NUCLEAR HYDROGEN PRODUCTION SUITED FOR CANADIAN SUPERCRITICAL WATER-COOLED REACTORS

S. Suppiah, L. Stolberg, S. York and A. Shkarupin
Atomic Energy of Canada Limited, Chalk River Laboratories, Ontario, Canada

Abstract

The Copper-Chlorine thermochemical cycle, a moderate temperature hydrogen production process comprising chemical and electrochemical steps requiring a maximum temperature of only about 550°C, is well suited for integration with the Supercritical Water-Cooled Reactor under development in Canada. The technical feasibility of all the steps of this process has been confirmed. Significant advancements in the production of hydrogen from direct electrolysis of CuCl/HCl as the electrochemical step in this cycle have been demonstrated at the Chalk River Laboratories of Atomic Energy of Canada Limited. This progress has been achieved through a fundamental understanding of the electrochemical reactions and selection of suitable operating conditions.

1. Introduction

Several countries around the world have embarked on developing advanced reactor systems operating at temperatures higher than the current reactor systems to increase the overall efficiency of heat and/or power production. The heat available at the higher temperatures can be used for various thermochemical cycles and/or high temperature electrolysis to produce hydrogen more efficiently. Many countries are developing the Very High Temperature Reactors (VHTRs) that can provide the high temperature (>800ºC) needed for thermochemical cycles such as Sulphur-Iodine and Hybrid-Sulphur. Canada is developing the moderate temperature Supercritical Water-Cooled Reactor (SCWR), capable of providing a maximum reactor outlet temperature of about 625°C, as its Generation IV reactor system. Since the Copper-Chlorine (Cu-Cl) Thermochemical Cycle only requires a maximum temperature of 550°C, it is ideally suited for integration with the Canadian SCWR. The Cu-Cl thermochemical cycle is a hybrid process that uses both heat and electricity to carry out a series of chemical and electrochemical reactions (shown below) with the net overall reaction being the splitting of water into hydrogen and oxygen.

Table 1. Reactions in the four step Cu-Cl cycle.

Reaction Stoichiometry	Temperature (°C)	Equation
$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$	425-450	(1)
$4CuCl(a) \rightarrow 2CuCl_2(a) + 2Cu$ (electrochemical)	<100	(2)
$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2\ (s) + 2HCl(g)$	300-375	(3)
$Cu_2OCl_2\ (s) \rightarrow 2CuCl(l) + \frac{1}{2}O_2(g)$	450-530	(4)

Lewis et al. [1, 2] at Argonne National Laboratory (ANL) have confirmed that all the reactions shown in Table 1 are thermodynamically feasible. They have also conducted proof of principle experiments for the generation of H_2 (Equation 1), Cu (Equation 2), HCl (Equation 3) and O_2 (Equation 4). However, there are numerous challenges associated with each step involved in this cycle, in addition to the challenges related to the integration of this cycle to the SCWR. The challenges involved in the development of the electrochemical step (Equation 2) of disproportionating CuCl in an aqueous system are considered to be quite significant from technological and economical points-of-view. The electrochemical step (Equation 2) has provided a major technical challenge to the development of the Cu-Cl process. Also the energy requirement for this step is a significant fraction of the overall process [1,2]. As a result, a concerted effort has been focused on the development of this step to advance the overall cycle development.

While the above four-step process was drawing attention internationally, AECL focused on a variant of the above cycle, proposed by Dokiya and Kotera [3] involving direct generation of hydrogen through the following electrochemical step, Equation (5), replacing steps shown in Equations (1) and (2) above.

$$2CuCl + 2HCl \rightarrow H_2 + 2CuCl_2 \qquad <100°C \qquad (5)$$

Obviously, combining the two steps into one and avoiding solid copper handling issues would minimize the complexity of the process. The efforts at AECL have focused on advancing the above hydrogen production step through a fundamental understanding of the anode and cathode electrochemical reactions and developing suitable membranes and cell designs in addition to determining the appropriate cell operating conditions. Some of the latest results from this work are presented here.

2. Experimental

Single cell CuCl/HCl electrolysis experiments have been carried out in the test facility shown in Figure 1. In general, the anolyte and catholyte are recycled through the electrolysis cell after their compositions are adjusted approximately to the desired levels at the inlet of the cell. Some of the studies also included single pass flow through the cell maintaining a given current density for which the flow rate was reduced from $1.0\ L\cdot min^{-1}$ to $3.5\ mL\cdot min^{-1}$. The cell design is similar to a PEM fuel cell in which a membrane separates the anode and cathode compartments. The cathode and anode areas are each $25\ cm^2$ and they are fabricated from graphite separator plates spray-coated with platinized carbon. In general, the catholyte is 6 M HCl and the anolyte 1 M CuCl dissolved in 6 M HCl. Some of the experiments involved studying the effect of different concentrations of these components and they are specified where necessary in the following sections. All experiments are carried out at ambient temperature and pressure.

The voltage or current applied across the electrolysis cell is supplied by the “Potentiostat” and “Power Supply”. This instrumentation is controlled by the ‘Computer’, which also collects and stores experimental data.

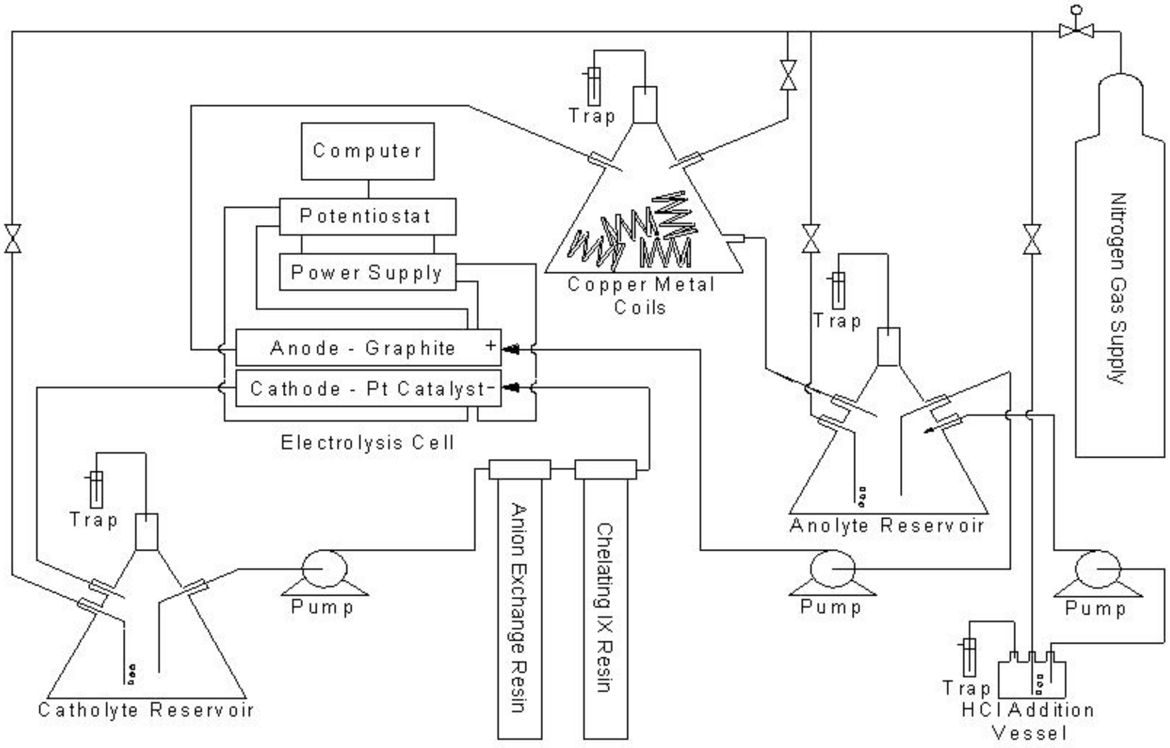

Figure 1 Schematic of the experimental facility used in the single cell experiments.

3. Results and discussion

Using the single cell experimental facility shown in Figure 1, Stolberg et al. [4] demonstrated that a current density of 100 mA·cm^{-2} could be measured at a cell voltage of 0.622 V in a study carried out with 6 M HCl as catholyte and 1 M CuCl in 6 M HCl as anolyte. However, the cell voltage was 0.11 V greater than the value predicted from the half-cell experiments, obviously reflecting the resistances within the cell. In their study a maximum current density of 429 mA·cm^{-2} was achieved at 0.9 V. While this level of current density is attractive for cell operation for the Cu-Cl cycle, the cell voltage is too high to be economical since Lewis et al. [1,2] determined the optimum voltage required to be about 0.6 V. In addition, the performance of the electrochemical cell needs to be maintained above a desired level over several years for economical application of the Cu-Cl cycle for hydrogen production.

Figure 2 shows the cell potential as a function of time at a constant cell current density of 100 mA·cm^{-2} at 1.0 L·min^{-1} of each catholyte and anolyte recycle flow through the cell. As can be seen, a steady increase in the measured voltage was recorded at the constant current density. This steady decline in cell performance was typical of the experiments carried out with catholyte recycled through the cell. Visual observations indicated the presence of traces of copper on the membrane and on the cathodes. Also, copper species were detected in the catholyte. Obviously, the ion-exchange method used to remove the copper species prior to the catholyte being recycled is inadequate. It was suspected that the presence of copper may be responsible for the instability observed in the cell potential during constant current single-cell electrolysis experiments where the catholyte solution was recycled. Under the actual operating conditions of the cell, one would not expect the catholyte to be recycled as done in the experiments in the laboratory. In order to determine if the observed instability was mostly an artifact of the laboratory experimental procedure used, experiments were conducted with once through catholyte and recycled anolyte flows through the cell. The catholyte flow had to be reduced to 3.5 mL·min^{-1} and the current applied to the cell was also reduced. Thus, the electrode and membrane areas were reduced considerably to maintain the current density at 100 mA·cm^{-2}. As can be seen from Figure 3, over the 72 hours of operation, the cell potential increased only marginally (0.016V), compared to the recycled flow conditions, confirming the positive effect of once-through catholyte flow through the cell. The reason for the oscillatory nature of the results seen in Figure 3 is not known. However, the results are encouraging considering the minimum values observed for the cell potential all lie within the 0.58 V to 0.59 V potential region.

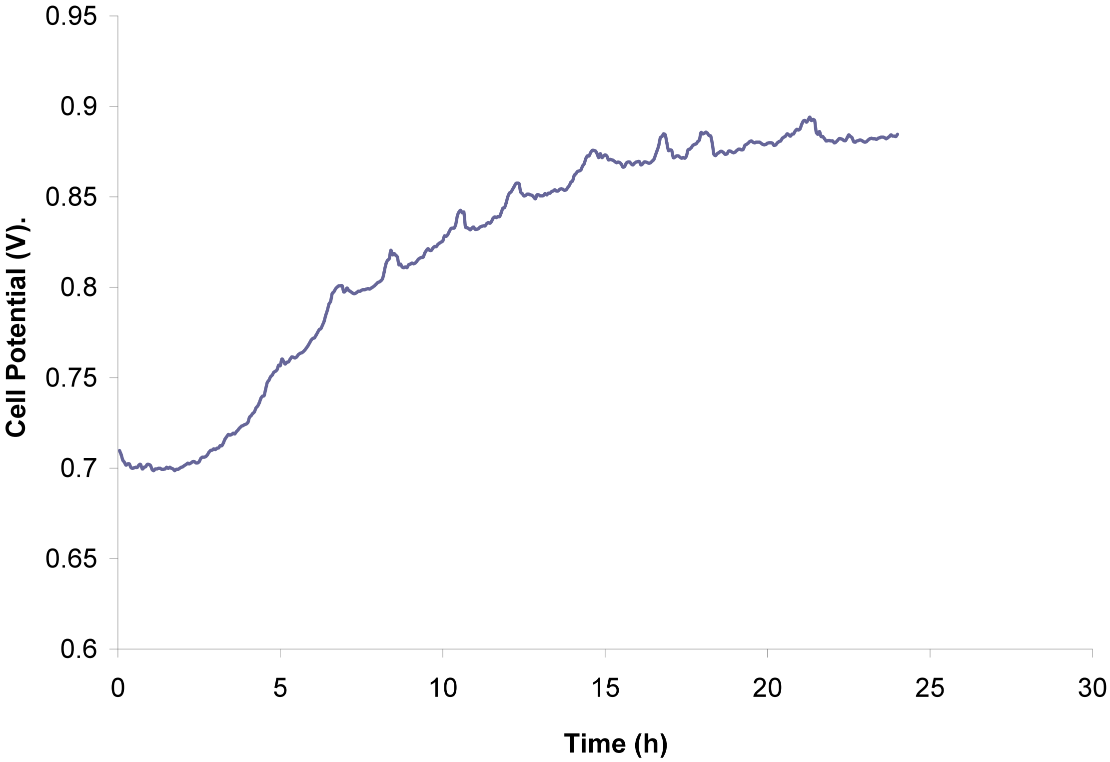

Figure 2 Cell potential recorded during a constant current single-cell electrolysis experiment.
Current density 100 mA·cm-2 and catholyte and anolyte recycled at 1 L·min-1.
6 M HCl catholyte and 1 M CuCl in 6 M HCl anolyte.

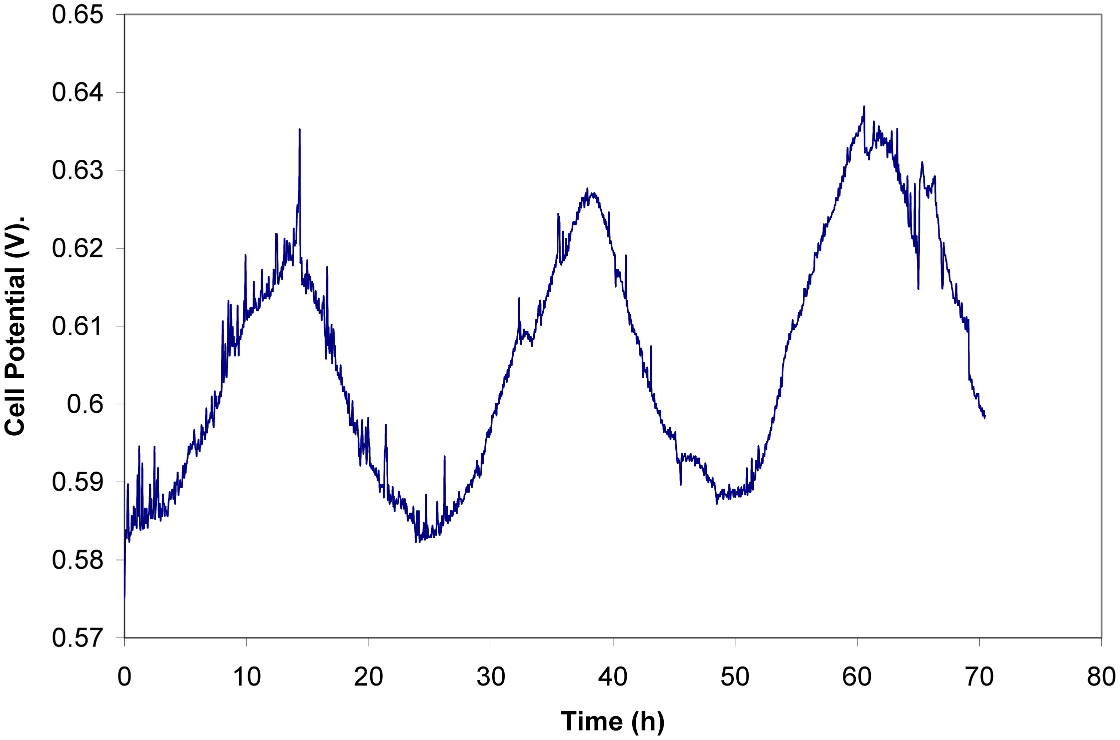

Figure 3 Cell potential recorded during a constant current single-cell electrolysis experiment. Current density 100 mA·cm-2 and catholyte once-through flow and anolyte recycled flow at 3.5 mL·min-1.

As part of the effort to understand the effects of experimental conditions on the stability of the voltage with time, the effect of increasing the HCl concentration was studied, and some of the results are shown in Figure 4. In this study the HCl concentration was the same for both the anolyte and catholyte solutions, but was adjusted from 6 M to 10 M. The anolyte was 1.0 M CuCl in HCl. It is clear from these results that a high HCl concentration yielded a more stable cell performance, though the performance decreased at all conditions studied. However, the time dependence profile at 10 M HCl concentration is much weaker than at 6 M HCl concentration.

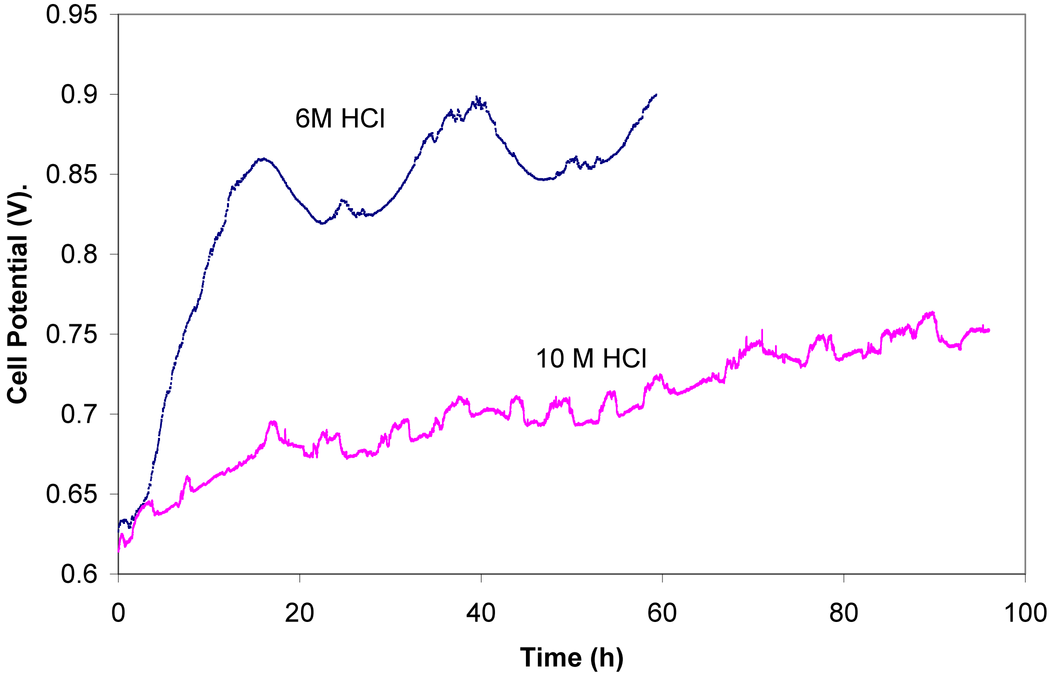

Figure 4 Cell potential against time at two different HCl concentrations. Current density 100 mA·cm-2 and catholyte and anolyte recycled at 1 L·min-1.

Figure 5 shows plots of total catholyte copper (in mg) against time for 6 M and 10 M HCl concentrations. The copper concentration was measured by UV-visible spectrophotometry. In general, the amount of copper present in the catholyte increased fairly linearly with time. The slope of these linear plots decreased with increasing HCl concentration, showing the positive effect of providing high HCl concentration. Lower copper concentrations in the catholyte at high HCl concentrations could explain the more stable voltage with time observed at high HCl concentrations compared to lower HCl concentrations (Figure 4).

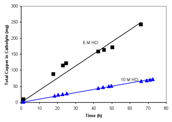

Figure 5 The amount of copper present in catholyte as a function of experimental time. Current density 100 mA·cm-2 and catholyte and anolyte recycled at 1 L·min-1.

The experimental results presented in the preceding section have shown that there is a clear benefit to increasing the HCl concentration. Higher HCl concentration means that higher CuCl concentrations can be studied because the solubility of CuCl increases with increasing HCl concentration (actually increasing chloride concentration). Higher CuCl concentrations mean that lower over potentials may be required to generate a specific current density. Thus, it was of interest to see what effect increasing the CuCl concentration has on the concentration of copper entering the catholyte and consequently on the stability of the voltage with time.

Figure 6 shows the amount of total copper measured in the catholyte as a function of time and CuCl concentration in the anolyte. The HCl concentration was 10 M for each test. In general, the amount of copper present in the catholyte increased linearly with time during the electrolysis experiment. As can be seen, for a given length of the test, the amount of copper present in the catholyte increased with increasing CuCl concentration in the anolyte. Since all conditions except the CuCl concentration was constant, the Cu(II) concentration should be independent of the CuCl concentration. Hence, the increased presence of copper in the catholyte with increasing CuCl concentration in the anolyte cannot be due to a simple increase in $CuCl_2$ concentration in the anolyte. However, it has to be due to increased differential in the copper concentration between the anolyte and catholyte and the consequent increase in the diffusion of all copper species.

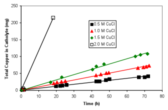

Figure 6 Effect of CuCl concentration in the anolyte on the amount of copper present in the catholyte. Current density 100 mA·cm-2 and anolyte and catholyte with 10 M HCl recycled at 1 L·min-1.

4. Conclusions

The results have shown that direct electrolysis of CuCl/HCl anolyte and HCl catholyte system to produce hydrogen in a PEM-type cell is feasible at a voltage as low as 0.59 V and 100 mA·cm^{-2} current density. A significant concentration of copper was found in the HCl anolyte due to the diffusion of copper species through the membrane. Increasing the concentration of HCl in the anolyte and catholyte reduced the amount of copper present in the anolyte. A corresponding improvement in the stability of the voltage was observed with time. There is evidence that the ion-exchange method used to remove the copper species for the purpose of recycling the catholyte was inadequate. Tests carried out at the same current density with once-through anolyte flow through the cell produced significantly greater stability of the voltage with time. Increasing the CuCl concentration in the anolyte also increased the concentration of copper species in the catholyte. Based on the finding that the presence of copper was responsible for the instability of voltage during the tests, reducing the CuCl concentration should lead to improved stability of the performance of the cell.

5. References

[1] Lewis, M. A. and M. Serban, "Hydrogen production at 550 C using low temperature thermochemical cycle", Proceedings of the OECD/NEA Meeting, Argonne National Laboratory, October 2-3, 2003.

[2] Lewis, M.A., M. Serban and J. Basco, "Generating hydrogen using a low temperature thermochemical cycle", Proceedings of the ANS/ENS 2003 Global International Conference on Nuclear Technology, New Orleans, 2003.

[3] M. Dokiya M. and Y. Kotera, "Hybrid cycle with electrolysis using Cu-Cl system", Presented at the U.S.-Japan Seminar on Key Technologies for the Hydrogen System, Tokyo, Japan, July 1975.

[4] Stolberg, L., H.Boniface, S. Suppiah, S. McMahon and S. York, "Electrolysis of the CuCl/HCl aqueous system for the production of nuclear hydrogen", Proceedings of the 4th International Topical Meeting on High Temperature Reactor Technology", HTR2008, Washington, DC, USA, September 2008.