

HYBRID CYCLE WITH ELECTROLYSIS USING Cu-Cl SYSTEM†

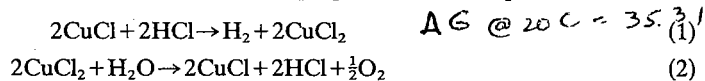
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Abstract—A hybrid thermochemical-electrolysis water splitting cycle is proposed and preliminary experimental results are presented. The electrolytic step of the cycle consists of the cathodic reduction of hydrochloric acid and the anodic oxidation of Cu⁺ to Cu²⁺. The cycle is closed by the reaction of CuCl₂ with steam at a temperature above 600°C to produce O₂, CuCl and HCl.

INTRODUCTION

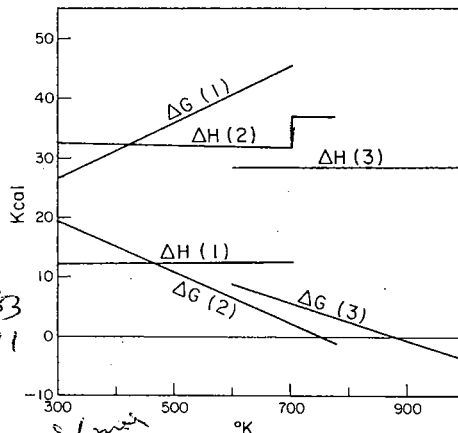
ONE METHOD of reducing the cell voltage required for water electrolysis is to conduct the reaction at elevated temperatures. An alternative method is to combine the electrolysis with thermochemical reactions. This latter method is considered to be one solution to the difficult problem of producing hydrogen from water. In the construction of such a hybrid cycle, it is desirable that the voltage required by the electrolytic step be as low as possible and that the cycle have few thermochemical steps. The Cu-Cl hybrid cycle proposed here is expressed as:



The first reaction is an electrolysis conducted at room temperature. The second reaction may be expressed more precisely in the following two reactions (2', 2''), even though these two reactions can be performed in a single reactor vessel.



The thermochemical property changes of these reactions are shown in Fig. 1.



Handwritten notes:
 $2\text{CuCl} + 2\text{HCl}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + 2\text{CuCl}_2(\text{aq})$
 $\Delta G(20^\circ\text{C}) = 25.83$
 $\Delta H(20^\circ\text{C}) = 21.11$
 $\Delta H \text{ Cu-Cl}(\text{aq}) = 13.66 \text{ kcal/mole}$
 $\Delta G(20^\circ\text{C}) = 8.37$

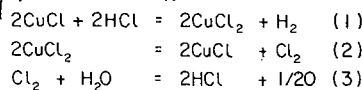
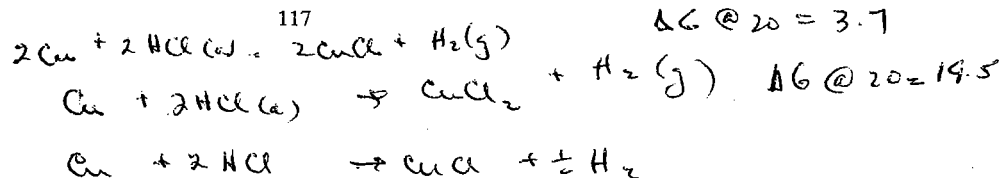


FIG. 1. ΔG and ΔH of cycle.

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Handwritten notes:
 0.8V = quiet
 0.5 mAmps
 $\Delta G = -RT \ln K$
 $= -RT \ln \frac{(\text{CuCl})(\text{H}_2)}{(\text{CuCl}_2)^2}$
 $= -RT \ln 5$

PRELIMINARY EXPERIMENT

The electrolysis cell consisted of two chambers separated by an anion exchange membrane (Celmem, manufactured by Asahi Glass Co., Ltd.) The cathode portion of the cell was a copper plate immersed in hydrochloric acid (5-35%), and the anode was a platinum plate in a solution of CuCl and CuCl₂ in hydrochloric acid (0-2.5 mol). A calomel electrode was used as the standard electrode. The potential and current of the electrolysis system were measured with a potentiostat.

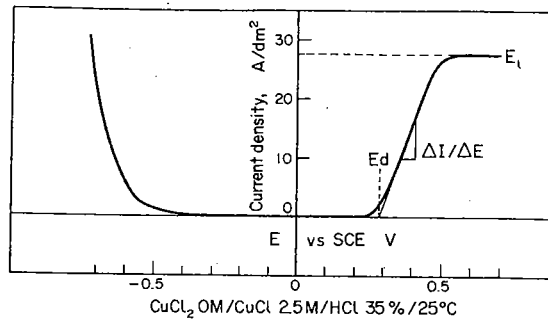
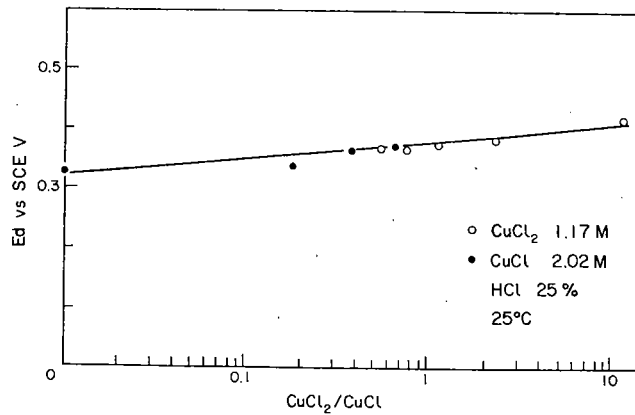
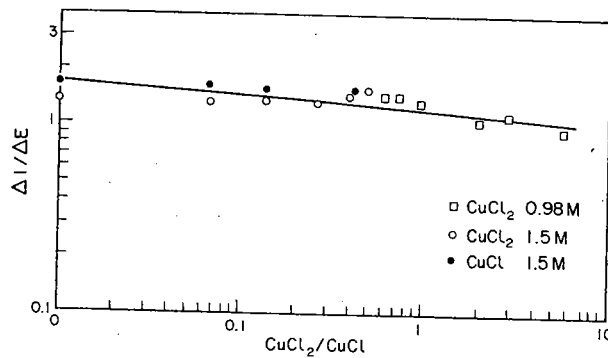
FIG. 2. i/E curve.

FIG. 3. Anode decomposition potential.

FIG. 4. Variation of $\Delta I/\Delta E$.

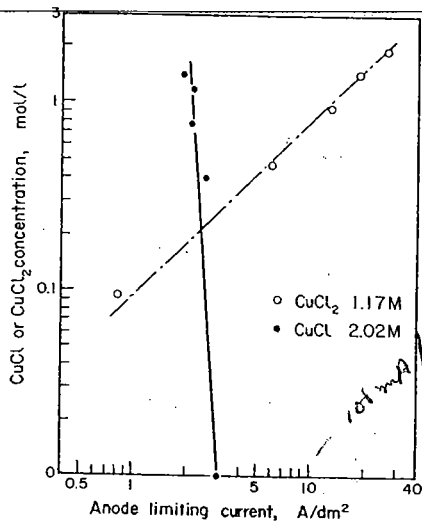


FIG. 5. Anode limiting current.

$10 \text{ dm}^2 = 10 \text{ cm}^2$

$\frac{A}{\text{dm}^2} = \frac{10^3 \text{ mA}}{10^2 \text{ cm}^2} = 10 \frac{\text{mA}}{\text{cm}^2}$

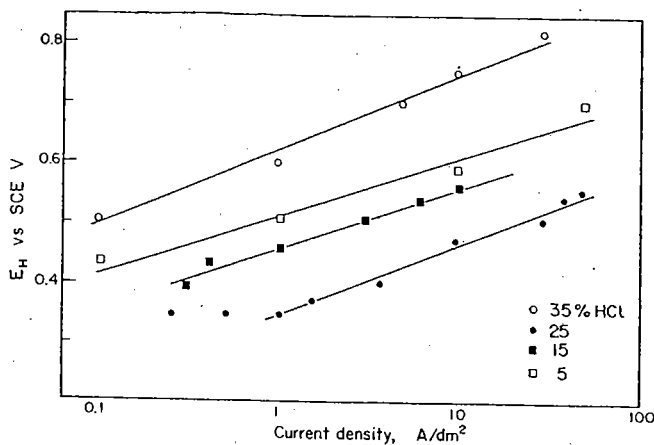


FIG. 6. Cathode i/E curve.

$1 \text{ m}^2 = 100 \text{ dm}^2 = 10^4 \text{ cm}^2$

$10 \times \frac{10 \text{ A}}{\text{dm}^2} = 10 \times \frac{10^3 \text{ mA}}{10^2 \text{ cm}^2}$

$\frac{10 \text{ A}}{\text{dm}^2} = \frac{100 \text{ mA}}{\text{cm}^2}$

TABLE I. Anode decomposition voltage

HCl wt. %	a	b
35	0.34	0.02
25	0.38	0.04
15	0.36	0.04
5	0.36	0.04

$E_{d,vsSCE}(V) = a + b \log \frac{C_{CuCl_2}}{C_{CuCl}}$

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TABLE 2. Current slope at anode

HCl wt. %	log i/\log (CuCl)	log i/\log (CuCl ₂)
35	0.96	-0.32
25	1.08	-0.20
15	1.04	-0.16
5	1.06	-0.26
av.	1.04	-0.24

TABLE 3. Cathode tafel coefficient

HCl wt. %	a	b
35	0.51	0.12
25	0.23	0.12
15	0.35	0.10
5	0.43	0.11

$$E_{vsSCE}(V) = -a - b \log i \text{ (mA/cm}^2\text{)}.$$

Some experimental results obtained with this system are shown in Figs. 2-6 and Tables 1-3. From these results, the empirical formula, at the anode, relating the current density and cell voltage of this cell is expressed as:

$$I = k \tanh \left[n \frac{i}{E} (E - Ed) \right] C_{HCl}^{-0.5} C_{CuCl}^{1.04} C_{CuCl_2}^{-0.24} \quad (3)$$

Where:

$$i = (\text{A/cm}^2)$$

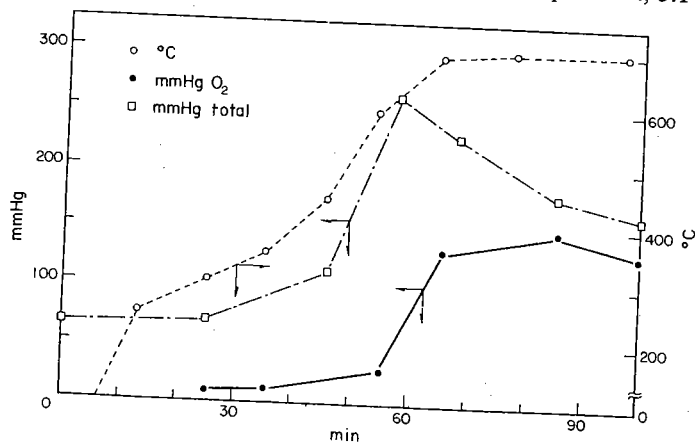
$$E - Ed = V$$

$$k = k^* \exp(-E_{act}/RT) = 0.6 \text{ (25}^\circ\text{C)}$$

$$n = 10$$

$$i/E = 1.5.$$

For the thermochemical reaction expressed in Eq. (2), the apparatus used was an ordinary glass reactor with a recirculating pump and an attached vacuum system. A gas chromatograph attached to the system was used for sample analysis. At the start of the experiment, 5.1 g of CuCl₂ were

FIG. 7. O₂ evolution.

placed in the reactor and the vessel was evacuated. Throughout the experiment, the vapor pressure of H_2O was maintained at 92 mm Hg in the reactor. All of the gases were recirculated in an inert He atmosphere. The total vapor pressure and the partial vapor pressure of O_2 are shown in Fig. 7.

CONCLUSIONS

The merit of a hybrid cycle lies in the possibility of obtaining low cell voltage in the electrolytic step. The cell voltage of the Cu-Cl system proposed here is found to be 0.6–1.0 V, according to the current density in this preliminary experiment. At present, it cannot be determined if this is an acceptable value. The ease of conducting the thermal reactions is a very attractive feature of this cycle. From these preliminary results, it may be concluded that this cycle merits further investigation as a candidate for water decomposition. More details are needed on electrode materials, the diaphragm membrane, and the reaction kinetics of O_2 evolution before a conclusive analysis of the total system can be made.

Figs. 2-6 and Tables 1-3.
re current density and cell

(3)

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