RECENT PROGRESS IN THE DEVELOPMENT OF THE CuCl/HCl ELECTROLYSIS REACTION FOR NUCLEAR HYDROGEN PRODUCTION

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Abstract

The hybrid Copper-Chlorine (Cu-Cl) thermochemical cycle is being developed in Canada for nuclear hydrogen production. The Cu-Cl cycle consists of both chemical and electrochemical reaction steps. Atomic Energy of Canada Limited (AECL) has been focusing on the development of the electrochemical reaction step. The energy required by the Cu-Cl cycle can be supplied by the Super Critical Water Reactor (SCWR), under development at AECL, since the highest temperature required by the Cu-Cl cycle is 530 °C.

This paper will mainly focus on recent progress that has been made at AECL towards the development of the CuCl/HCl electrolyzer. In order to assess the progress that has been made the performance of the electrolyzer will be evaluated by examining the time dependence of the cell voltage.

1. Introduction

One approach to large-scale hydrogen production involves the use of thermochemical cycles. One such cycle, the hybrid copper-chlorine (Cu-Cl) thermochemical cycle, uses both heat and electricity to carry out a series of chemical and electrochemical reactions with the net reaction being the splitting of water into hydrogen and oxygen. Lewis et al. [1] identified the Cu-Cl cycle as one of the most promising lower temperature cycles for hydrogen production. The Cu-Cl cycle is of interest to Atomic Energy of Canada Limited (AECL) because all of the chemical and electrochemical reactions can be carried out at temperatures that do not exceed approximately 530 ºC. This means that the heat requirement of this process can be supplied by intermediate temperature sources such as the Generation IV Super Critical Water Reactor (SCWR) being developed in Canada by AECL. It is expected that the SCWR will generate heat having a temperature that may be as high as 625 ºC.

There are two variations on the Cu-Cl cycle. In the original five-step process copper metal is produced electrochemically by the disproportionation of cuprous chloride (CuCl), which is dissolved in a hydrochloric acid (HCl) electrolyte. Hydrogen gas is then produced by a chemical reaction that takes place between copper metal and gaseous HCl at a temperature of 430-475 ºC. The four-step process was born when it was recognized that these two reaction steps could be replaced by a single electrolysis reaction that generates hydrogen gas directly at the cathode. The CuCl/HCl electrolysis reaction was first reported in Reference [2] as:

Overall Cell Reaction: $2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq)$ (1)

In this reaction Cu^+ in CuCl is oxidized at the anode to Cu^{2+} in $CuCl_2$ (cupric chloride) while at the cathode protons are reduced and form H_2 ($2H^+ + 2e^- \rightarrow H_2$). The electrochemical reaction defined by Equation (1) was successfully demonstrated in the laboratory only when a cation exchange membrane was used to separate the anode and cathode compartments of the electrolysis cell [3]. Since this demonstration, research groups in both Canada and the United States have been focusing on developing the four-step Cu-Cl cycle [4].

The main reactions that makeup the four-step Cu-Cl cycle are summarized in Table 1. The electrolysis reaction, Step 1, produces hydrogen and cupric chloride. In Step 2, the $CuCl_2$ produced in Step 1 is dried in preparation for reaction Step 3 in which $CuCl_2$ reacts with steam at about 400 °C to produce copper oxychloride ($CuO•CuCl_2$) and gaseous HCl. In Step 4, the copper oxychloride is decomposed to CuCl and oxygen. The overall reaction is the decomposition of water into H_2 and O_2 with $CuCl_2$, CuCl and HCl being recycled within the process.

Table 1 Reaction Steps in the Four-Step Cu-Cl Cycle

Step	Reaction	Temperature / °C
1	$2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq)$	> 100 Electrolysis
2	$CuCl_2(aq) \rightarrow CuCl_2(s)$	< 100 Drying Step
3	$2CuCl_2(s) + H_2O(g) \rightarrow CuO•CuCl_2(s) + 2HCl(g)$	400
4	$CuO•CuCl_2(s) \rightarrow 2CuCl(l) + ½O_2(g)$	530

The CuCl/HCl electrolysis reaction uses a solution of CuCl dissolved in HCl as the anolyte while the catholyte is HCl. The HCl concentration range that we previously reported on was 6 to 10 M while the CuCl concentration range was 0.5 to 1.5 M [5]. In the present study we will be presenting data for 11 M HCl solutions. The CuCl concentration will be 0.5 M. Depending on the HCl concentration, species such as $CuCl_2^-$, $CuCl_3^{2-}$ and $CuCl_4^{3-}$ can form when CuCl dissolves in HCl [6], [7] and [8]. Based on data presented in Reference [8], the anodic half-cell reactions in 6 and 11 M HCl solutions can be written as follows:

Anode Reaction (6 M HCl): $CuCl_2^- \rightarrow CuCl^+ + Cl^- + e^-$ (2)

Anode Reaction (11 M HCl) $CuCl_4^{3-} \rightarrow CuCl_2 + 2Cl^- + e^-$ (3)

During single-cell CuCl/HCl electrolysis experiments copper species enter the catholyte by crossing the cation exchange membrane that separates this solution from the anolyte. When CuCl is dissolved in 6 M HCl the copper (II) species that could cross the membrane during electrolysis is $CuCl^+$ (Equation (2)) while in 11 M HCl the copper (II) species is $CuCl_2$ (Equation (3)). During CuCl/HCl electrolysis studies $CuCl^+$ can be transported across the cation exchange membrane by diffusion and migration while $CuCl_2$ can be transported across the membrane by diffusion only. Thus, for a given current density, the flux of copper species across the membrane is expected to be higher in a 6 M HCl electrolyte than for an 11 M HCl electrolyte. As a result, lower catholyte copper species concentrations are expected when higher acid concentrations are used and this has been observed experimentally [5] and this also explains why CuCl/HCl electrolysis studies are presently being carried out in concentrated HCl solutions. It should be noted that we have also been able to confirm that copper (I) species, which are anionic, also cross the cation exchange membrane during CuCl/HCl electrolysis.

During studies of the CuCl/HCl electrolysis reaction the anolyte and catholyte are continuously recycled. As a result, the catholyte copper species concentration increases with time. It has been observed that copper species in the catholyte can cause the cell voltage to increase during constant current electrolysis experiments as a result of copper metal being deposited on the platinum electrocatalyst. Whether or not copper metal deposition occurs would seem to depend on the HCl concentration and current density [8]. The cell voltage can also increase when the copper (II)/copper (I) concentration ratio in the anolyte increases. This occurs because the equilibrium potential of the cell depends in part on the redox conditions at the anode. Since the anolyte is recycled, this ratio will increase during CuCl/HCl electrolysis. Thus, in order to keep this ratio as small as possible, copper (II) is converted back to copper (I) during the process by a reaction with copper metal.

Much of the research work that has been carried out at AECL has been focused on improving the performance of the CuCl/HCl electrolysis cell in terms of cell voltage stability. In this paper experimental data will be presented which will show the current status of the project.

2. Experimental

2.1 Electrodes and electrode configuration

In the present study a cell configuration similar to the membrane electrode assembly (MEA) found in fuel cells was used. A typical MEA consists of a proton exchange membrane (PEM) sandwiched between two catalyst treated gas diffusion layers (GDLs). In the CuCl/HCl electrolyzer, only the GDL that is on the cathode side of the electrolysis cell is treated with a catalyst. The GDL on the anode side of the cell is catalyst free. A Nafion® PEM is sandwiched between these two GDLs. With this configuration an electrical connection between the graphite separator plates (current collectors) and the GDLs must be established. To establish these connections, pieces of Duocel® Reticulated Vitreous Carbon are placed between the GDLs and the graphite separator plates. The electrical properties of Reticulated Vitreous Carbon (RVC) make it an excellent candidate as a current collector in the electrolysis cell. Because of its high degree of porosity, 97%, it also allows the catholyte and anolyte solutions to freely flow through their respective compartments. It should be noted that since the copper (I) oxidation reaction is facile on graphite surfaces the GDL, the RVC and the graphite separator plate all act as an anode. For this reason the reported current density is based on the geometric area of the cathode GDL.

2.2 Experimental parameters

The experimental parameters used to obtain the electrochemical data presented in this paper are summarized in Table 2.

Table 2 Experimental Parameter Values that were used to Study the CuCl/HCl Electrolysis Reaction

Experimental Parameter	Parameter Value
Catholyte	11 M HCl
Anolyte	0.5 M CuCl + 11 M HCl
Catholyte Flow Rate / L•min^{-1}	1.5
Anolyte Flow Rate / L•min^{-1}	1.25
Temperature used to Study CuCl/HCl Electrolysis / °C	45
Current / A	2.5
Geometric Area of the Cathode / cm^{2}	25
Current Density at the Cathode / A•cm^{-2}	0.1
Cathode	Pt on XC-72R Carbon Powder
Cathode Substrate Material	GDL
Anode	Graphite Separator Plate, GDL, RVC
Temperature of the Sample Holder during UV-Visible Spectrophotometric Measurements / °C	25

2.3 Process description

A simplified schematic of the CuCl/HCl process is shown in Figure 1. The catholyte is held in a 4 L glass vessel called the catholyte reservoir. A peristaltic pump is used to pump the catholyte from the catholyte reservoir into the cathode compartment of the electrolysis cell. After passing through the cathode compartment, the catholyte is returned to the catholyte reservoir and is recycled.

During electrolysis experiments the catholyte copper species concentration is measured *in-situ* using a UV-visible spectrophotometer. A sipper pump is used to pump the catholyte into an 80 μL flow cell that is held in a temperature controlled sample holder. Following the absorbance measurement, the catholyte is returned to the catholyte reservoir. Computer software is used to control the functionality of the UV-visible spectrophotometer.

The anolyte is also held in a 4 L glass vessel called the anolyte reservoir. The anolyte is pumped into the anode compartment of the electrolysis cell using a peristaltic pump. The anolyte, like the catholyte, is recycled. Therefore, in order to maintain the copper (I) concentration at its initial value as well as keep the copper (II)/copper (I) concentration ratio as small as possible the anolyte is directed into a vessel that contains copper metal coils once it exits the anode compartment. Within this vessel copper (II) reacts with copper metal giving two moles of Cu^{+} for every mole of Cu^{2+} that enters the flask. Following this reaction, the anolyte is returned to the anolyte reservoir. Protons from the anolyte cross the Nafion® membrane during CuCl/HCl electrolysis at the same rate that copper (I) is oxidized to copper (II). As a result, 11 M HCl is added to the anolyte reservoir at a rate of 3.11 mL•min^{-1} (this value is determined by the current and CuCl concentration) to replenish the supply of protons. This addition of HCl also dilutes the anolyte copper (I) concentration maintaining it at the initial value.

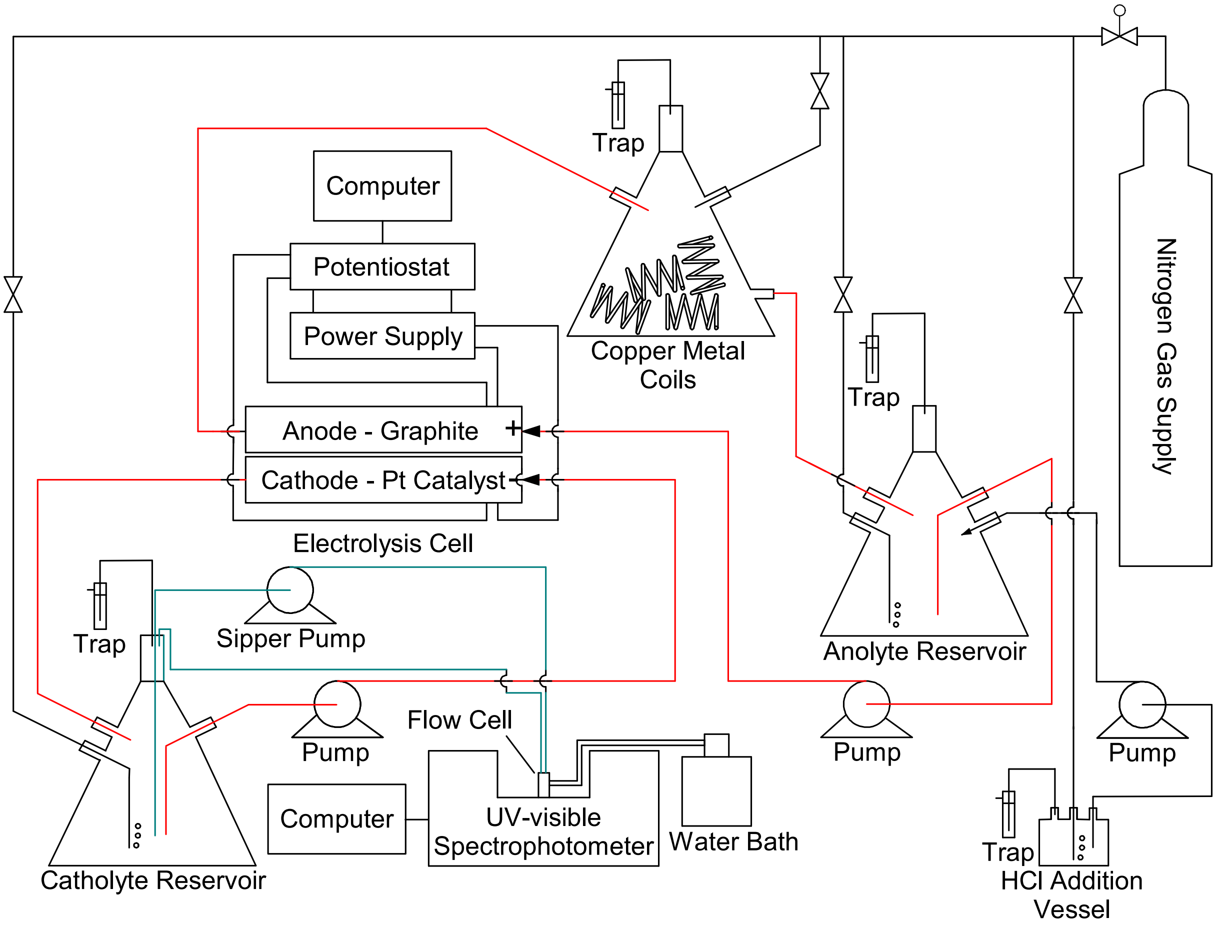

Figure 1 CuCl/HCl Process Flow Diagram.

The catholyte reservoir, anolyte reservoir and the vessel containing copper metal coils are all housed in a high density polyethylene tank that is about one third full with water (~20 L). Also present in this tank is a copper heat exchanger which runs along the inside surfaces of the tank and outside surfaces of the catholyte and anolyte reservoirs. The heat exchanger connects to the inlet and outlet ports of a circulating water bath. Thus, the temperature of the water inside the high density polyethylene tank, and consequently, all the solutions in the glass vessels are temperature controlled during electrolysis experiments.

Nitrogen gas is bubbled through the catholyte and anolyte reservoirs prior to and during electrolysis experiments. The nitrogen gas purge helps to keep these solutions oxygen free.

A PAR VersaSTAT^3 Potentiostat/Galvanostat connected to a KEPCO Model BOP 20-20M Power Supply was used to control current and measure the cell voltage during galvanostatic experiments. The KEPCO power supply extends the maximum current range of the VersaSTAT^3 to 20 A. The VersaSTAT^3 Potentiostat/Galvanostat was interfaced to a microcomputer through a USB cable. The experimental data was collected using the V^3-Studio^{TM} software package.

3. Results and discussion

Figure 2 displays the time dependence of the cell voltage as observed during a constant current single-cell electrolysis experiment. The various experimental parameters used to obtain this data have been summarized in Table 2.

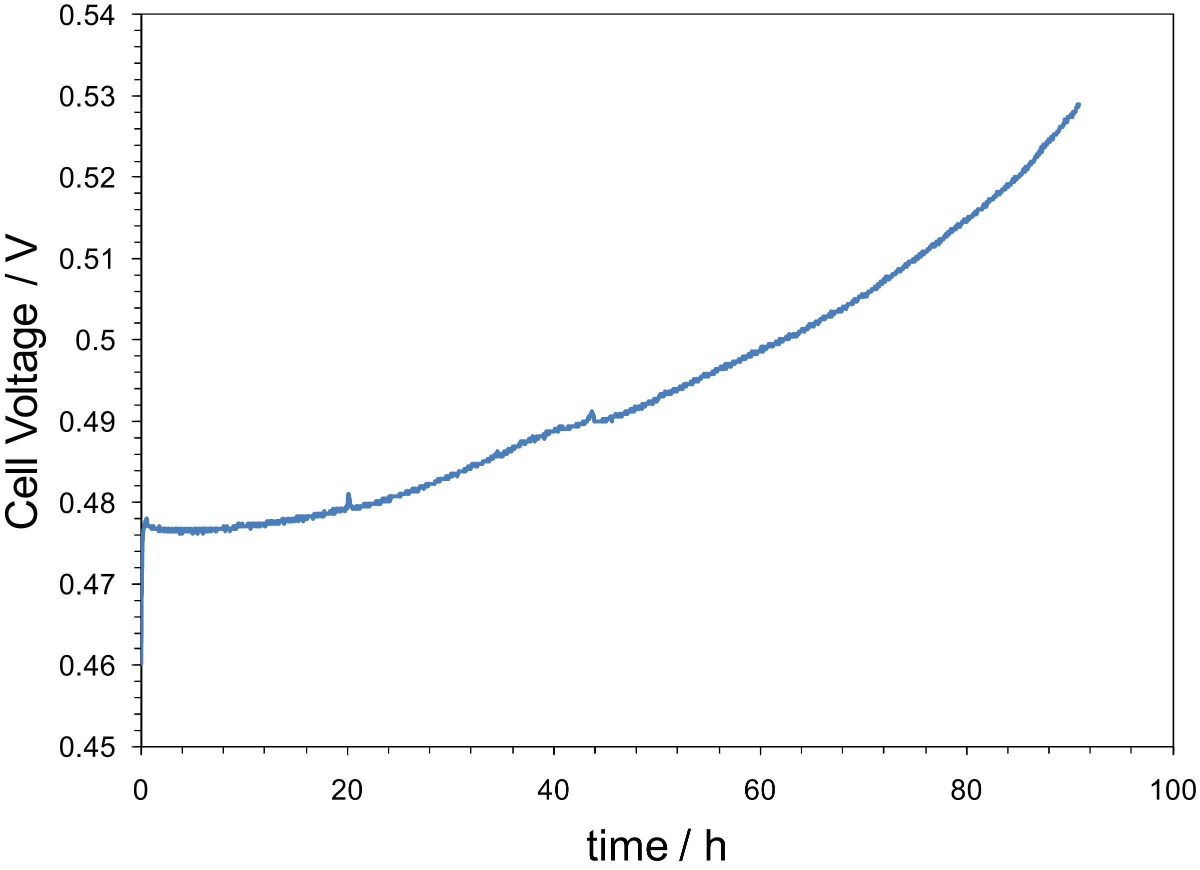

Figure 2 Time Dependence of the Cell Voltage.

The data presented in Figure 2 show that the performance of the electrolysis cell, in terms of cell voltage, is stable only during the first 10 h of the experiment. After 10 h the cell voltage increases with time for the duration of the experiment. Thus, the performance of the electrolysis cell in terms of cell voltage stability is, overall, rather poor. However, the values themselves for the cell voltage are excellent even after 90 h of constant current electrolysis. All of the cell voltage values displayed on Figure 2 are below 0.53 V. A cell voltage of about 0.476 V, observed during the first 10 h of electrolysis, is particularly encouraging. One important objective in the development of the CuCl/HCl electrolysis reaction is to develop a process that can operate at a cell voltage that is in the range of 0.6 to 0.7 V. Thus, the data presented in Figure 2 clearly demonstrates the potential of the CuCl/HCl electrolysis reaction for hydrogen production.

The cell voltages observed in Figure 2 for a zero-gap-cathode/zero-gap-anode electrode configuration are about 0.12 V lower than those observed when a wide gap-cathode/wide-gap-anode electrode configuration was used under similar experimental conditions. In the latter case the gap between the cathode and anode was 4 mm. This difference in cell voltage is significant and shows that there is a great benefit to using a zero gap configuration.

It should be noted that the small sudden rise (spikes) in the cell voltage seen at about 20 and 43 h in Figure 2 occurred when the anolyte solution was manually drained from the anolyte reservoir. During this draining process the anolyte was exposed to atmospheric oxygen for a short time which may have caused the copper (II)/copper (I) concentration ratio to increase. We have demonstrated that increasing this ratio in the anolyte causes the cell voltage to increase.

During CuCl/HCl electrolysis experiments copper species enter the catholyte from the anolyte by crossing the cation exchange membrane which separates these two solutions. The total concentration of copper species found to be present in the catholyte during the electrolysis experiment described above (Figure 2) can be found as a function of time in Figure 3.

The copper concentrations displayed on Figure 3 were obtained using *in-situ* UV-visible spectrophotometry. We apply this technique by continuously circulating the catholyte through a temperature controlled flow cell (see Figure 1). Every 2 h the flow is stopped for 10 s so that an absorbance measurement can be recorded. A multi component calibration curve was prepared for mixtures of copper (I) and copper (II). This calibration curve was then used to determine the concentration of these species in the catholyte based on the experimentally measured absorbance data. The total catholyte copper species concentration is the sum of the copper (I) and copper (II) concentrations. Each point on Figure 3 represents a single measurement. Since only a single measurement is taken it is difficult to define what the experimental error is. The experimental error will have at least two contributions. The first is the error associated with the construction of the calibration curve while the second is associated with the measurement of the catholyte copper (I) and copper (II) concentrations. As part of future experimental work the error associated with our determination of the catholyte copper species concentration will be assessed.

The data presented in Figure 3 show that the copper species concentration in the catholyte steadily increases during the electrolysis experiment. After 90 h the total catholyte copper species concentration was found to be about 40 ppm and this copper was present as copper (I). Electrolysis experiments have also been carried out under identical experimental conditions to those reported above but with a 2 mm gap lying between the cathode and membrane (a 4 mm gap between the cathode and anode). In these experiments the catalyst is applied directly to the graphite separator plate. When this configuration was used both copper (I) and copper (II) were found to be present in the catholyte. This would suggest that, in the present study (zero-gap-cathode/zero-gap-anode), copper (II) was immediately reduced to copper (I) as soon as it crossed the membrane and came into contact with the cathode catalyst and GDL. This would explain why no copper (II) was observed in the present experiment.

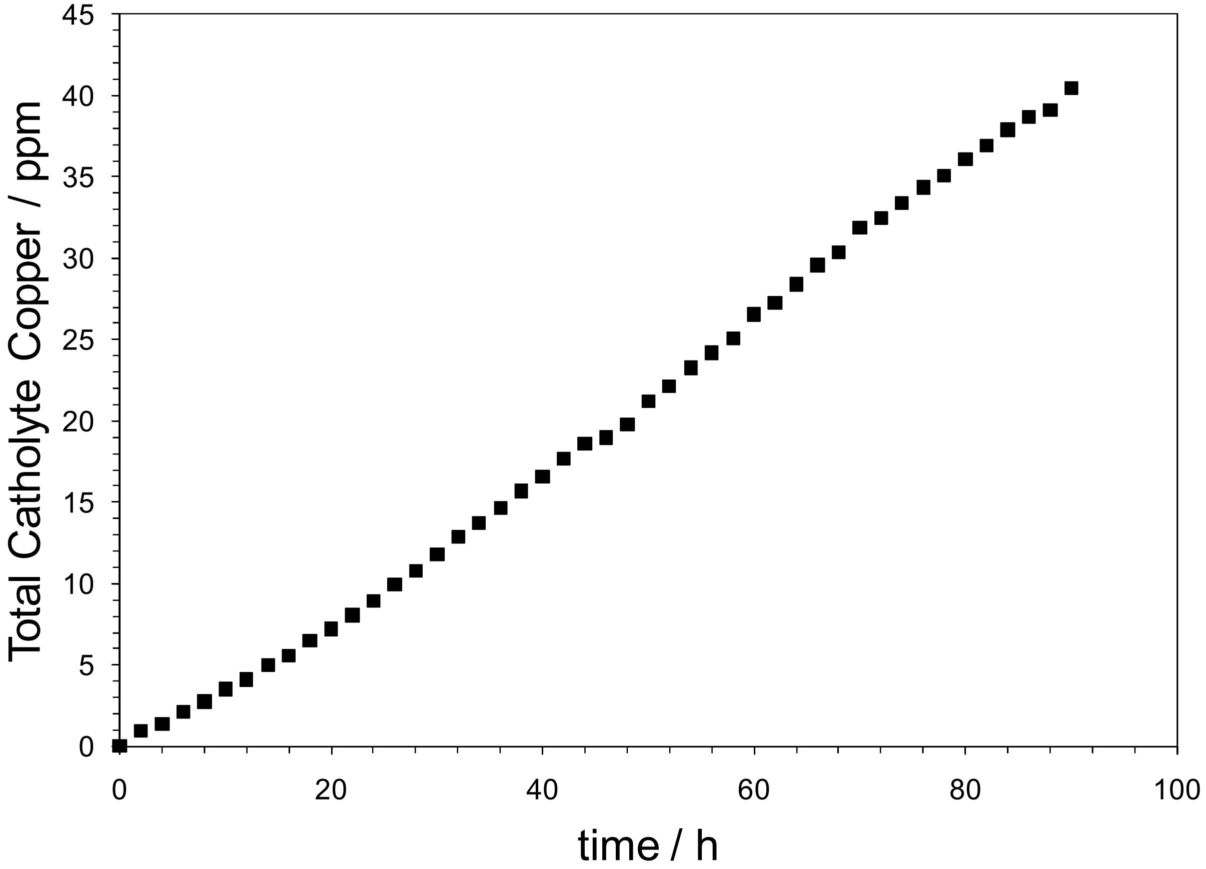

Figure 3 Total Copper Concentration in the Catholyte during a Single-Cell Electrolysis Experiment.

A SEM/EDX analysis of the cathode used to obtain the data presented in Figure 2 showed that there was no metallic copper present on the cathode following the electrolysis experiment. This would suggest that the time dependent cell voltage that was reported above for this experiment cannot be accounted for by copper metal deposition on the cathode electrocatalyst. According to Reference [8], copper deposition on the cathode is not expected to take place under the experimental conditions used to obtain the data presented in Figure 2 (i.e. current density and HCl concentration). Thus, the experimental data is consistent with literature data. The rise in cell voltage could be the result of an increasing copper (II)/copper (I) concentration ratio. Even though copper (II) is converted back to copper (I) by reaction with copper metal, the efficiency of the process, based on numerous experiments, would seem to be about 99%. It is also possible that the resistance of the cation exchange membrane could be increasing due to the presence of copper species in the membrane. If the resistance of the membrane increases then the cell voltage would be expected to increase as well.

We are interested in developing an electrolyzer that can operate at a current density of about 0.5 A•cm^{-2} with a cell voltage lying between 0.6 and 0.7 V. At this high current density copper deposition could be an issue if an 11 M HCl catholyte were used and will definitely be an issue, even at lower current densities, if the HCl concentration is dropped to say 6 M [8]. If copper deposition is an issue then the zero-gap-cathode/zero-gap-anode configuration can no longer be adopted. As a result, ways of preventing copper species from entering the catholyte during CuCl/HCl electrolysis are being investigated.

One area of active research that we are engaged in involves the development of alternative membranes that are capable of stopping copper species from crossing over and entering the catholyte. This research is ongoing and will not be discussed here. A second avenue of research and development has been the design of a new electrolysis cell that can prevent copper species from entering the catholyte. The design of this cell is proprietary and a patent for its design will be applied for. Therefore, details of the cell design will not be disclosed here. However, preliminary experimental data will be presented.

A plot of cell voltage versus time which was obtained using our newly designed electrolysis cell is presented in Figure 4. The experimental conditions used to obtain this data can be found in Table 2. As Figure 4 shows, the performance of the CuCl/HCl electrolysis cell in terms of cell voltage stability has improved significantly. After 50 h of continuous operation the cell voltage was found to be 0.625 V which is 0.004 V lower than the 0.629 V observed 72 s after the experiment began. During this experiment the copper (I) and copper (II) concentrations in the catholyte where measured *in-situ* using UV-visible spectrophotometry. The data showed that no copper species were present in the catholyte during this experiment. Comparing Figure 2 and Figure 4 it is clear that lower cell voltages are observed with our conventional cell design (Figure 2). We are attributing the higher cell voltages observed with our new cell design to a higher internal cell resistance. As part of future work we will be investigating ways to reduce the internal resistance of the cell in an effort to lower the cell voltage.

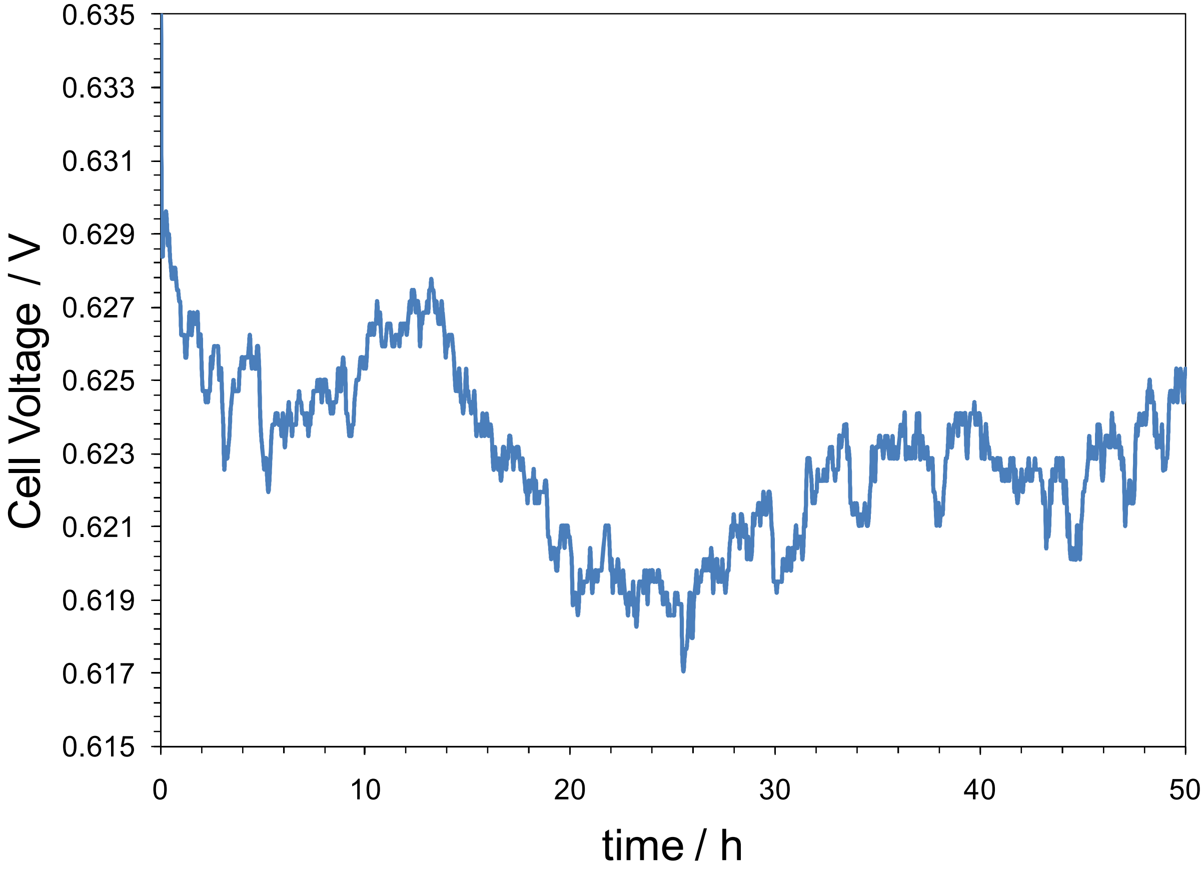

Figure 4 Cell Voltage versus Time Data obtained from an Electrolysis Cell having a Proprietary Design.

4. Conclusions

Based on the experimental data presented the following conclusions can be drawn:

- The performance of the CuCl/HCl electrolyzer (of conventional design) in terms of cell voltage stability was good only during the first 10 h of constant current electrolysis. After this initial period the cell voltage increased.

- The cell voltage values that were observed did not exceed 0.530 V even after 90 h of constant current electrolysis. This demonstrates the potential of the CuCl/HCl electrolysis reaction for hydrogen production.

- Since copper species cross the membrane from the anolyte to the catholyte during CuCl/HCl electrolysis, the time dependence of the cell voltage may be due to the presence of copper species in the membrane. Alternatively, the increase in cell voltage could arise from an increase in the copper (II)/copper (I) concentration ratio.

- When an electrolysis cell (proprietary cell design) capable of keeping copper species out of the catholyte was used the performance of the cell in terms of cell voltage stability was significantly improved. With this cell a stable cell voltage was observed for 50 h of constant current electrolysis. The cell voltage values observed during this period were around 0.623 V which are higher than the values observed from an electrolysis cell of conventional design. The higher cell voltages are being attributed to a higher internal cell resistance.

5. References

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