ANODE ELECTRODE MATERIALS FOR USE IN THE Cu-Cl THERMOCHEMICAL CYCLE
FOR THE PRODUCTION OF HYDROGEN

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Abstract

In this paper we have investigated the anode electrochemical kinetics of CuCl electrolysis under conditions relevant
to the Cu-Cl thermochemical cycle. Experiments were carried out using both solid platinum and glassy carbon
electrodes. Cyclic voltametry (CV) at a rotating disk electrode (RDE) was used to investigate the electrochemical
kinetics in order to ascertain if a noble metal based electrode was required for the anode. Inverse Levich analysis of
our results show that the under strongly acidic conditions (e.g pH < 2), the oxidation of Cu⁺ occurs at about ca. 3-
times faster rate on a Pt surface. However, at higher pH, the difference between Pt and glassy carbon electrode is
greatly reduced. Furthermore, this difference in intrinsic activities can be more than compensated at all pH’s by the
use of high surface area carbon blacks. We have also investigated Ceramic Carbon Electrodes (CCE) for use at the
anode. Preliminary experiments show CCE based anodes enhanced anode performance.

1. Introduction

The need for hydrogen is predicted to increase over next 10 years. The very rapid increasing demand for hydrogen
has catalyzed research in various ways of producing hydrogen. Most of the world’s hydrogen (about 97%) is
currently derived from fossil fuels. Thus, a key future challenge will be sustainable large-scale production of
hydrogen at low costs. One of the most efficient and viable way is the splitting of water at high temperature.
Research into water-splitting focus on two main methods - thermochemical cycles and high-temperature electrolysis.
More than 100 cycles have been proposed for the production of hydrogen (Carty et al., 1981, and Brown et al.,
2000), but the viability of only a few cycles have been demonstrated. The copper chloride cycle is as most promising
that has been demonstrated by researchers at Argonne laboratory (Lewis et al., 2003). The main advantage of this
cycle is that the operating temperature is < 550°C. One of the main challenges of this process is to achieve high
efficiency during the electrolysis of CuCl (Serban et al., 2003).

The Cu-Cl cycle decomposes water into hydrogen and oxygen through intermediate copper chloride compounds. A
series of chemical reactions form a closed internal loop that re-cycles all chemicals on a continuous basis. The series
of reactions in the Cu-Cl thermochemical cycle are shown in the Table.1

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Temp. Range (°C)</th>
<th>Feed/Output*</th>
</tr>
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</table>
| 1    | 2Cu(s) + 2HCl(g) → 2CuCl(l) + H₂(g) | 430 - 475 | Feed: Electrolytic Cu + dry HCl + Q  
                        |          | Output: H₂ + CuCl(l) salt |
| 2    | 2CuCl(s) → 2CuCl(aq) → CuCl₂(aq) + Cu(s) | Ambient (electrolysis) | Feed: Powder/granular CuCl and HCl + V  
                        |          | Output: Electrolytic Cu and slurry containing HCl and CuCl₂ |
| 3    | CuCl₂(aq) → CuCl₂(s) | <100 | Feed: Slurry containing HCl and CuCl₂ + Q  
                        |          | Output: Granular CuCl₂ + H₂O/HCl vapours |
| 4    | 2CuCl₂(s) + H₂O(g) → CuO*CuCl₂(s) + 2HCl(g) | 400 | Feed: Powder/granular CuCl₂ + H₂O(g) + Q  
                        |          | Output: Powder/granular CuO*CuCl₂ + 2HCl (g) |
| 5    | CuO*CuCl₂(s) → 2CuCl(l) + 1/2O₂(g) | 500 | Feed: Powder/granular CuO* CuCl₂(s) + Q  
                        |          | Output: Molten CuCl salt + oxygen |

Note: Alternative 4-step cycle combines above steps 1 and 2 to produce hydrogen directly as follows:
2CuCl(aq) + 2HCl(aq) → H₂(g) + 2CuCl₃(aq)

* Q = thermal energy, V = electrical energy
For the electrochemical step, the anode feed of CuCl (aq) must also contain chloride ion at a concentration greater than 1M in order to prevent the precipitation of CuCl(s). In addition, when the chloride ion concentration is greater that 1M, Cu(I) can form several anionic species (e.g. CuCl\(^{2−}\), CuCl\(^{3−}\)) (Xiao et al). Thus, the cell reactions can be expressed as follows:

\[
\begin{align*}
\text{CuCl}_2^{-}(aq) & \rightarrow \text{CuCl}_2^{-}(aq) + e^- \\
\text{CuCl}_2^{-}(aq) + e^- & \rightarrow \text{Cu}(s) + 2\text{Cl}^{-} \\
2\text{CuCl}_2^{-}(aq) & \rightarrow \text{CuCl}_2^{-}(aq) + \text{Cu}(s)
\end{align*}
\]

Alternatively, H\(_2\)(g) could be produced at the cathode (instead of solid copper). Because of this, our initial investigations have focused on the electrochemical kinetics at the anode since that reaction is common to both cycles.

Here we report a rotation disk electrode (RDE) study of the anode electrochemical kinetics on a pure Pt surface and on pure glassy carbon (GC) surface at variable pH. The primary goal was to determine if there is any performance gain by employing a noble metal based electrode material.

We have also studied the feasibility of using Ceramic Carbon Electrode (CCE) for the electrolysis of CuCl (Santhanam and Easton, 2008). The CCEs consist of electronically conductive carbon particles that are bound together by a ceramic binder formed through the sol-gel process (Tsionsky et al., 1994, Rabinovich and Lev, 2001). These ceramic carbon electrodes have been found to be promising system for many electrochemical systems due to their high surface area and durability. The CCE have found numerous electrochemical applications including fuel cells (Lev et al., 1997). For example, Anderson et al., have also reported the use of CCE-based electrodes for direct methanol fuel cells (Anderson et al., 2002). We have investigated CCE that formed from an amino-functionalized silane that should enhance the diffusion of Cu(I) species with the electrode layer.

2. Experimental

a. CCE Preparation

The ceramic carbon electrode (CCE) material used for this study was prepared by using a base-catalyzed sol-gel method. 200mg of Vulcan XC72 carbon black (Cabot Corp.) was mixed with the 13.5mL methanol (Fisher), 2.3mL of deionized water. 5.2 µL of 6M ammonium hydroxide was added to the mixture and stirred for 10 min. 4 mL of 3-aminopropyl trimethoxy silane (Aldrich, 97%) was added drop wise using a syringe. The reactant mixture was then stirred overnight in a covered beaker. Solvent was then allowed to slowly evaporate to form the gel. Electrodes were prepared by dip-coating a piece of carbon fiber paper (CFP) (TPGH-090, BASF) with the gel, which was subsequently dried at room temperature for 6hr, followed by drying in an oven at 80°C for 12 hours. The remaining gel was transferred to a petri dish where the gel was allowed to dry at room temperature for 6hr followed by drying at 80°C for 12 hours. The remaining gel was kept for characterization.

b. Electrochemical Experiments

All electrochemical experiments were performed in a one-compartment cell equipped with a Pt wire counter electrode and a saturated calomel electrode (SCE) reference electrode. Measurements were made at room temperature in a nitrogen- purged aqueous solution containing 1 mM CuCl (Alfa Aesar, 98%) and 1.5 M HCl. Solution pH was manipulated by drop wise addition of NaOH. Electrochemical measurements were performed using a Solartron 1470E Multichannel Potentiostat controlled using Multistat software (Scribner Associates). Solid Pt and glassy carbon (5mm diam, Pine Instruments) rotating disk electrodes (RDE) or CFP-based electrode were employed as the working electrodes.
3. Results and Discussion

(a) Pt vs Carbon Based Electrodes

The anodic oxidation step copper chloride was examined using platinum (Pt) and glassy carbon electrode (GC). The cyclic voltammograms (CVs) obtained at a stationary working electrode is presented in Fig.1. The results show that there is no difference in the potential requirements to drive the reaction on either a Pt or GC electrode surface. However the limiting current densities achieved using Pt electrode surface were approximately three times higher than that achieved with glassy carbon electrode under these conditions. Also, the Pt electrode seems to resolve two different Cu(I) species as indicated by two different peaks in the Fig.1.

![Fig.1. Cyclic Voltammetry for stationary Pt and GC electrode, Solution: CuCl = 1mM; HCl = 1.5M at room temperature.](image)

The use of a rotating disk electrode (RDE) allows for control over the mass transport conditions of the system which can be described by the Levich equation:

\[ i_{\text{lim}} = (0.620) n F A D^{1/3} \omega^{1/2} v^{1/6} C \]  

(1)

where \( i_{\text{lim}} \) is the limiting current density (A/cm²), \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( D \) is the diffusion coefficient, \( v \) is the kinematic velocity, \( \omega \) is the rotation rate of the electrode, and \( C \) is the concentration of the analyte.

A series of experiments at different electrode rotation rates were performed with both the Pt and GC electrode. A Levich plot was constructed and is shown in Fig. 2. Typical linear Levich behaviour was observed for both Pt and GC. However, the limiting currents were larger for Pt, indicating that reaction rate for the electron transfer is higher on Pt surface.

The RDE experimental results can also be interpreted using the inverse Levich equation:

\[ \frac{1}{i_{\text{lim}}} = \frac{1}{i_k} + \frac{1}{i_{\text{mt}}} \]  

(2)
Where $i_{\text{mt}}$ is the mass transport limited current and $i_k$ represent the kinetic current density in the absence of mass transfer effect. Thus the kinetic current is the intrinsic rate of charge transfer between the analyte and the electrode surface. The $i_k$ values for Pt and GC electrode are found to be 130 $\mu$A cm$^{-2}$ and 40 $\mu$A cm$^{-2}$ respectively. These experiments would imply that better anode performance would be achieved if a Pt-based electrode material was employed on the anode due to its larger intrinsic specific activity, and would in fact be somewhat contrary to AECL’s full cell results (Stolberg et al., 2008). However, when one considers that a typical carbon supported Pt catalyst employed in an electrolysis cell contains only 20 wt% Pt (and 80 wt% carbon black), the performance gained by the addition of Pt is unnoticeable due to the overwhelmingly larger (ca. 14,000 times) carbon surface area. Thus, high surface area carbon blacks are the electrode materials of choice based upon their performance as well as their substantially lower cost.

(b) pH Dependence

In order for CuCl to remain in solution, the concentration of Cl$^-$ must be maintained above 1M. However, the source of Cl$^-$ does not need to originate from HCl; it could originate from pH neutral salts such as NaCl (Winter et al., 2007). There may be some benefits in the thermochemical cycle if less acidic conditions could be employed. A less corrosive environment may allow for lower cost materials to be used. However, the introduction of a salt like NaCl into the Cu-Cl cycle may complicate the extraction and separation of copper chloride compounds. In order to understand the impact of pH, RDE experiments were performed for each electrode material over a pH range of 1-3.5. Solution pH was increased by dropwise addition of NaOH(aq). Kinetic currents were determined as a function of pH and results are shown in Fig.3. When the pH is less that 2, $i_k$ for Pt is approximately three times larger than it is for GC. Above pH 2 there is a significant increase in $i_k$ was observed for the both electrodes. Furthermore, the difference between the $i_k$ values for the GC and Pt electrodes become substantially smaller. For example, at pH 3.5 the value of $i_k$ is 89 $\mu$A cm$^{-2}$ and 109 $\mu$A cm$^{-2}$ for GC and Pt, respectively. This further indicates the kinetic advantage of Pt is even smaller at high pH.

(c) Ceramic Carbon Electrode

The viability of CCE’s for anode were evaluated by cyclic voltammetry. Fig. 4 shows the comparison of the CV’s obtained for aminosilicate-based CCE with that obtained with a bare carbon fibre paper electrode. These clearly show a significant enhancement of current (ca. 25-fold) when the CCE electrode was used. One reason for this is the increased active area of the electrode. In addition, the presence of protonated amino functional groups on the silicate acts as anion conductors that increases the diffusion rate of anionic Cu(I) species within the layer. Further
Fig. 3: Kinetic current ($i_k$) for the Cu$^+$/Cu$^{2+}$ redox couple as a function of pH for glassy carbon (GC) and Pt electrodes (concentration of Cl$^-$ was 1.5M in all cases).

Experiments are in progress using the electrolysis of CuCl using CCE. Ongoing studies are focused on optimizing the CCE structure to further increase performance.

Fig. 4: CV of the CuCl-HCl using carbon paper coated with ceramic carbon gel.
4. Conclusions

The CV’s of CuCl-HCl system using platinum electrode seems to resolve two different species of copper (I) chloride. Furthermore, Pt based electrodes do exhibit a three-fold larger kinetic current than that of carbon-based electrode. However, the substantially larger specific surface areas of carbon blacks, coupled with the fact that they are much cheaper than Pt, make them a more appealing anode electrode material. Further increases in anode activity can be achieved by forming ceramic carbon electrodes, which promote the transport of reactant within the electrode layer.

5. References


