State-of-Health of the CuCl electrolyzer during a 168-hour test

Sanchit Khurana^{a,b}, Derek M. Hall^{a,b}, Rich S. Schatz^{a,b}, Mark V. Fedkin^{a,b}, and Serguei N.
Lvov^{a,b,c,#}

^aDepartment of Energy and Mineral Engineering

^bThe EMS Energy Institute

^cDepartment of Materials Science and Engineering

The Pennsylvania State University, University Park, PA 16802, USA

[#]Corresponding author: lvov@psu.edu

Abstract

A state-of-health test of the CuCl/HCl electrolytic cell was carried out by maintaining a constant current density of 0.3 A cm^{-2} for 168 h at 80 °C and ambient pressure. While the most common method used to characterize the electrochemical performance of a CuCl electrolytic cell is to record current-voltage (*I-V* curves), it is also essential to separate the electrochemical and ohmic components of the polarization curve. In our study, the AC impedance characteristics of a single cell were studied along with the DC polarization curves. After the durability test, the potential required to maintain the cell at 0.3 A cm^{-2} increased from 630 mV of the fresh membrane electrode assembly (MEA) to 710 mV due to some degradation processes in the electrolytic cell. Quantitative analysis of the performance decay was carried out by Electrochemical Impedance Spectroscopy (EIS). EIS measurements showed an increase in the area specific ohmic resistance

of the MEA from $0.6 \Omega \text{ cm}^2$ to $0.85 \Omega \text{ cm}^2$ and area specific charge-transfer resistance from $0.61 \Omega \text{ cm}^2$ to $0.8 \Omega \text{ cm}^2$ measured at an overpotential of 0.2 V. The degradation in the cell is attributed to the decrease in membrane conductivity and an increase in the charge-transfer resistance.

Keywords:

Hydrogen Production; Performance Degradation; Electrochemical Impedance Spectroscopy;
CuCl/HCl thermochemical cycle

1 Introduction

There is growing interest in studying the Cu-Cl thermochemical cycle for generating hydrogen as the technology has about four times lower decomposition potential of the CuCl/HCl electrolytic cell as compared to water electrolysis [1] as well as significantly lower temperature requirements compared to other thermochemical cycles along with a better overall efficiency [2,3]. As discussed by Naterer et al. [4], the Cu-Cl cycle has a reduced electrical power requirements compared to water electrolysis, and as such, the difference in the electrical energy is equal to the amount of thermal energy needed by the remaining steps in the Cu-Cl cycle. While the Cu-Cl thermochemical cycle is among the most attractive technologies proposed for hydrogen production, it is essential to study the performance degradation in order to meet the DOE's target of producing hydrogen at the cost of \$6/kg by 2015 and further reducing it to \$4/kg by 2025 [4].

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic method that helps to better understand the degradation mechanisms in electrochemical systems as the technique can provide information on individual cell potential losses. EIS has a great prospective to

quantitatively analyze electrochemical systems [5,6,7] and extract the electrochemical cell components [8,9]. Recently, few authors have applied EIS to study the characteristics of the CuCl/HCl electrolytic cell [1, 10, 11] but there is no published data to characterize and separate the components leading to degradation in the CuCl/HCl electrolytic cell. In this study, we quantify the contribution of different physical processes to the main losses in the electrolyzer and investigate the main cause of degradation over time. An *in situ* EIS approach has been used to monitor the evolution of both the ohmic and charge-transfer resistances with time at different applied potentials.

2 Experimental

2.1 Cell preparation

In the investigated membrane electrode assembly (MEA), Nafion 117 ionomer membrane was used. The pretreatment method was the same as discussed previously [12]. Two 5 cm² carbon-cloth electrodes, painted with 4 mg cm⁻² of XC-72 R catalyst (0.8 mg cm⁻² Pt), were applied to each side of the membrane without hot pressing. Two 85 cm² graphite blocks having serpentine flow channels were obtained from Electrochem Inc. and used as the end plates. A solution of 2 mol of CuCl(s) in 7 mol L⁻¹ HCl(aq) was the anolyte and 7 mol L⁻¹ HCl(aq) was the catholyte. The experimental system which was used was similar to our previous studies [12].

The cell was maintained at 80 °C during the experiment and the solutions were pumped at a flow rate of 130 ml min⁻¹. For stable operation, a constant current density of 0.3 A cm⁻² was maintained for 168 h. Since the aim of this study was to test the durability of the electrolyzer in the Cu-Cl cycle, the regeneration column which was used to convert the Cu²⁺(aq) to Cu⁺(aq), acted as a substitute for the hydrolysis and the thermolysis steps in the complete cycle. As a

result, the regeneration column essentially doubled the concentration of the converted CuCl(aq) at each pass, making the possibility of precipitation of CuCl(s) much more likely overtime than in a real system. Therefore, in order to avoid any possible precipitation of CuCl(s) resulting from the increase in concentration of CuCl(aq) , the solutions were replaced every night and the experiment was paused every night for 6-8 hours, making the test semi-continuous in nature. However, it should be noted that the cell was maintained at a temperature of $80\text{ }^{\circ}\text{C}$ for the whole test period and the effective duration for which the membrane was soaked in the HCl(aq) at $80\text{ }^{\circ}\text{C}$ was over 400 h.

2.2 Electrochemical characterization

Electrochemical characterization of the cell was performed by EIS in the frequency range from 10 mHz to 50 kHz with 15 points per decade interval. EIS was used to keep a periodic track of degradation with time and observe the effect of applied potential. The data were obtained at the decomposition potential (DP) and at overpotentials of 0.2, 0.4 and 0.5 V. Before starting each EIS measurement, the cell was pre-polarized for at least 3 minutes at the measured potential to reach a steady state. The current densities before and after measurement were recorded to prove stability of the cell during the test time. For continuous monitoring of the ohmic resistance with time, measurements were taken periodically after every 4 h. Consistency and quality of data were established by Kramers-Kronig validation [13]. The Kramers-Kronig transformation constrains the real and imaginary components of the impedance for systems that satisfy the conditions of causality, linearity and stability. Polarization curves, using liner sweep voltammetry (LSV) were obtained after every 4 h to observe the cell behavior over a potential range from 0 to 0.7 V and observe the maximum current density at 0.7 V.

2.3 Membrane conductivity

The conductivity of the pretreated, Nafion 117 membrane was obtained using a through-plane glass clip conductivity cell [12] with the active area of 0.74 cm^2 .

The cell consists of parallel disk electrodes and measurements were performed in a 7 mol L^{-1} HCl(aq) solution. The membrane was equilibrated with a [2 mol L^{-1} CuCl(aq) + 7 mol L^{-1} HCl(aq)] for 20 h and the cell conductance was measured at atmospheric pressure and ambient temperature of $25 \text{ }^{\circ}\text{C}$. EIS was used to calculate the conductivity using Gamry electrochemical system and data were taken in a frequency range of 30 - 500 kHz. The resistance of the pre-pressed Nafion 117 membrane was obtained as the difference between the high frequency intercept obtained with and without the membrane.

3 Results and discussion

3.1 AC impedance analysis and polarization curves

LSV measurements were carried out periodically and Figure 1. shows the steady decrease in the current density of the cell over time from 0.46 A cm^{-2} at the beginning, to 0.31 A cm^{-2} at the end of the test at the applied potential of 0.7 V .

Figure 1. Decrease in the current density during the 168 h test.

Since the electrolyzer was operated in daily cycles and the anolyte solution was diluted every night, it is important to observe the daily trend in the system performance to reflect the DP changes as well as in the consumption of Cu (I). Figure 2 represents the gradual decrease in the total impedance of the cell (left) at DP over 16 hours of operation on the first day, and a corresponding increase in the current density was observed (right).

Figure 2. Gradual change in the EIS spectra at DP during a 16 h daily cycle (left) and I - V curve showing the corresponding increase in the current density with time (right) as the cell impedance decreased.

However, as shown in Figure 3, in the end of testing there was no significant decrease in the total impedance, and correspondingly, the current density did not improve over time. This is attributed to the fact that the magnitude of the DP decreased during every 16 h of daily cycles in the first 6 days of testing and reached a stable value in the concluding phases (Figure 4). The lower absolute value of the DP and the dynamic behavior of the system in the initial phases is believed due to a freshly packed regeneration column and freshly prepared anolyte solution resulting in more efficient conversion of Cu^{2+} aqueous species to Cu^+ aqueous species.

Figure 3. EIS spectra obtained at DP in the concluding phase of the test representing the degraded nature of the CuCl/HCl electrolyzer (left) and I - V curve representing the stable current density (right).

Figure 4. Variation of experimentally obtained DP as a function of operational time.

The obtained impedance spectra were described by an equivalent circuit model of the elementary impedance elements. The circuit represents various impedance elements as physical representation of the membrane, charge-transfer and mass-transfer resistances. Figure 5

represents the equivalent circuit model along with the simulation results for the experimental EIS data obtained at 0.2 V overpotential.

The model consists of R_{ohm} , which is the high frequency intercept of the impedance semi-cycle with the real axis and represents the ohmic resistance of the cell, R_{ct} , which is the charge transfer resistance calculated by the difference between the maximum value of the high frequency resistance (R_{maxHF}) and the ohmic resistance ($R_{maxHF} - R_{ohm}$), and R_m , which is the mass transfer resistance observed in the low-frequency region. The constant phase elements (CPEs) were incorporated in place of capacitors to account for the inhomogeneity in the system. The CPE is defined by two values, $CPE-T$ and $CPE-P$. Mathematically, it is expressed as $Z = 1/(T\omega^P)$, where ω is the angular frequency of the AC signal. In the above abbreviations, $CPE-T$ and $CPE-P$, T is capacitance and P is non-homogeneity constant. The circuit model precisely fits the experimental data and the fit converged satisfactorily. The chi-squared parameter [14], which quantifies the goodness of fit, was $< 8 \times 10^{-4}$.

Figure 5. Equivalent circuit model with the simulation of the experimental data obtained at the overpotential of 0.2 V.

Figure 6 compares the EIS data taken at the overpotential of 0.2 V after 15, 90 and 156 h of operation and as shown in Table 1, the area specific ohmic resistance of the membrane increased from 0.60 to 0.85 $\Omega \text{ cm}^2$ over a period of 168 hours, while the increase in the area specific charge-transfer area specific resistance was more pronounced as it increased from 0.51 $\Omega \text{ cm}^2$ to 0.80 $\Omega \text{ cm}^2$. The change in the mass-transfer area specific resistance was not so significant as it only increased from 0.15 $\Omega \text{ cm}^2$ to 0.18 $\Omega \text{ cm}^2$.

Figure 6. EIS spectra at 0.2 V overpotential representing the degradation of the CuCl/HCl electrolyzer with time.

Table 1. Parameters of equivalent circuit model shown in Figure 5 used in simulating the CuCl/HCl electrolyzer individual reaction process related to the ohmic, charge-transfer and mass-transfer resistances.

Equivalent circuit element	Fresh cell	Degraded cell (after 168 h of testing)
Area specific ohmic resistance ($\Omega \text{ cm}^2$)	0.62	0.85
Area specific charge-transfer resistance ($\Omega \text{ cm}^2$)	0.61	0.80
Area specific mass-transfer resistance ($\Omega \text{ cm}^2$)	0.15	0.18

One can see from the EIS results that the contribution of each component on the performance degradation was as follows: ohmic resistance (37 %, $0.23 \Omega \text{ cm}^2$) > charge-transfer resistance (31 %, $0.19 \Omega \text{ cm}^2$) > mass-transfer resistance (20 %, $0.03 \Omega \text{ cm}^2$). While the increase in the charge-transfer resistance is primarily related to the available active surface area and an improvement in this regard has already been discussed elsewhere [11], the possible reasons of the increase in ohmic resistance are decrease of conductivity by chemical degradation and delamination between catalyst layer and membrane. The mass transfer resistance is not a dominant parameter in degradation due to the high flow rate and high concentrations of solutions.

Figure 7 represents the evolution of the ohmic resistance with time and the test can be divided into three phases: (1) 0-90 h - where the ohmic resistance is relatively constant and no significant degradation was observed, (2) 90-130 h – representing the progressive membrane degradation where the ohmic resistance increased by 25 % in 40 h, and (3) 130-168 h – slow degradation, where the ohmic resistance showed a moderate increase and the current density reached a stable value of 0.31 A cm^{-2} at the applied potential of 0.7 V.

Figure 7. Evolution of ohmic resistance over 168 h of operation.

While the continuous monitoring of the system over time helps to identify any possible degradation, it is also essential to observe the cell behavior at different applied potentials to find out the contribution of different parameters while the cell is operating on-line. Figure 8 represents the EIS data at DP and at overpotentials of 0.2 and 0.4 V after 90 h of testing.

Figure 8. Experimentally obtained EIS data at DP and overpotentials of 0.2 and 0.4 V.

As expected, the charge transfer resistance decreases from 0.6 to 0.35 $\Omega \text{ cm}^2$ upon increasing the overpotential from 0.2 to 0.4 V, while the mass-transfer resistance remains same at 0.17 $\Omega \text{ cm}^2$. This characteristic decrease in the charge-transfer resistance with increasing applied potentials is attributed to the higher reaction rate at high overpotentials. As shown in Figure Table 2, the mass-transfer resistance has a relatively higher contribution towards total impedance at 0.4 V overpotential whereas the cell was charge-transfer controlled at low overpotentials.

Table 2. Percentage contribution of each resistance at overpotentials of 0.2 and 0.4 V.

Equivalent circuit element	Overpotential = 0.2 V	Overpotential = 0.4 V
Ohmic resistance contribution (%)	47	47
Charge-transfer resistance contribution (%)	41	30
Mass-transfer resistance contribution (%)	12	23

3.2 Membrane Conductivity

The membrane conductivity, if properly measured, should be directly related to the ohmic resistance (R_{ohm}), and it is given by equation:

$$k = \delta / (R_{\text{ohm}} \times A) \quad (1)$$

where the membrane thickness, δ , in our studies was 0.0195 cm for the tested Nafion 117 membrane, and the exposed surface area (A) of the membrane was 5 cm^2 in the electrolyzer. The ohmic resistance of the membrane was also determined separately by the single through-plane

conductivity cell (R_{con}) and was found to be $0.89 \, \Omega$. The active area in the single conductivity cell was $0.74 \, \text{cm}^2$. Putting these values in (1), the conductivity of the membrane is calculated as $0.029 \, \text{S cm}^{-1}$. The ohmic resistance calculated from the equivalent circuit model used to simulate the electrolyzer is $0.12 \, \Omega$. Thus, the membrane conductivity in the electrolyzer using equation (1) comes out to be $0.032 \, \text{S cm}^{-1}$. Therefore, we conclude that the ohmic resistance of the cell is the resistance of the membrane and an increase in the ohmic resistance represents degradation of the membrane. The small difference in the conductivities obtained using two independent methods could be due to the contact resistance between the flow field and the carbon cloth or other reasons.

3.3 *Electrolysis efficiency*

The current efficiency, η_c in %, of the CuCl electrolyzer can be estimated from the comparison between the experimentally produced amount of hydrogen, $m[\text{H}_2(\text{exp})]$, per unit of time and the theoretical rate of hydrogen gas generation at a particular current density, $m[\text{H}_2(\text{theor})]$, as calculated from Faraday's law:

$$\eta_c = 100 \times m[\text{H}_2(\text{exp})]/m[\text{H}_2(\text{theor})]$$

The average current efficiency calculated for all experimental points obtained from the CuCl/HCl electrolyzer was always above 95 % (Figure 9), which indicates that the hydrogen production reaction $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{gas})$ was the only process taking place at the electrolyzer cathode and, therefore, no parasitic reactions were apparent at the cathode.

Figure 9. H₂(g) production in CuCl/HCl electrolyzer using [2 mol/L CuCl(aq) + 7 mol·L⁻¹ HCl(aq)] anolyte and 7 mol·L⁻¹ HCl (aq) catholyte at 80 °C.

The voltage efficiency, $\eta_{v,}$, was estimated in this study as the percent ratio of the experimentally obtained decomposition potential, $-E_D$ (exp) which was 0.18 V, to the applied voltage, E_{app} . The variation of voltage efficiency with increasing current density is shown in Figure 10.

Figure 10. Voltage efficiency of the CuCl/HCl electrolytic cell. The dotted line represents the extrapolation to the theoretical efficiency at DP.

The voltage efficiency decreases from 47.5 % at 0.1 A cm⁻² to 32 % at 0.3 A cm⁻² due to the increased overall losses in the system at higher current densities. Consequently, more efficient electrolysis is needed to overcome the voltage losses and increase the voltage efficiency.

3.4 *Experimental and Theoretical Decomposition Potential for the CuCl Electrolyzer*

One of the significant sources of degradation in the cell performance during the durability test was from rising the decomposition potential magnitude as the test proceeded. One possible explanation for this increase is an increase in the permeation of copper and copper chloride aqueous species through the membrane throughout the duration of the test. Further testing is needed to determine the possible origin of this problem. Another explanation is an increase of Cu(II)(aq) species in the anolyte during the electrolysis. To address this second possibility, the

effect of the change in Cu(II) concentration needed to change the decomposition potential was quantified. Predicting trends of the decomposition potential for the CuCl/HCl electrolytic reaction requires thermodynamic properties of the aqueous species present in the anolyte and catholyte solutions. Using the Gibbs energy minimization approach described previously [1], equilibrium activities of the CuCl_x complexes involved in the electrolytic reaction were evaluated. Helgeson-Kirkham-Flowers (HFK) [1, 15] model values for calculating apparent standard Gibbs energy values for aqueous species were collected from literature for the following ionic species; $\text{Cl}^-(\text{aq})$, $\text{Cu}^+(\text{aq})$, $\text{Cu}(\text{OH})_2^-(\text{aq})$, $\text{CuCl}_2^-(\text{aq})$, $\text{CuCl}_3^{2-}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, $\text{CuOH}^+(\text{aq})$, $\text{HCuO}_2^-(\text{aq})$, $\text{CuO}_2^{2-}(\text{aq})$, $\text{CuCl}^+(\text{aq})$, $\text{CuCl}_3^-(\text{aq})$ and $\text{CuCl}_4^{2-}(\text{aq})$ [15–17]. Neutral species considered were $\text{HCl}^0(\text{aq})$, $\text{CuOH}^0(\text{aq})$, $\text{CuCl}^0(\text{aq})$, $\text{CuO}^0(\text{aq})$ and $\text{CuCl}_2^0(\text{aq})$ [18-20]. As the actual reaction for this electrolytic cell is not known, an assumed reaction was selected. All decomposition potentials were calculated for the following reaction:

This reaction was selected because of its simplicity, i.e. least number of active species, and the concentration of $\text{CuCl}_3^{2-}(\text{aq})$ is the dominant Cu(I) species in high concentrations of $\text{HCl}(\text{aq})$ [21]. Though the actual reaction(s) may differ slightly, after accounting for activity effects, all possible electrolytic reactions within this cell will have the same potential at equilibrium [22]. The apparent Gibbs energy values used for the species in the reaction at 80 °C and 1 bar are summarized in the Table 3.

Table 3. Apparent Gibbs energy values of Reaction (2) species at 80 °C and 1 bar [20].

Species	$\Delta G_i / (\text{kJ/mol})$
$\text{CuCl}_3^{2-}(\text{aq})$	-382.70
$\text{CuCl}_3^-(\text{aq})$	-315.98

H ₂ (g)	-7.33
H ⁺ (aq)	0

Using the values in Table 3, the Gibbs energy of reaction at unit activity in the infinitely dilute solutions (molal standard state) is 68.056 kJ/mol with a standard cell potential of -0.654 V, which is very different from the experimentally measured cell potential of -0.12 V.

As demonstrated previously [21,23], highly concentrated HCl(aq) solutions have activity coefficients considerably larger than unity. Therefore, in addition to the values of the standard Gibbs free energy of reaction, the activity coefficients should be considered for the catholyte and anolyte solutions composed of highly concentrated HCl(aq). To account for the non-ideality of the charged species within the aqueous phase, the mean activity coefficients of HCl(aq) solution can be used because HCl(aq) is the dominating electrolyte. The activity coefficients, $\gamma_{\pm}$, for a wide range of concentrations from 1 to 11 mol kg⁻¹ HCl(aq) solutions are available from 25 to 80 °C [22].

Table 4. The activity coefficients of HCl(aq) at 80 °C and 1 bar as a function of molality b [21]

$b / (\text{mol/kg})$	$\gamma_{\pm}$
7.93	3.225
9.251	4.197
10.092	4.860
11.102	5.650

The equation used to model the mean activity coefficient of the dominant electrolyte using experimental data was the third approximation of the Debye-Hückel theory [24]

$$\log_{10}(\gamma_{\pm}) = \frac{A|z_+z_-|\sqrt{I_m}}{1+B\lambda\sqrt{I_m}} + CI_m - \log_{10}\left(1 + \frac{b_t}{55.51}\right) \quad (3)$$

Here 55.51 is the number of moles of water in one kilogram of water, $b_t = \sum b_i$ refers to the sum of molalities for all of the solute species, A and B are the Debye-Huckel parameters [25], z_+ and z_- are the charge of the anion and cation, respectively, in the dominant electrolyte, $\dot{a}$ is the empirical radius of the aqueous component, C is the empirical parameter of the supporting electrolyte [HCl(aq)] and I_m is the ionic strength of the solution on the molal scale. For these calculations, 0.45 nm was used for the $\dot{a}$ parameter of each species considered.

In order to predict trends with the decomposition potential, cell conditions and species activities were needed for calculations. Cell temperature was held constant at 80 °C and pressure was 1 bar. The solution in contact with the anode was 2.49 mol of CuCl(s) in 8.71 mol kg⁻¹ HCl(aq) anolyte. The cathode was in contact with 7.75 mol kg⁻¹ of HCl(aq) catholyte with a gas blanket of H₂(g) at 1 bar of pressure. Using Gibbs energy minimization [26], the [2.49 mol of CuCl(s) + 8.71 mol kg⁻¹ HCl(aq)] anolyte should have CuCl₃²⁻(aq) and CuCl₃⁻(aq) concentrations of 2.47 mol kg⁻¹ and 5.53 10⁻⁸ mol kg⁻¹, respectively. Furthermore, the resulting ionic strength of the solution was determined to be 11.18 mol/kg. With these operating conditions, the Nernst equation of the CuCl/HCl electrolytic cell expressed by the following electrochemical diagram:

can be given as:

$$E = -\frac{\Delta_r G}{nF} = -\frac{\Delta_r G^o}{nF} + \frac{RT}{nF} \ln \left(\frac{\Pi (b_i^{v_i} \gamma_i^{v_i})_R}{\Pi (b_i^{v_i} \gamma_i^{v_i})_P} \right) \quad (5)$$

where $\Delta_r G^\circ$ is the standard Gibbs energy of reaction, n is the electron number in the 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, ν_i is the stoichiometric coefficient of the i -th species, γ_i is the activity coefficient of the i -th species, $\Pi(b_i^{\nu_i} \gamma_i^{\nu_i})_R$ is the product of the reactant activities and $\Pi(b_i^{\nu_i} \gamma_i^{\nu_i})_P$ is the product of the product activities taking into account the stoichiometric coefficient ν_i . Using Eq. (5), apparent Gibbs energy values from Table 3, the mean activity coefficients from Table 4, and composition of anolyte and catholyte given in Diagram (4), the Gibbs energy of reaction (2), $\Delta_r G$, was calculated to be 8.39 kJ/mol and, therefore, the theoretical DP is -0.087 V.

When compared to the experimental values measured, the theoretical DP was slightly lower. One reason for the deviation between the theoretical and experimental DP was that the concentration of the $\text{Cu(II)Cl}_x(\text{aq})$ species in the anolyte was not readily known throughout the test. Furthermore, the presence of the regeneration column ensures the values of the $\text{Cu(II)Cl}_x(\text{aq})$ species were very low ($b < 1 \text{ mmol kg}^{-1}$). This was justified by the clear to faint yellow fluid leaving the electrolytic cell. Still, this presented an issue for predicting the decomposition potential of the electrolytic cell. Therefore, we used the experimental DP measurements to estimate the $\text{CuCl}_3^-(\text{aq})$ concentrations. Experimental DP measurements, $E_{(\text{cell})}$, were measured for a series of points during the test. As pH and hydrogen gas pressure was constant throughout the test, the cathode potential, $E_{(\text{cathode})}$, could be considered relatively constant. By calculating the cathode potential, $E_{(\text{anode})}$ was determined from the conditions outlined above and the $E_{(\text{cell})}$ values measured. Potential values for the anode, cathode and cell are displayed in Table 4.

Using the Gibbs free energy values and the activities obtained from literature values, it is possible to estimate the $\text{CuCl}_3^-(\text{aq})$ concentrations needed to obtain the $E_{(\text{anode})}$ values displayed

in Figure Table 4. Table 4 displays the estimated $\text{CuCl}_3^-(\text{aq})$ values expected throughout the duration of the test, assuming the deviation in the cell potential is due entirely to the presence of additional copper concentration.

Table 4: Estimations of $\text{CuCl}_3^-(\text{aq})$ concentrations for the 168 hour test using measured DP

Duration/h	$E_{(\text{cell})} = E_{(\text{anode})} - E_{(\text{cathode})}/\text{V}$	$E_{(\text{cathode})}/\text{V}$	$E_{(\text{anode})}/\text{V}$	$b_{\text{CuCl}_3^-(\text{aq})}/\mu\text{mol kg}^{-1}$
0	-0.180	-0.096	-0.276	1.15 ± 0.05
90	-0.190	-0.096	-0.286	1.60 ± 0.05
120	-0.230	-0.096	-0.326	6.00 ± 0.25
168	-0.245	-0.096	-0.341	9.70 ± 0.25

Results from these calculations indicate that the decomposition potential could depend strongly on fluctuations in the $\text{Cu}(\text{II})$ species due to an increased permeation through membrane.

4 Conclusions

The Cu-Cl electrolyzer was operated for 168 h and a goal to maintain the cell at 0.3 A cm^{-2} under 0.7 V was successfully met. EIS was applied to monitor the system behavior over time and an equivalent circuit model was used to quantify the physical parameters contributing to the overall impedance of the cell. It was concluded that the primary cause of degradation during the 168 h of operation was the increase in the ohmic and charge-transfer resistances. The through-plane conductivity cell proved to be a reliable and time-efficient set up to calculate the membrane conductivity and screen new and existing membranes before testing in the electrolyzer. Electrochemical kinetics was improved at higher overpotentials, as the first loop shows in the

EIS spectrum, which is related to the charge-transfer resistance, decreased with increasing the applied potential. A rise in the magnitude of DP was observed with an increase in the total impedance over time and a thermodynamic analysis was carried out to estimate the parameters effecting the DP. A current efficiency of greater than 95 % was maintained throughout the experiment which confirmed that there were no side reactions taking place in the cell. The test summarizes the effectiveness of EIS as an aging protocol and it is recommended that it should be more widely employed towards the development of the CuCl electrolyzer to characterize the degradation mechanisms.

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