic equilibrium for a given system occurs where the Gibbs energy function reaches a global minimum at the calculated species concentration for a given temperature and pressure [37]. In the Gibbs energy minimization calculations with mass and charge constraints, the Lagrangian method can be used to find the global minimum and therefore thermodynamic equilibrium [36]. Each mass constraint can be represented as follows:

$$\Phi_j = b_j - \sum_{p=1}^{\psi} \sum_{k=1}^N v_{kj}^p n_k^p \quad (5)$$

where b_j is the total input amount of the j -th element, ψ is the number of phases, N is the number of species within p -th phase and v_{kj}^p is the stoichiometric number of j -th element in k -th species [36]. For systems involving electrolytes, electrical neutrality of the solution is another constraint to be met by the equilibrium composition. The electrical neutrality constraint is met when the net charge of the solution in the system is zero. Combining the Gibbs energy function along with the necessary constraints results in a Lagrangian function, L :

$$L = G - \sum_{j=1}^l \lambda_j \phi_j \quad (6)$$

where λ_j are the Lagrangian factors and Φ_j are the constraints [36]. The Gibbs energy minimum can be obtained by identifying the extreme points of the Lagrangian function using the partial derivatives of the Lagrangian function with respect to species concentrations and phases [36]. The constraints together with the partial derivatives result in a series of equations and unknowns to be solved. This approach supplies quantities for species concentrations and phases when the system is at equilibrium. As usual, the Gibbs energies of formation for all species are used instead of the unknown chemical potentials without changing position of the global minimum with respect to the phase and component composition of the system.

Several different programs exist for performing Gibbs energy minimization calculations using the Gibbs energies of formation of all potentially existing species. This study employed the program HCh [38], developed by Y. Shvarov for multicomponent/multiphase systems including a multicomponent aqueous phase. In this work, the Gibbs energy minimization approach was used to determine the concentrations and phases thermodynamically stable in the anolyte

solution for three different sets of standard thermodynamic properties (Speciation 1, 2 and 3) for CuCl(aq) and CuCl₂(aq) complexes at their different concentration ratios.

With values for the concentrations of species obtained in the anolyte using Gibbs energy minimization, equilibrium electrode potential can be calculated for any redox half-reaction involving CuCl(aq) and CuCl₂(aq) species using the Nernst equation

$$E_{eq} = -\frac{\Delta_r G}{n_e F} = -\frac{\Delta_r G^o}{n_e F} + \frac{RT}{n_e F} \ln \left(\frac{\prod (b_i^{v_i} \gamma_i^{v_i})_R}{\prod (b_i^{v_i} \gamma_i^{v_i})_P} \right) \quad (7)$$

which requires activity coefficients, concentrations and standard Gibbs energy of reaction. In Eq. (7), E_{eq} is the equilibrium potential of an electrode of interest versus the standard hydrogen electrode (SHE) half-reaction, $\Delta_r G^o$ is the standard Gibbs energy of the half-reaction, n_e is the electron number in the half-reaction, F is Faraday's constant of 96485 C/mol, R the molar gas constant of 8.3145 J/(mol K), T is the thermodynamic temperature in K, b_i is the molality of the i -th species, v_i is the stoichiometric coefficient of the i -th species, γ_i is the ionic activity coefficient of the i -th species, $\prod (b_i^{v_i} \gamma_i^{v_i})_R$ is the product of the reactant activities and $\prod (b_i^{v_i} \gamma_i^{v_i})_P$ is the mathematical product of chemical product activities taking into account the stoichiometric coefficient v_i . Values of the standard Gibbs energy of formation were obtained from the HKF model values provided in literature [8,27,28]. For all ionic activity coefficients, the third approximation of Debye-Hückel equation was used with the empirical parameter b_γ and b_n calculated using the corresponding literature data for the mean activity coefficients of HCl(aq) as already described. At equilibrium, the anolyte and catholyte redox solution potentials were the same as the potentials calculated for specific half reactions via the Nernst equation.

3 Experimental Systems

An experimental approach was developed to enable equilibrium potential measurements in the anolyte solution with known concentrations of CuCl(aq) and $\text{CuCl}_2\text{(aq)}$. Potential measurements of the anode versus a reference electrode were conducted in a multi-port glass electrochemical cell made by Pine Instruments. Concentrations for all tests were prepared in such a way that a $\text{CuCl}_2\text{(aq)}$ solution consisted of X mol of $\text{CuCl}_2\text{(aq)}$ mixed with Y mol of HCl(aq) for a kilogram of water in a solution. References to this type of solution preparation will be labelled as X mol of $\text{CuCl}_2\text{(aq)}$ in Y mol/kg HCl(aq) . $\text{CuCl}_2\text{(aq)}$ containing solutions were prepared using 97 % pure copper (II) chloride powder from Sigma Aldrich. The powder was mixed with 37 % mass basis hydrochloric acid from Sigma Aldrich and deionized water from a Millipore water purification system. All CuCl(aq) was prepared by converting $\text{CuCl}_2\text{(aq)}$ to CuCl(aq) using 0.8 – 2 mm solid copper shot with a purity of 99.5 % (metals basis) from Alfa Aesar in a de-aerated environment. The general method of converting $\text{CuCl}_2\text{(aq)}$ to CuCl(aq) was described in more details previously [16]. For the glass cell, a freshly prepared 2 mol of CuCl(aq) in 8 mol/kg HCl(aq) solution was injected into the glass cell pre-flushed with an argon gas atmosphere. The total mass of the solution was weighed enabling calculation of the CuCl(aq) and HCl(aq) concentrations. Once weighed, a glass bubbler, a Cole Parmer Ag(s)/AgCl(s) reference electrode with 4.57 mol/kg (4 mol/L) KCl(aq) and a platinum electrode were all added to the cell ports. The cell assembly described is shown in Figure 2.

A Gamry reference 3000 was used to make the OCP measurements between the platinum wire and reference electrode. The glass bubbler was used to ensure the solution was constantly blanketed with argon gas and avoid conversion of CuCl(aq) to $\text{CuCl}_2\text{(aq)}$ in presence of $\text{O}_2\text{(g)}$

which could be dissolved into the test solution. The solution was at ambient conditions at temperature of 25 ± 0.3 °C and pressure of 1.00 ± 0.02 bar. After each OCP measurement, $\text{CuCl}_2(\text{aq})$ was added to the test solution via small injections of solution containing 1 mol of $\text{CuCl}_2(\text{aq})$ in 8 mol/kg $\text{HCl}(\text{aq})$. The mass of the $\text{CuCl}_2(\text{aq})$ containing solution injected was determined by measuring the syringe before and after each injection. A ScienceTek scale with precision to ± 0.0001 g was used.

The anode equilibrium potentials were measured for five different ratios of $\text{CuCl}(\text{aq})$ to $\text{CuCl}_2(\text{aq})$. The redox reaction of $\text{CuCl}(\text{aq})$ to $\text{CuCl}_2(\text{aq})$ was previously reported to be very fast and reversible at low concentrations of $\text{Cl}^-(\text{aq})$ on glassy carbon [39]. With known mass fractions for the each chemical [$\text{H}_2\text{O}(\text{l})$, $\text{HCl}(\text{aq})$, $\text{CuCl}(\text{aq})$ and $\text{CuCl}_2(\text{aq})$], the molality of $\text{CuCl}(\text{aq})$ [sum of the molalities for all $\text{Cu}(\text{I})(\text{aq})$ species] and $\text{CuCl}_2(\text{aq})$ [sum of the molalities for all $\text{Cu}(\text{II})(\text{aq})$ species] are calculable for each test solution after an injection. The resulting concentrations were used to compare the experimental OCPs with theoretically predicted values for the same molal concentrations of $\text{CuCl}(\text{aq})$ and $\text{CuCl}_2(\text{aq})$.

The second experimental system used was a lab scale $\text{CuCl}(\text{aq})/\text{HCl}(\text{aq})$ electrolytic cell described previously [14,15,17]. This system was used to provide the current-potential relationship and $\text{H}_2(\text{g})$ production measurements needed to calculate the current and voltage efficiency of the $\text{CuCl}(\text{aq})/\text{HCl}(\text{aq})$ electrolytic cell. The anolyte solution was prepared by dissolving 1.25 mol of $\text{CuCl}_2(\text{s})$ into 8.71 mol/kg $\text{HCl}(\text{aq})$. Anolyte was then circulated through a glass column packed with copper shot and glass beads to regenerate $\text{CuCl}_2(\text{aq})$ species to $\text{CuCl}(\text{aq})$ species, forming a highly reduced environment. Conversion of $\text{CuCl}_2(\text{aq})$ to $\text{CuCl}(\text{aq})$ could be identified visually by the color of the anolyte switching dramatically from a dark green to a very transparent solution with a yellow tinge. The resulting solution was fed directly into the

electrolytic cell. The catholyte solution was 7.75 mol/kg HCl(aq) blanketed with 1 bar of H₂(g). The anolyte and catholyte flow rates were 220 mL/min. A schematic of the system used for testing the CuCl(aq)/HCl(aq) electrolytic cell is presented in Figure 3.

The system presented in Figure 3 was used to determine the voltage and current efficiencies of a CuCl(aq)/HCl(aq) electrolytic cell. Component numbers 8 through 11 represent the section of the system that purifies the gas stream from the cathode then measures the hydrogen gas production rate. For a constant current density of 0.3 A/cm², steady state hydrogen production was measured for 30 minutes to compare with the theoretical output of H₂(g) from the constant current density. The value of 0.3 A/cm² was used because it was a DOE design target, as indicated in a previous study [17]. To determine the current-potential relationship for a series of potentials, linear sweep voltammetry (LSV) was conducted with a Gamry 3000 potentiostat. The resulting polarization curve obtained from LSV was used to calculate the voltage efficiency of the electrolyzer. Additional descriptions of system operation and design are provided in detail within previous publications [8,14,16,17].

4. Results and Discussion

4.1 Anolyte Redox Potentials and the Effect of Anolyte Speciation

The anode redox potential data collected comprised of an experimental cell potential at OCP ($E_{cell(OCP)}$) paired with a concentration ratio of CuCl(aq) to CuCl₂(aq), as described in section 3. Solutions 1 through 5 were prepared in the manner described for the glass electrochemical cell within the experimental section. The major difference between each solution was the amount of injected mass of 1 mol CuCl₂(aq) with 8 mol/kg HCl(aq). $E_{cell(OCP)}$ was observed via OCP measurements between the CuCl(aq)/CuCl₂(aq) redox electrode versus a Ag(s)/AgCl(s)

reference electrode in a 4.57 mol/kg KCl(aq) solution. The concentrations for each OCP measured are presented in Table 1. The standard deviation of the average $E_{\text{cell(OCP)}}$ value measured is the random error associated with each measurement in Table 1.

Table 1. Composition of CuCl(aq)/CuCl₂(aq) solutions used in redox equilibrium potential, $E_{\text{cell(OCP)}}$, measurements at 25±0.3 °C and 1.00±0.02 bar.

	Solutions used in OCP measurements				
	1	2	3	4	5
total mass / g	111.9398	112.5899	113.2364	114.4063	115.6927
mass added / g	0.6398	0.6501	0.6465	1.1699	1.2864
HCl(aq) / g	21.9234	22.0564	22.1886	22.4279	22.6910
CuCl(s) / g	14.7934	14.7934	14.7934	14.7934	14.7934
CuCl ₂ (s) / g	0.0603	0.1216	0.1826	0.2928	0.4141
H ₂ O(l) / g	75.1627	75.6185	76.0718	76.8922	77.7942
HCl(aq) / (mol/kg)	8.00	8.00	8.00	8.00	8.00
CuCl(aq) / (mol/kg)	1.99	1.98	1.96	1.94	1.92
CuCl ₂ (aq) / (mmol/kg)	6.0	12.0	18.0	28.0	40.0
$E_{\text{cell(OCP)}} / \text{mV}$	234±0.1	251±0.1	261±0.05	274±0.05	282±0.1

The OCP data collected are displayed in Figure 4. The linear relationship between the $E_{\text{cell(OCP)}}$ and the logarithm of CuCl₂(aq) concentration demonstrates good consistency between the data points collected.

The contribution from the anode to the CuCl(aq)/HCl(aq) electrolytic cell's decomposition potential (E_{DP}) is equal in magnitude but opposite in sign to $E_{\text{cell(OCP)}}$. This equilibrium potential can be determined from experimental OCP measurements of the anode

versus a reference electrode with a known potential of the reference electrode versus the SHE.

Using this approach, experimental OCP values for the anode versus the reference electrode in the multi-port electrochemical cell were compared with theoretical predictions of the potential using the Nernst equation discussed in Section 2.3. As the tests employed a liquid junction between the test and reference electrode solutions, a diffusion potential (E_{diff}) correction is needed for accurate comparisons. Previous works have successfully used the Henderson equation to account for E_{diff} [40]. The Henderson equation was used to estimate the E_{diff} resulting from contact between 8 mol/kg HCl(aq) test solution and 4.57 mol/kg KCl(aq) reference electrode. The Henderson equation is as follows [40]:

$$E_{diff} = -\frac{RT}{F} \left[\frac{\sum \frac{|a_{i(II)} - a_{i(I)}| \lambda_i |z_i|}{z_i}}{\sum |a_{i(II)} - a_{i(I)}| \lambda_i |z_i|} \right] \ln \left\{ \frac{\sum a_{i(II)} \lambda_i |z_i|}{\sum a_{i(I)} \lambda_i |z_i|} \right\} \quad (8)$$

where E_{diff} is the diffusion potential between solution I and solution II, $a_{i(II)}$ is the activity of the i -th ionic species in solution II, $a_{i(I)}$ is the activity of the i -th species in solution I, z_i is the charge of the i -th ionic species and λ_i is the molar ionic conductivity of the i -th ionic species. In this cell setup, solution I was the 4.57 mol/kg KCl(aq) and solution II was 8 mol/kg HCl(aq) at an ionic strength of 10. The activities for the ions considered in solutions I and II were taken to equal 2.62 and 92.79, respectively. The molar conductivities for KCl(aq) at 4.57 mol/kg and HCl(aq) at 8 mol/kg were taken from Ref. data as 92.70 S cm²/mol [41] and 134.04 S cm²/mol [42], respectively. The relationship between ionic conductivities (λ_+ , λ_-) and molar conductivity (Λ) are as follows;

$$\lambda_+ = \frac{t_+ \Lambda}{v_+} \quad (9)$$

$$\lambda_- = \frac{t_- \Lambda}{v_-} \quad (10)$$

where t_- and t_+ are the transport numbers for the cation and anion, respectively. For the E_{diff} calculations, the transport numbers for KCl(aq) and HCl(aq) at infinite dilution were used to estimate the ionic conductivities, a common assumption, due to a relatively small concentration dependence of the transport numbers in these solutions [43]. From Ref. [43], the transport number for $H^+(aq)$ in HCl(aq) was 0.8209. From Ref. [43], the transport number for $K^+(aq)$ in KCl(aq) was 0.4905. Using Eqs. (9) and (10), the resulting ionic conductivity values used to estimate the E_{diff} within the Henderson equation for KCl(aq) were 45.47 S cm²/mol and 47.25 S cm²/mol for the cation and anion, respectively. For HCl(aq), the molar ionic conductivity values were 109.98 S cm²/mol and 24.00 S cm²/mol for the cation and anion, respectively. At 25 °C, the calculated E_{diff} was -66 mV. Additional sources of uncertainty from the E_{diff} calculation, not readily quantifiable, are deviations in the transport numbers, activity coefficients and contributions from the copper containing complexes. Even with these additional uncertainties, the first approximation of a E_{diff} as -66 mV is more preferable than ignoring E_{diff} entirely.

Determining the anode potential (E_{anode}) vs. the SHE from the measured $E_{cell(OCP)}$ required adjusting for the reference electrode potential (E_{ref}) vs. the SHE and the E_{diff} previously discussed. For the reference electrode, the electrochemical couple was the Ag(s)/AgCl(s) with a standard electrode potential of 0.2223 V [44] and the $Cl^-(aq)$ activity was the same value used in the Henderson equation for the KCl(aq) solution ions, 2.62. The resulting potential for the Ag(s)/AgCl(s) reference electrode versus the SHE was 198±3 mV. The accuracy of the E_{ref} vs.

the SHE was limited to 3 mV, which was the potential difference measured between two Ag(s)/AgCl(s) reference electrodes in the same reference solution, prior to being applied in the experimental system. Calculating the E_{anode} versus the SHE, E_{anode} can be determined by the following equation:

$$E_{anode} = E_{cell(OCP)} + E_{ref} - E_{diff} \quad (11)$$

where E_{ref} is the Ag(s)/AgCl(s) reference electrode potential versus the SHE and E_{diff} is the diffusion potential calculated using the Henderson equation. Using Eq. (8), the experimental $E_{cell(OCP)}$ values were used to determine E_{anode} for each ratio of CuCl(aq)/CuCl₂(aq). The estimated E_{anode} are given in Table 2.

Theoretical predictions of E_{anode} vs. the SHE were made for the three different variations of CuCl(aq) speciation discussed in Section 2.1 using the available HKF model parameters and empirical activity coefficient parameters as described in Section 2.2. The resulting theoretical E_{anode} vs. the SHE were compared with the experimentally determined E_{anode} vs. the SHE. Table 2 is a summary of the theoretical E_{anode} values predicted for the different ratios of CuCl(aq)/CuCl₂(aq) for the three CuCl(aq) Speciation sets.

Table 2. Comparison of experimental and theoretical values for the anodic equilibrium potential

Anodic potential / mV	Solutions used in measurements (see Table 1)				
Experimental E_{anode}	498±3.1	515±3.1	525±3.05	538±3.05	546±3.1
Predicted E_{anode}^1	407	425	436	448	457
Predicted E_{anode}^2	452	471	481	493	502
Predicted E_{anode}^3	508	526	535	548	557
¹ Speciation 1, ² Speciation 2, ³ Speciation 3					

From the results shown in Table 2, all the models predicted the magnitude of E_{anode} within 90 mV. Another observation is that all speciation models predicted the change in potential between each test condition with an accuracy of 1 mV. The most defining difference between the speciation models was their accuracy in predicting the correct magnitude of the E_{anode} . Of the three CuCl(aq) Speciation sets, the values from Speciation 3 provided predictions within 12 mV of the experimentally determined anode potential as a function of CuCl(aq) and CuCl₂(aq) concentrations, which was quite close considering the uncertainties associated with high ionic strength solutions.

When compared to the 40 mV deviation of Speciation 2 predictions and the 90 mV deviation of Speciation 1 predictions, Speciation 3 predictions are considerably more accurate with respect to equilibrium potential predictions for the anolyte. However, as demonstrated in the Balashov et al. (2011) paper, the solubility predictions from Speciation 3 and Speciation 2 deviate considerably from the existing experimental solubility data. This disagreement between models and experimental data indicates that additional studies are still needed to further refine the thermodynamic properties of the CuCl(aq) and CuCl₂(aq) species. In this work, we will use the Speciation 3 model as most suitable for analysing the CuCl(aq)/HCl(aq) electrolytic cell. Nevertheless, the experimental redox potential data presented in this study provide additional data to further investigate the uncertainty related to the CuCl(aq) and CuCl₂(aq) speciation models and their thermodynamics.

4.2 Speciation of CuCl(aq) Species in the Anolyte

Using the CuCl(aq) Speciation 3 values, a concentration diagram of the CuCl(aq) species in the anolyte were produced for high ionic strengths. This diagram identifies the dominant species in CuCl(aq) solution predicted to exist at equilibrium. Speciation of the anolyte was predicted as a function of HCl(aq) with high concentrations of CuCl(aq) in a highly reduced environment when the extent of reaction is low. Figure 5 presents the CuCl(aq) species concentrations predicted to exist at high concentrations of HCl(aq) when 2 mol/kg of CuCl(aq) is used at 25 °C and 1 bar. As shown in Figure 5, the species $\text{CuCl}_3^{2-}(\text{aq})$ is predicted to be orders of magnitude higher in concentration than all other Cu(I) species. $\text{CuCl}_2^-(\text{aq})$ was the second largest concentration. The concentration of $\text{Cu}^+(\text{aq})$ and $\text{CuCl}_2^-(\text{aq})$ is very small of an order of magnitude, respectively, 10^{-11} and 10^{-8} mol/kg. Considering the high current densities experimentally measured from this cell ($0.2 - 0.5 \text{ A/cm}^2$), the primary electrochemically active bulk species is likely to be $\text{CuCl}_3^{2-}(\text{aq})$. For $\text{CuCl}_2(\text{aq})$ species, $\text{CuCl}_3^-(\text{aq})$ and $\text{CuCl}_4^{2-}(\text{aq})$ were the most prevalent. Given that $\text{CuCl}_3^{2-}(\text{aq})$ is the most likely CuCl(aq) species, the simplest mechanism for a dominant electrochemical reaction that is fast and reversible would indicate $\text{CuCl}_3^-(\text{aq})$ is the dominant $\text{CuCl}_2(\text{aq})$ electrochemically active species of the anode half reaction.

Figure 6 presents the concentrations of $\text{CuCl}_2(\text{aq})$ species predicted when 2 mol of CuCl(s) is dissolved into various concentrations of HCl(aq). Further confirmation of the mechanism can be obtained in future work through comparisons between concentrations predicted from electrochemical kinetic studies and the concentrations predicted here with using thermodynamic calculations.

4.3 Electrochemical Efficiency of the CuCl(aq)/HCl(aq) Electrolytic Cell

4.3.1 Current Efficiency

The current efficiency, otherwise known as faradaic efficiency, is frequently used to assess a contribution of undesired reactions to the total current generated in electrolyzer. In previous research [2], copper deposition at the cathode from copper permeation through the membrane was a significant obstacle. However, recent studies have since demonstrated that the obstacle can be overcome by increasing the concentration of HCl(aq) at the cathode [3,14–16]. When copper deposition is not occurring, the current efficiency measurements of hydrogen production in the electrolytic cell have consistently been greater than 90 %. The current efficiency, ε_c , is calculated as follows:

$$\varepsilon_c = H_2(\text{measured}) / H_2(\text{calculated}) \quad (12)$$

where $H_2(\text{measured})$ is the amount of H_2 gas experimentally produced for a given current density output and $H_2(\text{calculated})$ is the amount of H_2 gas calculated via Faraday's law of electrolysis using the measured current flowing through the cell. The water displacement technique, described previously [8,17], was used to measure H_2 production and verify the high current efficiency reported previously. After the $H_2(g)$ measurement apparatus reached a steady state, hydrogen production was measured for 30 minutes. Figure 6 presents an example of the ε_c data collected each minute for thirty minutes. Overall, these results were consistent with the values previously obtained. For example, Faraday's law predicted 11.95 mL/min of H_2 would be produced and for thirty minutes 11.5 ± 0.5 mL/min of H_2 was measured. The average ε_c

measured was 0.95 with a standard deviation of ± 0.05 mL/min. Therefore, we can conclude that this CuCl(aq)/HCl(aq) electrolytic cell experienced no significant parasitic electrochemical reactions.

4.3.2 Thermodynamic Efficiency

In electrochemical science and engineering, the thermodynamic efficiency describes the transfer of energy in a reversible electrochemical cell. Unlike thermodynamic efficiency for a heat engine, the thermodynamic efficiency for electrochemical cells is not necessarily constrained between 0 and 1 [45]. Investigating the thermodynamic efficiency for a CuCl(aq)/HCl(aq) electrolytic cell highlights some of the peculiarities and a possible misunderstanding that in aqueous solutions the standard thermodynamic state of ions is hypothetical. This hypothetical state is not representative of operating conditions where species activity coefficients are known not to be unity. An assessment of this electrolytic cell's reaction thermodynamics (1) showed a need to take into account the activity coefficients and (2) demonstrated that the anolyte speciation can significantly impact thermodynamic efficiency.

In order to calculate the thermodynamic efficiency, Gibbs energy of reaction and enthalpy of reaction were needed for the electrolytic reaction [45]. To account for activity coefficients, the enthalpy ($\Delta_r H$), Gibbs energy ($\Delta_r G$) and entropy ($\Delta_r S$) of reaction were calculated by the following equations:

$$\Delta_r H = \Delta_r H^\circ - RT^2 \left\{ \partial \left(\ln \left[\frac{\prod (b_i^{v_i} \gamma_i^{v_i})_{Ri}}{\prod (b_i^{v_i} \gamma_i^{v_i})_{Pi}} \right] / \partial T \right\} = \Delta_r H^\circ - RT^2 \partial \ln(Q) / \partial T \quad (13)$$

$$\Delta_r G = \Delta_r G^\circ - RT \ln \left[\frac{\prod (b_i^{v_i} \gamma_i^{v_i})_R}{\prod (b_i^{v_i} \gamma_i^{v_i})_P} \right] = \Delta_r G^\circ - RT \ln[Q] \quad (14)$$

$$\Delta_r S = (\Delta_r H - \Delta_r G) / T \quad (15)$$

The standard thermodynamic values were calculable using the HKF equations cited in Section 2.1. As the predominant electrolytic reaction had yet to be determined, three reactions were selected for comparison. However, at equilibrium a solution only has one redox potential and as such these redox reactions should have the same reaction thermodynamic values provided all reactions are sufficiently fast and reversible.

The equation for calculating the thermodynamic efficiency, ε_{TH} , of an electrolytic cell is as follows [46]:

$$\varepsilon_{TH} = \Delta_r H / \Delta_r G \quad (19)$$

which is inverse to the thermodynamic efficiency of a fuel cell [45]. To demonstrate the impact of activity coefficients and speciation on thermodynamic efficiency, the standard thermodynamic values, $\varepsilon_{TH}^o = \Delta_r H^o / \Delta_r G^o$, are presented for Reactions (16)-(18) in Table 3.

Table 3. Standard thermodynamic values of three electrochemical reactions for a $\text{CuCl}(\text{aq})/\text{HCl}(\text{aq})$ electrolytic cell at 25 °C and 1 bar.

Reaction #	$\Delta_r G^\circ$ / (J/mol)	$\Delta_r H^\circ$ / (J/mol)	$\Delta_r S^\circ$ / (J/[mol K])	$-E_{cell}^\circ$ / (mV)	ε_{TH}°
RXN 16	15627	-14727	-101.81	162	-0.94
RXN 17	55802	2891	-177.46	578	0.05
RXN 18	68931	-21187	-302.26	714	-0.31

As can be seen from Table 3, the standard thermodynamic properties, $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ of the three reactions are very different and, moreover, some of the standard thermodynamic efficiencies are negative at the hypothetical standard state. However, to calculate the thermodynamic values of an operating electrolytic cell, activity coefficients and aqueous speciation must be taken into account.

As demonstrated previously [5,8], current operating concentrations in the anolyte aimed to maximize CuCl(aq) species and minimize CuCl₂(aq) species. These conditions resulted in a highly reduced aqueous environment. At these conditions, the concentration of the total CuCl(aq) was well defined, but the concentration of total CuCl₂(aq) was rarely taken into account. To overcome this limitation, the concentrations of CuCl(aq) and CuCl₂(aq) species in RXNs (16) - (17) were determined from Gibbs energy minimization calculations for a case of dissolving 2.50 mol of CuCl(s) in 8.71 mol/kg HCl(aq). The resulting concentration ratio of Cu⁺ species to Cu²⁺ species from Gibbs energy minimization represents a thermodynamic minimum value of the Gibbs energy of reaction for the HCl(aq) and total aqueous copper species concentrations used at the anode. The catholyte concentrations used were 1 bar of H₂(g) and 7.75 mol/kg of H⁺(aq). The values of the anolyte species at temperature of 25 °C along with two neighboring temperatures of 20 and 30 °C are presented in Table 4.

Table 4. Anolyte concentrations and activity coefficients needed to calculate the thermodynamic efficiencies for the electrochemical reactions with 2.5 mol of CuCl(aq) in 8.71 mol/kg HCl(aq) forming a highly reduced environment at a total pressure of 1 bar

Species / (aq)	20 °C		25 °C		30 °C	
	$b_i / (\text{mol/kg})$	γ_i	$b_i / (\text{mol/kg})$	γ_i	$b_i / (\text{mol/kg})$	γ_i
CuCl ₃ ⁻	1.12 10 ⁻⁸	16.15	1.37 10 ⁻⁸	14.98	1.64 10 ⁻⁸	13.81
Cu ²⁺	6.48 10 ⁻¹¹	2.26	1.10 10 ⁻¹⁰	2.07	1.82 10 ⁻¹⁰	1.89
CuCl ₄ ²⁻	2.84 10 ⁻⁸	2.26	2.76 10 ⁻⁸	2.07	2.65 10 ⁻⁸	1.89
CuCl ₃ ²⁻	2.498	2.26	2.498	2.07	2.497	1.89
Cu ⁺	1.91 10 ⁻¹²	16.15	4.00 10 ⁻¹²	14.98	8.21 10 ⁻¹²	13.81
Cl ⁻	3.732	16.15	3.732	14.98	3.733	13.81

With the values given in Table 4 and Table A.3, reaction quotients, as a function of temperature for each reaction considered are presented in Table 5 as well as a linear approximation of the temperature derivative of the equilibrium constant, $[\partial \ln(Q)/\partial T]_P$. Only three temperature values were used for the linear interpolation as the coefficient of determination of the fittings was greater than 0.95.

Table 5. Reaction quotients for the reactions considered as a function of temperature.

Reaction #	$\ln(Q)_{@20^\circ\text{C}}$	$\ln(Q)_{@25^\circ\text{C}}$	$\ln(Q)_{@30^\circ\text{C}}$	$[\partial \ln(Q)/\partial T]_P$
RXN 16	21.046	20.78	20.525	-0.051
RXN 17	2.229	2.399	2.568	0.0338
RXN 18	26.177	26.076	25.982	-0.0188

Using values from Table 5 and the standard thermodynamic values in Table 3, thermodynamic values that account for the effects of activity coefficients and speciation can now be calculated.

Table 6. Thermodynamic values for the CuCl(aq)/HCl(aq) electrolytic cell taking into account the activity coefficients and concentration terms at 25 °C and 1 bar.

Reaction #	$\Delta_r G / (\text{J/mol})$	$\Delta_r H / (\text{J/mol})$	$\Delta_r S / (\text{J/[mol K]})$	$-E_{\text{cell}} / (\text{mV})$	ϵ_{TH}
RXN 16	9710	10350	2.15	100	1.07
RXN 17	9680	10340	2.21	100	1.07
RXN 18	9720	10370	2.18	100	1.07

The values in Table 6 clearly demonstrate the effect of operating conditions on the thermodynamic efficiency of an electrolytic cell. When accounting for the activity coefficients and speciation, the thermodynamic reaction values changed dramatically, this agreed with the trends observed in the experimental section. All reactions were non-spontaneous for this electrolytic process and required a reversible potential of -100 mV, which is the theoretically calculated magnitude of the decomposition potential. Furthermore, all the thermodynamic values for the three reactions were essentially the same, which agreed with the notion that the solution only had one redox potential at equilibrium. For the concentrations considered, the thermodynamic efficiency for all the redox reactions in this solution was 107 %. This positive efficiency is comparable to but less than the 120 % thermodynamic efficiency for water electrolysis [45]. An efficiency of 107 % indicated that the reaction requires a small amount of heat to be supplied to the system from the environment (or other processes in the cell such as Joule heating), in addition to the electrical work done by the environment on the system. The difference between the standard values and those determined by accounting for activity coefficients demonstrate the significant impacts possible from high ionic strength solutions on thermodynamic values in an electrolytic cell. Now that the decomposition potential is predictable, estimations of the real voltage efficiency are possible.

4.3.3 Voltage Efficiency

The electrochemical efficiency used to quantify the amount of work lost from irreversible processes of an electrochemical cell is commonly referred to as the voltage efficiency. Voltage efficiency for an electrolytic cell describes the additional work done on the system by the environment to overcome processes such as ohmic, charge transfer and mass transfer resistances. For the CuCl(aq)/HCl(aq) electrolytic cell, experimental data obtained from the electrolyzer system can be used to assess the voltage efficiency at 25 °C. The description of the voltage efficiency, ε_V , for an electrolytic cell is as follows:

$$\varepsilon_V = E_{DP}/E_{EC} \quad (20)$$

which is inverse to the definition for fuel cells [45]. In Eq. (20) E_{DP} is the theoretical cell decomposition potential and E_{EC} is the operating or applied potential of the cell at a specified current density output [47]. It is important to note that the applied potential is commonly shown as a positive value. However, from a thermodynamic perspective, all non-spontaneous reactions have a negative equilibrium potential.

To determine the voltage efficiency, current density as a function of applied potential is needed and can be obtained from a current-potential performance curve. In Figure 8, applied potentials for the lab scale electrolyzer was collected via an LSV curve, as described previously in the experimental system section. With the applied potential-current density curve and the theoretical decomposition potential calculated previously (-100 mV), the voltage efficiency can be calculated a function of measured current density.

Figure 9 shows the voltage efficiency as a function of current density measured using the described above $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolytic cell. Similar to water electrolysis, the voltage efficiency represents the largest inefficiency of the electrolyzer and can be improved through several approaches. For example, reducing charge transfer, mass transfer and ohmic losses in a cell design can be used to improve the voltage efficiency. Implementing better catalysts, membranes, and flow fields for this electrochemical cell are the areas with large possibilities to improve voltage efficiency and by association improve the overall efficiency of the $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolytic cell. Moreover, the overall cell performance can be improved by reducing the permeation of copper species through the membrane.

This voltage efficiency analysis of the $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolytic cell brings about an interesting conclusion on the practice of comparing voltage efficiencies between different electrochemical cells. Consider a case where the decomposition potential of an electrolyzer approaches zero. When the decomposition potential is sufficiently low, any appreciable application of potential will result in low voltage efficiency. Therefore, the term of voltage efficiency should not be used when the magnitude of the decomposition potential is close to zero. Also, we do not need the voltage efficiency to be used if the decomposition potential is the theoretical value. The product of the voltage and thermodynamic efficiencies eliminates the need using the voltage efficiency.

4.3.4 Overall Efficiency

With the current, thermodynamic and voltage efficiencies now known, it is possible to determine the overall efficiency[45] for the first time. Overall efficiency for an electrolytic cell represents the total electrical energy input that is stored within a desired form of chemical energy. For the

CuCl(aq)/HCl(aq) electrolytic cell, we identify CuCl₂(aq) and H₂(g) as the desired chemical products. The common equation of electrolytic efficiency is as follows [45]:

$$\varepsilon_{EC} = \varepsilon_V \varepsilon_{TH} \varepsilon_c \quad (21)$$

which also be rearrange to an equation where the voltage efficiency is not used:

$$\varepsilon_{EC} = (\Delta_r H / \Delta_r G) (E_D / E_{EC}) \varepsilon_c = [\Delta_r H / (n_e F E_{EC})] \varepsilon_c \quad (22)$$

Figure 10 shows the overall efficiency, calculated by Eq. (22), as a function of current density measured using the described above CuCl(aq)/HCl(aq) electrolytic cell.

As with the voltage efficiency plot, a significant decrease in efficiency is observed at low current densities. This sudden drop is the primary source of inefficiency in the current design and operating conditions of the electrolytic cell. The most probable sources of this inefficiency given the experimental observation here and in previous works [8,17] are permeation of copper through the membrane, membrane resistance, diffusion overpotentials and an increasing CuCl₂(aq) concentration at the anode. Additional studies are needed to further differentiate the losses in performance from these known issues.

To put the efficiency of the electrolytic cell into context with the Cu-Cl cycle, the total potential energy stored by the cycle is quantified by the enthalpy of water vapour decomposition (lower heating value of H₂, LHV_{H2}) [10,11], which is 241.8 kJ/mol [48] . When compared to the enthalpy of this step, 10.3 kJ/mol in highly reduced conditions, the overall efficiency of the electrolytic process dictates the storage efficiency of less than 5 % of the total energy stored by

the Cu-Cl thermochemical cycle. As such, the efficiency of the electrolytic cell does not have the largest impact on the total efficiency of the cycle. To demonstrate, the data and equations provided in Ref. [10] for the steps of the Cu-Cl cycle, can be used to calculate the cycle efficiency, ε_{cycle} , that corresponds to different values of ε_{EC} for the CuCl(aq)/HCl(aq) electrolytic cell operating at 25 °C. According to Ref. [10], the efficiency of the Cu-Cl cycle with a process design that uses the CuCl(aq)/HCl(aq) electrolytic cell is as follows:

$$\varepsilon_{cycle} = \frac{LHV_{H_2}}{Q_{net} + W} = \frac{241.8 \text{ kJ/mol}}{343.4 \text{ kJ/mol} + \left(\frac{41.2 + (-E_{EC})}{0.4} \right) \text{ kJ/mol}} \quad (23)$$

where Q_{net} is the total heat and W is the total work input (electrical energy) required by the cycle [10]. The value 343.4 kJ/mol represents the total heat and the value 41.2 kJ/mol represents the electrical energy needed by the cycle excluding the electrical energy needed by the electrolytic cell taken from Ref. [10]. The conversion factor 0.4 represents the conversion efficiency from heat to electricity taken from Ref. [10]. Using the E_{EC} that corresponded with each ε_{EC} , ε_{cycle} was calculated for each value of the ε_{EC} . Figure 11 presents the calculated Cu-Cl ε_{cycle} for each ε_{EC} . As demonstrated in Figure 11, decreasing ε_{EC} 85 % only decreased ε_{cycle} by 18 %. When E_{EC} was increased in magnitude to increase the current density, the cycle efficiency decreased as expected. By decreasing the amount of overpotential needed to reach appreciable current densities through improvements in design, the impact of the CuCl(aq)/HCl(aq) electrolytic cell on ε_{cycle} can be reduced.

5 Conclusions

Open circuit potential measurements coupled with Gibbs energy minimization calculations that accounted for the effect of activity coefficients and speciation demonstrated the predictability of the Gibbs energy of the anode reaction in the CuCl(aq)/HCl(aq) electrolytic cell. Using this approach, the uncertainty between three CuCl(aq) speciation models were examined. It was found that the E_{anode} values predicted with the Sverjensky et al., (1997) thermodynamic values (Speciation 1 model) were within 12 mV for all measured potentials, whereas Speciation 2 and 3 were off by -90 mV and 40 mV, respectively. Furthermore, the Sverjensky's speciation model provided evidence to $\text{CuCl}_3^{2-}(\text{aq})$ and $\text{CuCl}_3^-(\text{aq})$ being the electrochemically active species of the primary half reaction at the anode.

Using Speciation 1 model, thermodynamic values such as the Gibbs energy, entropy and thermodynamic efficiency of the electrolytic cell were calculated for a highly reduced anolyte at 25 °C and 1 bar. As expected, all redox reactions considered had the same thermodynamic values at equilibrium. The Gibbs energy, enthalpy and entropy of the electrochemical reaction were found to be, respectively, 9700 J/mol, 10350 J/mol, and 2.15 J/(mol K). These values resulted in a thermodynamic efficiency of 107 %. It was found that accounting for the effect of activity coefficients and aqueous phase speciation is critical when predicting representative thermodynamic and overall efficiency values. By accounting for these phenomena, the relationship between operating conditions and cell performance can be correctly understood. Using thermodynamic values predicted for the electrochemical reaction and experimental data, the overall efficiency of converting electrical energy to desired chemical energy was calculated for the first time. Depending on the current density, the overall efficiency ranged from 15 to 95 %.

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7 Nomenclature

$\dot{a}$ = Ionic radius

$a_{i(II)}$ = Activity of the i-th ion in solution II

$a_{i(I)}$ = Activity of the i-th ion in solution I

A_{DH} = Debye-Hückel parameter

b = Molality

b^o = Standard molality

b_i = Molality of the i-th species

b_n = Setchenow coefficient

b_t = Total molality of solute species

b_γ = Empirical term for the third approximation of Debye-Hückel

B_{DH} = Debye-Hückel parameter

C_p = Heat capacity

E_{eq} = Potential of a half reaction versus the SHE

E_{Anode} = Anode potential versus the SHE

$E_{cell(OCP)}$ = Cell potential at OCP

E_{diff} = Diffusion potential

E_{DP} = Decomposition potential

E_{EC} = Applied potential of an electrolytic cell

E_{ref} = Reference electrode potential versus the SHE

F = Faraday's constant

G = Gibbs energy function

$\Delta_f G^\circ$ = Standard Gibbs energy of formation

$\Delta_r G^\circ$ = Standard Gibbs energy of reaction

$\Delta_r G$ = Gibbs energy of reaction

$\Delta_f H^\circ$ = Standard enthalpy of formation

$\Delta_r H^\circ$ = Standard enthalpy of reaction

$\Delta_r H$ = Enthalpy of reaction

I_m = Ionic strength on the molal scale

j = Current density

L = Lagrangian function

LHV_{H_2} = Water vapor decomposition

n_e = Electron number

n_k^p = Molar amount of k-th species in the p-th phase

Q = Reaction quotient

Q_{net} = Total heat

R = Molar gas constant

S° = Standard entropy of formation

$\Delta_r S^\circ$ = Standard entropy of reaction

$\Delta_r S$ = Entropy of reaction

t_+ = Transport number of the cation

t_- = Transport number of the anion

T = Temperature

W = Work

z_a = Charge of the anion

z_c = Charge of the cation

z_i = Charge of the i-th ion

z_n = Zero charge of a neutral species

γ_i = Activity coefficient of the i-th species on the molal scale

γ_n = Activity coefficient of a neutral species on the molal scale

$\gamma_{\pm}$ = Mean activity coefficient of an ionic species on the molal scale

ϵ_c = Current efficiency (Faradaic efficiency)

ϵ_{TH} = Thermodynamic efficiency

ϵ_V = Voltage efficiency

ϵ_{EC} = Overall efficiency of an electrolytic cell

ϵ_{cycle} = Cycle efficiency

λ_+ = Molar ionic conductivity of the cation

λ_- = Molar ionic conductivity of the anion

λ_i = Molar ionic conductivity of the i-th ion

λ_j = Lagrangian factor

Λ = Molar conductivity

μ_k^p = Chemical potential of the k-th species in the p-th phase

ν_i = Stoichiometric coefficient of the i-th species

ν_{kj}^p = Stoichiometric number of j-th element of the k-th species in the p-th phase

$\Pi(b_i^{\nu_i} \gamma_i^{\nu_i})_R$ = Product of reactant activities

$\Pi(b_i^{\nu_i} \gamma_i^{\nu_i})_P$ = Product of product activities

Φ_j = Mass constraint on j-th element

ψ = the number of phases

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9. Appendix

Table A.1. Heat capacity values and standard thermochemical properties of solids at 298.15 K and 1 bar.

Formula	a	b	c	d	e	$S^\circ{}^{(b)}$	$\Delta_f G^\circ{}^{(a)}$	Ref.
CuCl(s)	75.271	$-2.683 \cdot 10^{-2}$	$2.569 \cdot 10^{-5}$	0	$-1.845 \cdot 10^6$	87.03	-120081	[18,19]
Cu(s)	29.764	$1.612 \cdot 10^{-2}$	$3.411 \cdot 10^{-7}$	$-1.007 \cdot 10^{-7}$	0	33.14	0	[20]
Cu ₂ O(s)	426.02	$-2.508 \cdot 10^{-2}$	$9.244 \cdot 10^{-5}$	$-6.078 \cdot 10^3$	$4.898 \cdot 10^6$	93.14	-146036	[20]
CuO(s)	30.967	$1.374 \cdot 10^{-2}$	0	$3.693 \cdot 10^2$	$-1.258 \cdot 10^6$	42.63	-129567	[20]
$C_p(T) = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$; $^{(a)}$ J mol ⁻¹ ; $^{(b)}$ J mol ⁻¹ K ⁻¹ ;								

Table A.2. Standard thermodynamic properties and Helgeson, Kirkham and Flowers (HKF) model parameters for aqueous species.

Species / (aq)	$\Delta_f G^\circ$ ^(a)	$\Delta_f H^\circ$ ^(a)	S° ^(b)	$a_1 \times 10$ ^(c)	$a_2 \times 10^{-2}$ ^(a)	a_3 ^(d)	$a_4 \times 10^{-4}$ ^(e)	c_1 ^(b)	$c_2 \times 10^{-4}$ ^(e)	$\omega \times 10^{-5}$ ^(a)	Ref.
Cl ⁻	-131290	-167080	56.74	16.87	20.087	23.276	-11.912	-18.41	-23.907	6.092	[24]
HCl ⁰	-95701	-103805	149.7	41.737	69.35	-3.2	-14.494	16.957	21.124	-1.751	[31]
Cu ⁺	49957	80416	70	5.924	-18.093	31.17	-10.879	47.99	-9.744	1.501	[24]
CuOH ⁰	-130093	-159862	101.21	6.251	-17.295	30.856	-10.912	245.01	-143.997	0	[24]
Cu(OH) ₂ ⁻	-325808	-443638	39.12	4.028	-22.723	32.989	-10.688	-2.453	-40.384	5.634	[24]
Cu ²⁺	65584	65689	-97.07	-4.611	-43.815	41.28	-9.816	84.935	-18.368	6.179	[24]
CuOH ⁺	-126357	-174473	-25.52	-0.116	-32.809	36.879	-10.271	89.982	0.94	2.708	[24]
CuO ⁰	-87027	-143093	-51.88	-1.647	-36.551	38.357	-10.116	50.831	-13.89	3.09	[24]
HCuO ₂ ⁻	-251458	-361079	1.26	5.524	-19.049	31.498	-10.84	-13.702	-33.748	2.286	[24]
CuO ₂ ²⁻	-172381	-311290	-96.65	2.52	-26.375	34.363	-10.537	32.021	-58.294	14.915	[24]
CuCl ⁺	-67990	-99776	-27.24	7.314	-14.687	29.802	-11.02	122.826	12.355	2.708	[27]
CuCl ₂ ⁰	-193058	-268445	3.26	21.257	19.359	16.42	-12.427	157.297	33.517	-0.159	[27]
CuCl ₃ ⁻	-315214	-447044	-9.25	40.275	65.794	-1.831	-14.347	267.308	48.998	6.948	[27]
CuCl ₄ ²⁻	-433375	-638202	-77.32	61.378	117.322	-22.084	-16.477	366.116	58.799	14.612	[27]
^(a) J mol ⁻¹ ; ^(b) J mol ⁻¹ K ⁻¹ ; ^(c) J mol ⁻¹ bar ⁻¹ ; ^(d) J K mol ⁻¹ bar ⁻¹ ; ^(e) J K mol ⁻¹											

Table A.3. Standard thermodynamic properties and Helgeson, Kirkham and Flowers (HKF) model parameters for CuCl(aq) species

Species / (aq)	Speciation Set	$\Delta_f G^\circ$ ^(a)	$\Delta_f H^\circ$ ^(a)	S° ^(b)	$a_1 \times 10$ ^(c)	$a_2 \times 10^{-2}$ ^(a)	a_3 ^(d)	$a_4 \times 10^{-4}$ ^(e)	c_1 ^(b)	$c_2 \times 10^{-4}$ ^(e)	$\omega \times 10^{-5}$ ^(a)	Ref.
CuCl ⁰	3	-94591.9	-110198	92.3	17.19	9.427	20.324	-12.017	72.505	4.046	-0.159	[27]
CuCl ⁰	2	-104885	-106717	138.49	17.188	9.443	19.12	-12.017	27.496	-11.249	-0.159	[28]
CuCl ⁰	1	-102901	-108048	127.4	18.426	12.433	19.171	-12.141	5	-19.927	0	[8]
CuCl ₂ ⁻	3	-242835	-305026	112.8	35.122	53.213	3.114	-13.827	153.785	15.416	5.112	[27]
CuCl ₂ ⁻	2	-243680	-274671	217.48	34.585	51.911	0.877	-13.773	-13.295	-36.145	3.524	[28]
CuCl ₂ ⁻	1	-243965	-291169	214.35	38.464	61.357	-0.059	-14.164	-23.867	-41.18	3.539	[8]
CuCl ₃ ²⁻	3	-376405	-495904	97.4	55.43	102.801	-16.376	-15.877	267.696	33.091	11.957	[27]
CuCl ₃ ²⁻	2	-371016	-449935	233.51	54.735	101.129	-20.254	-15.808	-83.539	-79.127	9.903	[28]
HCuCl ₂	1	-245220	-290106	171	34.752	52.295	3.504	-13.789	56.731	-1.947	0	[8]
Cu ₂ Cl ₃	1	-317474	0	201	39.504	63.898	-1.057	-14.269	34.972	-9.509	0	[8]
^(a) J mol ⁻¹ ; ^(b) J mol ⁻¹ K ⁻¹ ; ^(c) J mol ⁻¹ bar ⁻¹ ; ^(d) J K mol ⁻¹ bar ⁻¹ ; ^(e) J K mol ⁻¹												

Table A.4. Mean activity coefficients and corresponding b_γ of HCl(aq) at 1 bar [29]

Ionic Strength / mol kg ⁻¹	$\gamma_\pm$ at 20 °C	b_γ at 20 °C	$\gamma_\pm$ at 25 °C	b_γ at 25 °C	$\gamma_\pm$ at 30 °C	b_γ at 30 °C
8	6.23	0.1477	5.89	0.1449	5.56	0.1418
9	8.48	0.1478	7.96	0.1450	7.47	0.1419
10	11.40	0.1474	10.70	0.1448	9.94	0.1416
11	15.20	0.1466	14.10	0.1438	13.10	0.1409
12	19.90	0.1452	18.30	0.1414	16.90	0.1394

10. Figures

Figure 1. Diagram of the $\text{CuCl(aq)}/\text{HCl(aq)}$ electrolytic cell.

Figure 2. Multi-port glass cell for analyte redox potential measurements at 25 ± 0.3 °C and 1.00 ± 0.02 bar: 1 – test solution of 2 mol of $\text{CuCl}(\text{aq})$ in 8 mol/kg $\text{HCl}(\text{aq})$, 2,3 – argon gas inlet and outlet streams, 4 – 1 mol of $\text{CuCl}_2(\text{aq})$ with 8 mol/kg $\text{HCl}(\text{aq})$, 5 – platinum electrode, 6 – $\text{Ag}(\text{s})/\text{AgCl}(\text{s})$ reference electrode, 7 – argon gas blanket.

Figure 3. Schematic of the CuCl(aq)/HCl(aq) electrolyzer experimental system at 25 °C and 1 bar: 1 – catholyte tank, 2 – anolyte tank, 3 – catholyte pump, 4 – anolyte pump, 5 – damping column, 6 – regeneration column, 7 – electrochemical cell, 8 – HCl(g) removal, 9 – moisture removal, 10 - H₂(g) flow meter, 11 – H₂(g) storage tank.

Figure 4. $E_{\text{cell(OCP)}}$ for the $\text{CuCl}(\text{aq})/\text{CuCl}_2(\text{aq})$ redox electrode with different concentrations of $\text{CuCl}_2(\text{aq})$, as specified in Table 1, versus a 4.57 mol/kg $\text{KCl}(\text{aq})$ $\text{Ag}(\text{s})/\text{AgCl}(\text{s})$ reference electrode at 25 ± 0.3 °C and 1.00 ± 0.02 bar.

Figure 5. Logarithm of molal concentration of $\text{CuCl}(\text{aq})$ species in 2 mol/kg $\text{CuCl}(\text{aq})$ solution as a function of $\text{HCl}(\text{aq})$ concentration from 8 to 10 mol/kg in a highly reduced environment at 25 °C and 1 bar. [— $\text{Cu}^+(\text{aq})$, — · $\text{CuCl}^0(\text{aq})$, ···· $\text{CuCl}_2^-(\text{aq})$, — $\text{CuCl}_3^{2-}(\text{aq})$]

Figure 6. Logarithm of molal concentration of $\text{CuCl}_2(\text{aq})$ species in a 2 mol $\text{CuCl}(\text{aq})$ solution as a function of $\text{HCl}(\text{aq})$ concentration from 8 to 10 mol/kg in a highly reduced environment at 25 °C and 1 bar. [— = $\text{Cu}^{2+}(\text{aq})$, = $\text{CuCl}^+(\text{aq})$, --- = $\text{CuCl}_2^0(\text{aq})$, --- = $\text{CuCl}_3^-(\text{aq})$, - · - = $\text{CuCl}_4^{2-}(\text{aq})$]

Figure 7. ε_c data from the CuCl(aq)/HCl(aq) electrolyzer at a constant current density of 0.3 A/cm². Conditions: anolyte is 2.5 mol of CuCl(aq) with 8.71 mol/kg HCl(aq) in 1 kg of water, catholyte is 7.75 mol/kg HCl(aq) in contact with 1 bar of H₂(g), flow rates of both the anolyte and catholyte are 220 mL/min.

Figure 8. LSV with a 10 mV/s sweep rate for the CuCl/HCl electrolytic cell at 25 ± 0.1 °C:
 Anolyte is 2.5 mol of CuCl(s) in 8.71 mol/kg HCl(aq), and catholyte is 7.75 mol/kg HCl(aq) in
 contact with 1 ± 0.1 bar of H₂(g), flow rates are 220 mL/min.

Figure 9. Voltage efficiency estimated from the LSV curve in Figure 8 for the CuCl(aq)/HCl(aq)
 electrolytic cell as a function of current density at 25 ± 0.1 °C.

Figure 10. Overall efficiency for the CuCl(aq)/HCl(aq) electrolytic cell at 25 ± 0.1 °C for a range of current densities.

Figure 11. Cu-Cl ϵ_{cycle} for different ϵ_{EC} values of the electrolytic cell operating at 25 °C and 1 bar with highly reduced conditions at the anolyte.