Electrochemical Kinetics of CuCl(aq)/HCl(aq) Electrolyzer for Hydrogen Production via a Cu-Cl Thermochemical Cycle

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An electrochemical kinetics investigation of the CuCl(aq)/HCl(aq) electrolyzer identified methods to significantly reduce the platinum loadings required to achieve a high cell current density of 0.5 A/cm² at 0.7 V. As the CuCl(aq)/HCl(aq) electrolyzer is a key component of the Cu-Cl thermochemical cycle, the economic viability of the Cu-Cl thermochemical cycle was significantly improved by reducing the loading required to achieve 0.5 A/cm². Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) with a rotating disc electrode were employed to investigate the kinetics of the aqueous CuII/CuI chloride complexes reaction on platinum and glassy carbon using a three-electrode cell. It was found that the standard exchange current density of the anodic CuII/CuI electrochemical reaction on platinum, 4–12 A/cm², was significantly larger than the values reported for the HER cathodic reaction thus far. In addition, SEM was used to observe the effectiveness of different catalyst application techniques. Through SEM observations, and electrochemical data analysis, the amount of platinum used in a laboratory scale CuCl(aq)/HCl(aq) electrolyzer was reduced from 0.8 mg/cm² applied to both electrodes to 0.4 mg/cm² on the cathode and zero at the anode while still maintaining a current density of 0.5 A/cm² at 0.7 V of applied potential difference.

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As interest in an energy storage option capable of storing both thermal and electrical energy produced via solar resources increases, low temperature hybrid thermochemical cycles are becoming an attractive candidate to fill this role. In particular, the Cu-Cl hybrid thermochemical cycle’s high efficiency and moderate temperature requirements have established itself as a promising option for inexpensive hydrogen generation through harnessing excess thermal and electrical energy from solar resources. One of the most important components in the hybrid cycle is the CuCl(aq)/HCl(aq) electrolytic cell.11 In the electrolytic step of this cycle, the general electrochemical reaction consists of an anode reaction in which aqueous CuII chloride complex species are oxidized to aqueous CuI/CuII chloride complex species, and a cathode reaction in which HCl(aq) is reduced to H2(aq) with transfer of H+ (aq) through a cationic conductive membrane. This process is usually simplified as follows:

\[
\text{CuCl}(aq) + \text{HCl}(aq) = \text{CuCl}_2(aq) + 0.5 \text{H}_2(aq) \tag{1}
\]

To increase the solubility of CuCl(s) in the anolyte, a high concentration of HCl(aq) is typically used. Similarly, the catholyte comprises of highly concentrated HCl(aq) to avoid copper deposition at the cathode.9

Previous research established an electrolytic cell design that employed membrane electrode assemblies (MEAs) similar to water electrolysis cells. The conventional Pt-C catalysts were deposited on the electrodes to increase the rate of reaction for a given applied potential. Although effective, the cost of the platinum catalysts increased the capital cost of the cycle significantly. As with many electrolytic cells, reduction of the capital costs of the cell design is needed to attain a financially viable cycle. In this study, electrochemical techniques and scanning electron microscopy (SEM) were used to determine how to significantly decrease the amount of platinum on both electrodes while maintaining performance of 0.5 A/cm² at 0.7 V. Meeting this performance target with reduced Pt loadings is a key design milestone in economic viability the Cu-Cl thermochemical based on the DOE H2A production model.13 Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were used on a rotating disc electrode (RDE) cell to obtain values of the transfer coefficient and standard exchange current densities for a CuII/CuI electrochemical reaction on both glassy carbon and platinum surfaces in high HCl(aq) solutions. The collected EIS and LSV data indicated that the anodic reaction of the CuCl(aq)/HCl(aq) electrolytic cell was very fast relative to the hydrogen evolution reaction at the cathode.

**Experimental**

In this work two experimental systems were employed to study the CuCl(aq)/HCl(aq) electrolytic cell. One of the systems was a laboratory scale electrolytic cell with supporting systems capable of operating over 100 hours as previously established for durability tests.11,13–15 When discussing concentrations used in the experimental systems, CuCl(aq) refers to all CuI containing species in the aqueous phase, whereas CuCl2(aq) refers to a specific neutral species containing a CuII cation and a Cl− anion combined to an ion pair. This convention is used throughout the text for all aqueous species such as HCl(aq) and CuCl2(aq). Experimentally, concentrations for all tests were prepared in such a way that a CuCl2(aq) & CuCl(aq) solutions consisted of X mol of CuCl2(aq) and X mol of CuCl(aq) mixed with Y mol of HCl(aq) for every kilogram of water in a solution, where X is the same for both CuCl(aq) and CuCl2(aq). References to this type of solution preparation will be labeled as X mol of CuCl2(aq) & CuCl(aq) in Y mol/kg HCl(aq) to avoid confusion. In the laboratory scale system, the catholyte solution contained 7.75 mol/kg HCl(aq) purged and retained under a H2(g) blanket. The anolyte solution contained 2.5 mol of CuCl2(aq) in 8.71 mol/kg HCl(aq), where 1.25 mol CuCl2(aq) was converted to 2.5 mol CuCl(aq) by irreversibly reacting with Cu(s) shot packed in a regeneration column:

\[
\text{CuCl}_2(aq) + \text{Cu(s)} \rightarrow 2\text{CuCl}(aq) \tag{2}
\]

The regeneration column was a glass column filled with layers of copper shot and glass beads that functioned to convert CuII.
aqueous species to CuI aqueous species as the solution flowed vertically through it. Cell temperature in the laboratory scale system was determined by a type K Omega thermocouple inserted into the side of the graphite bipolar plate. For any given measurement, the cell temperature was considered stable when the temperature fluctuation was less than 0.5°C from the desired cell temperature. The pressure of the solution tanks were measured by Omega pressure transducers with an upper limit of 0.690 ± 0.070 MPa gauge.

The electrodes used within the laboratory scale electrocatalytic cell were made by either spray or brush painting a Pt/C ink onto 5 cm² carbon cloth. Spraying was performed via airbrush, while brush painting was carried out with a fine-tip sterile paint brush. Platinum catalyst was in the form of 20% platinum on carbon black Vulcan XC-72R. Catalyst ink was prepared by mixing 15% Nafion EW 1100 solution and 20% platinum on Vulcan XC-72R in a ratio of 2.86:1 Nafion to Vulcan XC-72R by weight. Deionized (DI) water and isopropyl alcohol were added in ratios of 4:1 DI water to Vulcan XC-72R and 20:1 isopropyl alcohol to Vulcan XC-72R to make the ink a desired consistency for airbrushing. Additional isopropyl alcohol was added to the mixture in small amounts to help suspend the catalyst as needed. The mixture was shaken thoroughly and sonicated until all catalyst particles were suspended and dispersed evenly. For spraying, argon gas was used to airbrush the desired loading. Electrodes were placed in a desiccator to completely dry before being weighed to calculate the final loading. The electrodes were used with a chemically pre-treated, hot-pressed Nafion 117 membrane to form the MEA. The pre-treatment process and hot-pressing techniques used were the same as described in previous studies. Fluorosilicone rubber gaskets were used to seal the MEA between graphite bipolar plates with 5 cm² serpentine flow channels.

The second system was used to investigate fundamental properties of the anode reaction on platinum and glassy carbon surfaces. For these studies, a glass multiport three-electrode cell from Pine Instruments equipped with a Pine RDE as the working electrode, platinum counter electrode and Ag(s)/AgCl(s) reference electrode was used. A 4.57 mol/kg KCl(aq) reference solution was used for the reference electrode. Measurements were performed with both platinum (Pt) and glassy carbon (GC) RDE tips, both having a geometric surface area of 0.19635 cm². Rotation rates were varied between 500 and 2000 RPM with a minimum of 3 rotation rates for each sample. Prior to testing, the working electrodes were polished with a mirror finish with a 0.05 μm alumina polish solution on a microfiber cloth. The glass cell was filled and blanket with a steady flow of Ar(g) during each test to isolate the test solution from oxygen exposure. A 0.5°C precision glass thermometer was sealed into one of the available ports for temperature measurements. All tests with this system were conducted at 25 ± 0.5°C. The atmospheric pressure was measured via a mercury barometer to obtain a constant pressure of 0.100 ± 0.002 MPa. Figure 1 presents the key components of the glass electrochemical cell.

For both Pt and GC RDE measurements, the solution concentrations tested were 1, 5, and 10 mmol (mmol = 10⁻³ mol) of CuCl(aq) & CuCl₂(aq) in 8 mol/kg HCl(aq). Each test was prepared by mixing pure CuCl(aq) and CuCl₂(aq) solutions to make the final concentration of CuCl(aq) and CuCl₂(aq) both equal to 1, 5 or 10 mmol per kilogram of water. Each CuCl₂(aq) solution was prepared with Alfa Aesar 97% copper(II) chloride powder and Sigma Aldrich 37 wt% ACS HCl(aq) stock solution. Each CuCl(aq) solution was prepared by converting a pure CuCl₂(aq) solution with half the desired concentration to CuCl(aq) using 0.8–2.0 mm diameter, 99.5% purity, Cu(s) shot. Each CuCl(aq) to CuCl₂(aq) conversion was performed by vigorously stirring the Cu(s) shot within the CuCl₂(aq) solution under an argon atmosphere until the solution turned from a transparent green to a colorless solution.

Experimental measurements in both systems were performed with a Gamry Reference 3000 system. Electrochemical techniques used in this study included potential sweeps of reactor potential difference (U) scans (polarization curves, E/j data), LSV, EIS, and open circuit potential (OCP) measurements. SEM and back scattered electron (BSE) images were obtained using a FEI Quanta 200 microscope to analyze the catalyst coating on the electrodes of the electrolytic cell. Quality of EIS data with respect to linearity, stability and causality were investigated with Kramers-Kronig transformations. It was found that all EIS data collected had goodness of fittings between 10⁻⁵ and 10⁻⁶ for Kramers-Kronig transformations, which indicated the data were of high quality.

Results and Discussion

RDE analysis.—To determine the possible effects of removing platinum catalyst at the anode on cell performance, kinetic parameters of the anode reaction were quantified. EIS and LSV data collected from the RDE system were analyzed to obtain values of the exchange current density (jₒ), transfer coefficient (α), and standard rate constant (kₒ) for the Cu²⁺(aq)/Cu⁺(aq) electrochemical reaction in highly concentrated HCl(aq) solutions. In solutions with high concentrations of Cl⁻(aq), CuCl₂(aq) species had the largest concentration among Cu⁺ complexes by about 3 orders of magnitude. For this kinetic study, the next closest Cu⁺ complex was CuCl₂⁺(aq) with a bulk concentration of 10⁻⁶ mol/kg, whereas CuCl₂⁻(aq) had a bulk concentration that was effectively 10⁻³ mol/kg. The large difference in Cu⁺ bulk concentrations in combination with the observed high current densities and limiting currents suggested that this species was a likely candidate as an electrochemically active species. Given the high concentrations of CuCl₂⁻(aq) and CuCl₂⁺(aq) from thermodynamic speciation calculations, Equation 3 is the simplest form of a possible anode reaction, written in its reduction form:17

\[
\text{CuCl}_2^-(aq) + e^- \leftrightarrow \text{CuCl}_2^2+(aq)
\]

The values obtained via LSV and EIS were compared to check for agreement between the two analytical techniques. The Koutecky-Levich method was used to extract jₒ and α values from LSV data. For EIS data, values of jₒ were quantified from the charge transfer resistance element within an equivalent circuit model that represented a possible reaction mechanism for the Cu³⁺/Cu⁺ reaction. Values of kₒ for platinum and glassy carbon were calculated from the jₒ values obtained via EIS and LSV. For the Cu³⁺/Cu⁺ reaction, LSV data were collected at a series of rotation rates with both Pt and GC materials as working electrodes. Figures 2–4 present the LSV data obtained from each concentration tested with corrections for the measured ohmic resistance and the OCP. Ohmic resistance values between the working electrode and reference electrode were consistently on the order of 1 to 2 Ω.
circuit values also varied slightly, but were consistently 375 ± 20 mV vs. the reference electrode. The OCP reported here, in addition to the ohmic resistance correction, were used to calculate all overpotentials in the RDE analysis. The OCP values measured did not depend on the working electrode material. Using the Nernst equation with available thermodynamic data, the reference electrode potential was determined to be 198 mV vs. the SHE.17 As the reference electrode used a porous frit to separate the test solution from the KCl(aq), the resulting diffusion potential formed was estimated as −66 mV.17 Applying an approach previously outlined with values for the reference electrode and diffusion potential,11 the experimental value of the working electrode equilibrium potential vs. SHE was determined to be 639 ± 20 mV, neglecting the uncertainty in the diffusion and reference electrode potential calculations. Using the Gibbs energy minimization for determining the half-cell electrode potential values with the best fitting thermodynamic values previously published,17 the theoretically predicted value for equation 3 is 656 mV vs. the SHE, which is within the range of experimental error. An in depth analysis of the values and equations needed to describe the equilibrium potentials were published previously.17

As can be seen from the LSV data collected, the small overpotentials needed to reach the limiting current densities suggested that the Cu²⁺/Cu⁺ reaction was very fast and required a very small overpotential on both Pt and GC. Furthermore, the increase in the limiting current as the rotation rate increased supported the assumption that diffusion of the active species was the source of the limiting current. To quantify kinetics of the Cu²⁺/Cu⁺ reaction from LSV data presented in Figures 2–4, the Koutecky-Levich equation was implemented as a method to take into account the effects of diffusion on the measured current values.18 The equation is as follows:

\[
\frac{1}{j_{∞}(\eta)} = \frac{1}{j_{∞}(\eta)} + \left( \frac{1}{j_{∞}(\eta)} \right) \frac{(1.62)k_{ox}v^{1/6}D_{ox}^{2/3} + (1.62)k_{ox}v^{1/6}D_{ox}^{2/3}}{ω^{1/2}}
\]

or

\[
\frac{1}{j_{∞}(\eta)} = \frac{1}{j_{∞}(\eta)} + \left( \frac{1}{j_{∞}(\eta)} \right) \frac{B}{ω^{1/2}}
\]

where \(\eta\) is overpotential, \(j_{∞}(\eta)\) is the current density of a specific overpotential at a specific rotation rate, \(j_{∞}(\eta)\) is the current density at a hypothetical rotation rate with no effects of diffusion, \(ω\) is the rotation rate, \(v\) is the kinematic viscosity, \(k_{ox}\) is the rate constant of the cathodic reaction, \(k_{ox}\) is the rate constant of the anodic reaction, \(D_{ox}\) is the diffusion coefficient of the CuCl(aq) active species, \(D_{ox}\) is the diffusion coefficient of the CuCl(aq) active species and \(B\) is an arbitrary constant when the overpotential is constant. Values of \(j_{∞}(\eta)\) for a number of overpotentials were determined from Koutecky-Levich plots of the conditions tested in the RDE. With the Koutecky-Levich equation, it is possible to extrapolate a plot of \(1/j_{∞}(\eta)\) vs. \(1/ω^{1/2}\) to an infinite rotation rate as a method of estimating \(j_{∞}(\eta)\).

Figures 5 and 6 are the Koutecky-Levich plots for 10 mmol CuCl(aq) with GC and Pt RDEs. As can be seen in Figures 5 and 6, the relationship between the experimental \(1/j_{∞}(\eta)\) and \(1/ω^{1/2}\) values were linear, as expected. The plotted 10 mmol LSV data, along with similar plots for 1 and 5 mmol CuCl(aq) & CuCl₂(aq) with GC and Pt RDEs, were used to estimate \(j_{∞}(\eta)\) for multiple overpotentials at each concentration and electrode material presented in Figures 2–4. The resulting \(j_{∞}(\eta)\) values were plotted as a function

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**Figure 2.** LSV data of 1 mmol of CuCl₂(aq) & CuCl(aq) in 8 mol/kg HCl(aq) at 25 °C and 0.1 MPa for GC(left) and Pt(right) RDEs at six different rotation rates. (Rotation rates: − = 500 RPM, − = 750 RPM, − = 1000 RPM, − = 1250 RPM, − = 1500 RPM, − = 2000 RPM).

**Figure 3.** LSV data of 5 mmol of CuCl₂(aq) & CuCl(aq) in 8 mol/kg HCl(aq) at 25 °C and 0.1 MPa for GC(left) and Pt(right) RDEs at six different rotation rates. (Rotation rates: − = 500 RPM, − = 750 RPM, − = 1000 RPM, − = 1500 RPM).

**Figure 4.** LSV data of 10 mmol of CuCl₂(aq) & CuCl(aq) in 8 mol/kg HCl(aq) at 25 °C and 0.1 MPa for GC(left) and Pt(right) RDEs at four different rotation rates. (Rotation rates: − = 1500 RPM, − = 1750 RPM, − = 1250 RPM, − = 1000 RPM, − = 750 RPM, − = 500 RPM).

**Figure 5.** Koutecky-Levich plots of the CuCl(aq)/CuCl₂(aq) reaction on GC at 25 °C and 0.1 MPa. Conditions: 10 mmol CuCl₂(aq) & CuCl(aq) in 8 mol/kg HCl(aq), η = [80 mV, η = [75 mV, η = [70 mV, η = [65 mV, η = [60 mV, η = [55 mV, η = [50 mV, η = [45 mV, η = [40 mV] (1) F108-F114 (2015)
of overpotential and analyzed with the Tafel equations to estimate \( \alpha_\text{c} \) and \( j_\infty \) values. For anodic polarizations, the Tafel equation is:

\[
\log_{10} j_\infty = \frac{(1 - \alpha_c) F}{RT \ln(10)} + \log_{10} j_0
\]

and for cathodic polarizations:

\[
\log_{10} |j_\infty| = -\frac{\alpha_c F}{RT \ln(10)} + \log_{10} j_0
\]

where \( R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \) is the molar gas constant, \( F = 96485 \text{ C mol}^{-1} \) is Faraday’s constant, and \( T \) is the thermodynamic temperature. Figure 7 presents the Tafel plots of anodic and cathodic polarizations of \( j_\infty(\eta) \) for 10 mmol CuCl(aq) & CuCl2(aq) with the two electrode materials.

Figure 7 demonstrates the large impact of diffusion on the \( j_\infty(\eta) \) values, as the \( j_\infty(\eta) \) values were significantly higher in magnitude than the \( j_\infty(\eta) \) values observed in LSV data. The sizable difference between \( j_\infty(\eta) \) and \( j_\infty(\eta) \) values indicated that the charge transfer reaction was significantly limited by the surface concentration of the electrochemically active species. With Tafel plots of \( j_\infty(\eta) \) for positive and negative overpotentials, it is possible to estimate values of \( \alpha_c \) and \( j_0 \) via a linear fit. Ideally, the values obtained from Tafel analyses of positive and negative polarizations would be the same. However, given the large extrapolation needed, the precision of this analytical method was limited to a small current density range.

As demonstrated in Table I, \( \alpha_c \) calculated from GC data demonstrated high consistency between opposite polarizations. Furthermore, the \( j_\infty \) values obtained from both cathodic and anodic polarizations at a particular concentration were comparable. The same procedure was used to analyze kinetics of the Cu\(^{2+}/\text{Cu}^{+} \) reaction on a Pt RDE. Table II displays the values obtained with a Pt RDE for the same concentrations as the GC tests.

Unlike the GC data, the Pt kinetic values showed more variation between opposite polarizations. However, more variation was expected given the order of magnitude difference between the extrapolated current density and measured current density values when compared to the GC LSV data and corresponding Tafel plots. With average values for \( \alpha_c \) and \( j_0 \), the \( k_0 \) can be approximated for the concentrations analyzed by the following equation, assuming the reaction is a one-step electron charge transfer reaction:

\[
j_0 = Fk_0 \left( \epsilon_{\text{cat}}^{1-x} \epsilon_{\text{red}}^{x} \right)\]

where \( \epsilon_{\text{cat}} \) is the concentration of the oxidant on the molar concentration scale and \( \epsilon_{\text{red}} \) is the concentration of the reductant on the molar concentration scale. Using the density of an HCl(aq) solution at the conditions of the test obtained from reference literature, 1106 g/L, \(^{20}\) the concentrations of 1, 5, and 10 mmol CuCl & CuCl2(aq) in 8 mol/kg HCl(aq) solutions were determined to be 0.86, 4.29 and 8.59 mmol/L, respectively. Molar concentrations were used with the average \( j_0 \) for each concentration and the average \( \alpha_c \) from all tests with a given material in Equation 8 to calculate the average \( k_0 \) for each material. When the concentrations in Equation 8 are equal to standard state (1 mol/L), \( j_0 \) is equal to the standard exchange current density (\( j_\infty \)), which is actually the effective standard value corresponding to the 8 mol/kg HCl(aq) solution. Values of \( k_0 \), \( j_0 \), and \( \alpha_c \) for Pt and GC are displayed in Table III.

Cases in which changes in activity coefficients of active species are negligible between tests, \( k_0 \) should be independent of concentration. As the ionic strength of the test solution was high and did not change significantly between each test, we assumed the activity coefficients did not change significantly. However, it is important to note that \( k_0 \) values can change with concentration due to the effects of changing activity coefficients when activity is not used in the equation for calculating \( k_0 \), as is the common approach. The noticeable difference in \( k_0 \) values between Pt and GC indicated that the reaction is indeed faster on Pt. Still, the reaction was very fast on both materials when compared to the hydrogen evolution reaction, which has a \( j_\infty \) value of around 10\(^{-3} \) A/cm\(^2\) on Pt. \(^{21}\) Literature values for the Cu\(^{2+}/\text{Cu}^{+} \) couple at 20°C with 0.5 mol/L KCl(aq) on GC reported an \( \alpha_c \) of 0.49 ± 0.03 and a \( k_0 \) of 4.6 μA/cm\(^2\) using the same LSV analysis methods. \(^{22}\) Similarities in \( k_0 \) values despite the small differences in test conditions added confidence to the successful application of the LSV analytical approach used in this work.

In addition to LSV data, EIS data were collected for three concentration sets of CuCl(aq) and CuCl2(aq) at multiple rotation rates for Pt and GC RDEs. Using an equivalent circuit model, the exchange current density values at different concentrations on each material were quantified. EIS spectra were collected with 10 mV root mean square.

### Table I. Kinetic values of the CuCl(aq)/CuCl2(aq) reaction on a GC RDE calculated from positive (\( \eta^+ \)) and negative (\( \eta^− \)) polarizations for a range of molalities (b) at 25°C and 0.1 MPa.

| b (mmol/kg) | \( j_{0,b^+} \) (mA/cm\(^2\)) | \( j_{0,b^-} \) (mA/cm\(^2\)) | \( \alpha_c(\eta^+) \) | \( \alpha_c(\eta^-) \) |
|------------|-----------------|-----------------|-----------------|-----------------|
| 1          | 0.51            | 0.35            | 0.36            | 0.46            |
| 5          | 4.27            | 2.51            | 0.47            | 0.47            |
| 10         | 5.37            | 5.75            | 0.46            | 0.36            |

### Table II. Kinetic values calculated from positive and negative polarizations for the CuCl(aq)/CuCl2(aq) reaction on a Pt RDE at 25°C and 0.1 MPa.

| b (mmol/kg) | \( j_{0,b^+} \) (mA/cm\(^2\)) | \( j_{0,b^-} \) (mA/cm\(^2\)) | \( \alpha_c(\eta^+) \) | \( \alpha_c(\eta^-) \) |
|------------|-----------------|-----------------|-----------------|-----------------|
| 1          | 2               | 1               | 0.54            | 0.56            |
| 5          | 15              | 21              | 0.35            | 0.66            |
| 10         | 83              | 20              | 0.78            | 0.37            |
rms, AC polarizations around the OCP. EIS data were collected with 10 points per decade over a frequency range of 300 kHz to 0.3 Hz. Figures 8 and 9 are examples of the EIS data collected for tests with concentrations of 1, 5, and 10 mmol CuCl(aq) & CuCl2(aq) in 8 mol/kg HCl(aq).

The EIS spectra in Figures 8 and 9 have two time constants. On both materials, the low frequency time constant was the largest contributor to the total impedance. A circuit model that represented a single-step charge transfer reaction limited by diffusion of the active species at sufficiently large overpotentials, the Randles circuit model, was used to analyze the data. Ohmic resistances, represented as the \( R_{\text{ohm}} \), consisted of the solution resistance between the RDE and reference electrode as well as the resistance from electrical connections to the potentiostat. The effects of the electrical double layer at the working electrode surface/solution interface were represented by the capacitor component \( C_{\text{dl}} \). The bounded Warburg element, \( W_r \), was used to represent the effect of active species diffusion through the boundary layer at the RDE surface on the impedance. Lastly, the charge transfer resistance, \( R_{\text{ct}} \), was used to represent the effects of the charge transfer reaction on the measured impedance. Close to the equilibrium potential, at which the relationship between current and potential can be approximated as linear, the value of \( R_{\text{ct}} \) can be used to compare the effectiveness of catalysts at high concentrations of HCl(aq). The equivalent circuit used to represent the proposed mechanism is presented in Figure 10. An example of EIS data fitted with the selected circuit model is displayed in Figure 11. The values obtained for each circuit element from the data fitted in Figure 11 is presented in Table IV.

According to the model results, the CuII/CuI reaction was significantly limited by mass transfer in high concentrated HCl(aq) solutions. From the value of \( R_{\text{ct}} \) within the circuit model, calculation of \( j_0 \) for a specific set of conditions such as activity, temperature, surface area and catalyst material, the exchange current density \( j_0 \) may be calculated from the value of \( R_{\text{ct}} \) within the circuit model, using the equation:

\[
j_0 = \frac{(RT)}{(F R_{\text{ct}} A)} \tag{[9]}
\]

where \( A \) is the surface area. Using Equation 9 and the \( R_{\text{ct}} \) values obtained from circuit model fittings, \( j_0 \) values were calculated for each of the concentrations tested. The values obtained for \( j_0 \) from Pt and GC RDEs are displayed in Table V.

A comparison between \( j_0 \) values calculated from EIS and LSV data indicated some differences between the two analytical techniques. To

### Table III. Average \( k_0 \), \( \alpha_c \), and \( j_0 \) values for the CuCl(aq)/CuCl2(aq) reaction in 8 mol/kg HCl(aq) determined from LSV data at 25°C and 0.1 MPa.

| Material | \( k_0 \) (\( \mu \)m/s) | \( \alpha_c \) | \( j_0^{(0)} \) (A/cm\(^2\)) |
|----------|-----------------|------|------------------|
| GC       | 6.7 ± 1.5       | 0.43 ± 0.05 | 0.65 ± 0.14     |
| Pt       | 41 ± 22         | 0.55 ± 0.17 | 4.0 ± 2.1       |

### Table IV. Values from circuit model fittings of EIS spectra in Figure 11.

| Element | GC values | GC error% | Pt values | Pt error% |
|---------|-----------|-----------|-----------|-----------|
| \( R_{\text{ohm}} \) / Ω cm\(^2\) | 3.28 | 3.7 | 0.456 | 2.01 |
| \( R_{\text{ct}} \) / Ω cm\(^2\) | 61.93 | 3 | 0.516 | 4.59 |
| \( W_T \) / Ω cm\(^2\) | 362.5 | 3.7 | 35.26 | 2.28 |
| \( W_p \) | 0.61 | 7.4 | 0.62 | 4.49 |
| \( W_p \) | 0.5 | Fixed | 0.5 | Fixed |
| \( C_{\text{dl}} \) / F cm\(^{-2}\) | 7.23 \times 10^{-5} | 14.9 | 3.95 \times 10^{-5} | 5.62 |
| \( C_{\text{dl}} \) | 0.9 | 1.6 | 1 | Fixed |

### Table V. Values of \( j_0 \) for the CuCl(aq)/CuCl2(aq) reaction obtained from EIS at 25°C and 0.1 MPa.

| \( b \) (mmol/kg) | \( j_0^{(GC)} \) (A/cm\(^2\)) | \( j_0^{(Pt)} \) (A/cm\(^2\)) |
|-----------------|------------------|------------------|
| 10              | 80 ± 21           | 13.5 ± 2.9       |
| 5               | 40 ± 10           | 4.9 ± 0.3        |
| 1               | 14 ± 3            | 2.9 ± 1.0        |

![Figure 8](image8.png)  
EIS data collected from a GC RDE for multiple rotation rates with 5 mmol CuCl(aq) & CuCl2(aq) in 8 mol/kg HCl(aq) at 25°C and 0.1 MPa. (Rotation rates: ● = 500 RPM, ○ = 1000 RPM, o = 1500 RPM).

![Figure 9](image9.png)  
EIS data collected from a Pt RDE for multiple rotation rates with 5 mmol CuCl(aq) & CuCl2(aq) in 8 mol/kg HCl(aq) at 25°C and 0.1 MPa. (Rotation rates: ● = 500 RPM, ○ = 1000 RPM, o = 1500 RPM).

![Figure 10](image10.png)  
Equivalent circuit model where \( R_{\text{ohm}} \) represents the ohmic resistance, \( R_{\text{ct}} \) represents the charge transfer resistance, \( C_{\text{dl}} \) is a constant phase element to represent the electrical double layer and \( W_r \) is a bounded Warburg to represent diffusion controlled mass transfer effects with a finite boundary layer governed by the hydrodynamics.

![Figure 11](image11.png)  
EIS data fitting of RDE data for GC (data = ●, fitting = •) and Pt (data = ○, fitting = ◦) working electrodes. Conditions: 500 RPM, 5 mmol CuCl(aq) & CuCl2(aq) in 8 mol/kg HCl(aq), 25°C and 0.1 MPa.
better compare the two techniques, average $k_0$ and $j_{0}^\alpha$ values, displayed in Table VI, were calculated from the $j_0$ values obtained via EIS and the $\alpha$ determined from LSV data.

Values of $k_0$ calculated from $R_\alpha$ were approximately two to three times larger than those determined from LSV data. This discrepancy could be related to the large extrapolations. resulting in a small current density window, used in the LSV method that were not needed in the EIS analysis. Despite the differences in the two approaches, one conclusion is clear. The kinetics of the Cu$^{II}$/Cu$I$ reaction on GC or Pt are significantly faster than the kinetics of the hydrogen evolution reaction on Pt in highly concentrated HCl(aq). Therefore, it is reasonable to assume that removing the platinum catalyst from the anode should not significantly reduce the performance of the CuCl(aq)/HCl(aq) electrolyzer. Additionally, given the large extrapolation in the Koutecky-Levich plots needed for LSV data and the large bounded Warburg impedance relative to the $R_\alpha$ from EIS data, it appears that the rate limiting step is primarily the transport of active species through the Nernst diffusion layer. As such, studies focused on the hydrodynamics of the anolyte within the electrolyzer would be needed to appreciably increase the rate of the anodic reaction.

**SEM Analysis.**— In addition to RDE tests, scanning electron microscopy (SEM) was used to diagnose the quality of catalyst application on electrodes for HCl(aq)/CuCl(aq) electrolytic cells. The two catalyst application techniques reviewed were the painted loading technique used previously14,15 and the sprayed painting technique. The resulting SEM image for a brush painted electrode is displayed in Figure 12 (right) and sprayed in Figure 12 (left). Figure 12 indicates that the brush painting technique provided a relatively thick and flat catalyst layer covering on the carbon weave support. From these observations, it was inferred that replacing brush painting with a spray painting technique could significantly improve the accessibility of the platinum catalyst. As seen in Figure 12, electrodes coated in catalyst with the spraying application technique were observed to have more effective surface area, which provided supporting evidence to this assumption. Comparisons between Figure 12 (left) and Figure 12 (right) show how the surface geometry of the bulk catalyst layer was altered between each application technique. It was has been suggested that switching from brushed electrodes to sprayed electrodes would improve the performance through an increase in electrode surface area and a decrease in inaccessible platinum. Polarization curves providing $E/j$ data between electrolytic cells assembled with brushed and sprayed electrodes under otherwise identical conditions were conducted to verify if the cell performance did in fact improve when changing the application procedure.

Observations made with SEM and the three-electrode cell led to the proposal of two methods for reducing the platinum catalyst loading while maintaining performance: switching from brush painting to spray painting at the cathode, and removing the platinum altogether from the anode. Figure 13 presents the data obtained from operating a full CuCl(aq)/HCl(aq) electrolytic cell at 80°C using electrode pairs with different catalyst application techniques. Figure 13 demonstrates that the current density obtained from the spray painted electrodes is significantly higher than that of the brush painted electrodes. The observed increase in performance confirmed the hypothetical benefits of the new catalyst topology seen in SEM images. By changing the loading technique to spray based application, the catalyst loading required to reach a 0.5 A/cm$^2$ design point was accomplished with 50% less loading than the 0.8 mg Pt/cm$^2$ used previously.11,13–15

After verifying the effectiveness of the sprayed catalyst application procedure, the platinum loading was removed from the anode while maintaining 0.4 mg Pt/cm$^2$ on the cathode to verify the conclusions made from the RDE analysis. To accomplish this, a bare carbon cloth was used as the anode. The corresponding $E/j$ data are shown in

| Material | $k_0$ / (μm/s) | $j_{0}^\alpha$ / (A/cm$^2$) |
|----------|---------------|----------------------------|
| GC       | 21 ± 12       | 2 ± 1                      |
| Pt       | 120 ± 43      | 12 ± 4                     |

Figure 12. SEM images for electrodes with sprayed(left) and painted(right) catalyst loading techniques both with 0.8 mg Pt/cm$^2$.

Figure 13. $E/j$ data with 10 mV/s scan rates of the CuCl(aq)/HCl(aq) electrolytic cells operating at 80°C and ambient pressure with using brushed (gray) and sprayed (black) electrodes. Conditions: 0.4 mg Pt/cm$^2$ loadings, 5 cm$^2$ carbon cloth electrodes, hot-pressed Nafion 117 membrane, anolyte of 2 mol CuCl(aq) in 7 mol/L HCl(aq), catholyte of 7 mol/L HCl(aq), flow rates of 400 mL/min.
By accomplishing the main objective of reducing the platinum loading weight per area, the CuCl(aq)/HCl(aq) electrolytic cell is now significantly closer to a economically viable cell design. Using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM), we identified and confirmed that a new catalyst application method can improve catalyst loading effectiveness for the CuCl(aq)/HCl(aq) electrolytic cell. Furthermore, catalyst loading can be decreased on the anode without adversely affecting performance to any significant degree due to the fast rate of the anode reaction.

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