CERAMIC CARBON ELECTRODE-BASED ANODES
FOR USE IN THE COPPER-CHLORINE THERMOCHEMICAL CYCLE

Santhanam Ranganathan and E. Bradley Easton
Faculty of Science, University of Ontario Institute of Technology,
2000 Simcoe Street North, Oshawa, Ontario, Canada, L1H 7K4
Email addresses: ranga@uoit.ca, Brad.Easton@uoit.ca

ABSTRACT
Sol-gel chemistry is becoming more popular for the synthesis of electrode materials. For example, the sol-gel reaction can be performed in the presence of a carbon black to form a ceramic carbon electrode (CCE). The resultant CCE structure contains electronically conductive carbon particle pathways that are bound together via the ceramic binder, which can also promote ion transport. Furthermore, the CCE structure has a high active surface area and is chemical and thermally robust.

We have investigated CCE materials prepared using 3-aminopropyl trimethoxysilane. Electrochemical experiments (cyclic voltammetry, electrochemical impedance spectroscopy) were performed to characterize their suitability as anode electrode materials for use in the electrochemical step of the Cu-Cl thermochemical cycle. Our initial results have shown that CCE-based electrodes vastly outperform a bare carbon electrode, and are thus highly promising and cost-effective electrode material. Subsequent experiments involved the manipulation of the relative ratio of organosilane carbon precursors to gauge its impact on electrode properties and performance. An overview of the materials characterization and electrochemical measurements will be presented.

INTRODUCTION
A thermochemical cycle is a process by which water is decomposed into hydrogen and oxygen through a series of chemical reactions. The chemicals that are used in these reactions are regenerated and recycled during the process. After the principle of the thermochemical cycle was discovered by Funk and co-workers in the year 1966, the Gas Research Institute (GRI) funded a long term program to evaluate 200 thermochemical cycles during mid 1980’s. They have evaluated these cycles for their kinetics, thermodynamics, material stability and cost analysis and found that 80 cycles were most promising and 15 were feasible (Beghi 1986, Carty et al., 1981, and Brown et al., 2000). However all cycles have faced different challenges and are yet to progress beyond the laboratory scale.

The Cu-Cl thermochemical cycle possesses various advantages such as low operation temperature, lower demands on material construction and recycle of the chemicals than the existing ones. The Cu-Cl cycle has been the primary focus of Canadian researchers due to the fact that the low operation temperature could allow for it to be linked to Generation IV SCWR (Super-Critical Water Cooled Reactor).

The latest advances by the Canadian research team have been reported in a recent review article by Naterer et al., (2009) One of the main challenges of this process is to achieve high efficiency during the electrolysis of CuCl (Serban et al., 2003). The reactions in the Cu-Cl thermochemical cycle are shown in the Table 1.

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. CuCl₂⁻, CuCl₃⁻) (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, H₂(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 variations.
The choice of electrode material can greatly impact the electrochemical kinetics. Our previous work has shown that the reaction rate for Cu(I) oxidation is approximately three times faster on a Pt electrode compared to a carbon surface (Santhanam and Easton, 2008). However, carbon black materials have a rather large specific surface area which more than compensate for their lower intrinsic activity. This coupled with its low cost, makes carbon the ideal anode electrode materials. Thus, our work has focused on designing electrodes structure with a high surface area and high anion conductivity.

Ceramic carbon electrode (CCE) posses various desirable electrode properties, including a wide operating potential, high surface area, and high chemical and thermal stability. CCE are prepared by mixing electronically conducting carbon particles with an organosilane monomer that is subsequently polymerized via the sol-gel reaction (Kazuhiro Fujiki et al., 1998, Tsionsky et al., 1994, Rabinovich and Lev, 2001). CCEs have been reported in the literature by numerous research groups in a wide variety of applications, including fuel cells. For example, Anderson et al., have also reported the use of CCE-based electrodes for direct methanol fuel cells (Anderson et al., 2002). Eastcott and Easton, (2009) have also reported the synthesis and electrochemical studies of CCE materials for H2 air fuel cells. We also studied the feasibility of using CCE coated onto the carbon fibre paper (CFP) for the electrolysis of CuCl (Santhanam and Easton, 2008).

Here we report the fabrication and characterisation and electrochemical studies of CCE materials prepared from Vulcan XC72 carbon black and 3-aminopropyl trimethoxy silane. Under acidic conditions, the resulting aminosiloxane polymer will be protonated and thereby enhance the transport of anionic species. One key advantage of this method is that the ionomer in added in monomer form and subsequently polymerise in the presence of the carbon. Hence the ionomer is evenly distributed throughout the porous catalyst materials. The structure of polymer 3-aminopropyl trimethoxy silane is shown in Fig.1. Anode performance has been studied as a function of silane loading within the CCE layer.

Table 1. Reactions in Copper-Chloride Cycle.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Temp. Range (°C)</th>
<th>Feed/Output*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2Cu(s) + 2HCl(g) → 2CuCl(l) + H2(g)</td>
<td>430 – 475</td>
<td>Electrolytic Cu + dry HCl + Q</td>
</tr>
<tr>
<td>2</td>
<td>2CuCl(s) → 2CuCl(aq) → CuCl2(aq) + Cu(s)</td>
<td>Ambient (electrolysis)</td>
<td>Powder/granular CuCl and HCl + V</td>
</tr>
<tr>
<td>3</td>
<td>CuCl2(aq) → CuCl2(s)</td>
<td>&lt;100</td>
<td>Slurry containing HCl and CuCl2 + Q</td>
</tr>
<tr>
<td>4</td>
<td>2CuCl2(s) + H2O(g) → CuO*CuCl2 + 2HCl(g)</td>
<td>400</td>
<td>Powder/granular CuCl2 + H2O/HCl vapours</td>
</tr>
<tr>
<td>5</td>
<td>CuO*CuCl2(s) → 2CuCl(l) + 1/2O2(s)</td>
<td>500</td>
<td>Powder/granular CuO*CuCl2(s) + Q</td>
</tr>
</tbody>
</table>

Note: Alternative 4-step cycle combines above steps 1 and 2 to produce hydrogen directly as follows: 2CuCl(aq) + 2HCl(aq) → H2(g) + 2CuCl2(aq)

* Q = thermal energy, V = electrical energy

Fig.1. Structure of protonated form the 3-aminopropyl trimethoxy silane polymer
EXPERIMENTAL

CCE Preparation

The ceramic carbon electrode (CCE) material used for this study was prepared by using a base-catalyzed sol-gel method (Tsionsky et al., 1994, Rabinovich and Lev, 2001). 400mg 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. 0.5 - 1 mL of 3-aminopropyl trimethoxy silane (Aldrich, 97%) was added drop wise using a syringe. The amount 3-aminopropyl trimethoxy silane was varied in order to prepare CCEs with varying silicate loadings. 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 coating the gel onto 1 cm² region of a strip of carbon fiber paper (TPGH-090, BASF), 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 and was used for characterization. Fig.2 shows the a picture of a coated electrode as well as a schematic representation of the CCE catalysts layer.

Fig.2. A) CFP coated with CCE; B) A pictorial representation of the distribution of silica with the electrode. The black spheres represent the carbon particles and white spheres represent the silica ionomer.

Electrochemical Experiments

All electrochemical experiments were performed in a three-electrode 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. The inert atmosphere was maintained throughout the experiment in order to prevent aerial oxidation CuCl. Electrochemical measurements were performed using a Solartron 1470E multichannel potentiostat controlled using Multistat software (Scribner Associates).

Thermal Analysis

Thermogravimetric analysis (TGA) was performed in order to determine CCE composition using TA instruments Q600 SDT thermal analyser. The composition of the CCE was calculated from the TGA plots using a method similar to that reported by Eastcott and Easton, (2009). Samples were heated from room temperature to 1000°C at the rate of 20°C / min under flowing air atmosphere (50mL/min). The mass at 100°C was defined as the dry mass and used as 100% value for analysing the data.
Scanning electron microscopy
Electron microscopy was used to investigate the porosity of the composite layer deposited onto the CFP. SEM images of the CCE layer were acquired using a JOEL JSM 6400 scanning electron microscope.

RESULTS AND DISCUSSION
TGA analysis

Fig. 3 shows the TGA curves obtained under flowing air for CCE layers with various silicate loadings. All CCE materials showed a water loss between 80 and 200°C and underwent combustion between 250 – 800°C. Fig. 3B clearly shows that the combustion process occurs in two distinct steps. The first step began around 250°C and was attributed to the combustion of the aminopropyl side chain (RNH₂). Above 600°C, all the carbon in CCE material is combusted to CO₂. The residue obtained at the end of the experiment was SiO₂. The weight percentage of residual SiO₂ was used to calculate the weight percentage of organosilicate polymer in the original CCE material, which can be described by the chemical formula SiO₁.₅RNH₂. Table 2 summarizes the composition of the CCE materials used in this study. Also apparent from the TGA results is that these electrode materials are oxidatively stable up to ca. 250°C which would be a requirement for high temperature electrochemical cell operation.

![TGA graph and Differential thermogram](image)

Table 2. The composition of different CCE material as determined by TGA

<table>
<thead>
<tr>
<th>Weight % of SiO₂</th>
<th>Weight % of SiO₁.₅RNH₂</th>
<th>Wt % of C</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.6</td>
<td>21.8</td>
<td>78.2</td>
</tr>
<tr>
<td>20.1</td>
<td>36.3</td>
<td>63.7</td>
</tr>
<tr>
<td>25.9</td>
<td>56.0</td>
<td>44.0</td>
</tr>
</tbody>
</table>

SEM Analysis

SEM was used to examine the morphology of the CCE layer. Fig. 4 shows the SEM image catalyst layer that contains 36% SiO₁.₅RNH₂. The low magnification image (Fig 4A) shows that a uniform coating of CCE material was applied onto the CFP. Fig 4B shows a higher magnification image which shows the CCE layers are highly porous and have a uniform distribution at the micro/nano scale.
Electrochemical Characterization

The cyclic voltammogram (CV) obtained for each CCE sample as well as a bare CFP electrode are shown in Fig. 5. This clearly shows that there is substantial enhancement (about 4-fold) of current for all CCE-compositions compared to the uncoated CFP. This can be attributed to the substantially larger electrochemically active surface area of the CCEs as well as enhanced transport of anionic Cu(I) species (e.g., CuCl$_2^-$) within the CCE layer. It was also observed that all the three different CCE coated CFP shows similar enhancement of electrochemical activity. CV studies repeated using the CCE electrode immersed in the electrolyte for a period of 24 h reveal no change in the electrochemical behaviour. This indicates the CCE materials are stable under the under acidic environments employed. Future study of longer term stability is required.

Also apparent from these CVs are the resolution of two distinct redox waves by the CCE materials. In order to confirm the second peak is related to a Cu species and not the CCE layer itself, CV's were obtained in both the presence and absence of CuCl for the electrode containing 36% SiO$_{1.5}$RNH$_2$, which are shown in Fig. 6. The peaks are absent from the solution that does not contain CuCl, and must therefore be due to copper, possibly two different species of Cu(I) in solution. We have reported similar electrochemical behaviour using a Pt rotating disk electrode (Santhanam and Easton, 2009).

Anodic polarization

In order to better gauge the performance of these electrodes in a CuCl electrolysis cell, anodic polarization curves were obtained for each electrode material, and are shown in Fig. 7 A and B. A similar onset potential was observed for all electrode materials. However, the peak and limiting current behaviour varied greatly. All CCE-based electrodes clearly outperformed the bare CFP.

Furthermore, the performance of the CCE electrode varied with SiO$_{1.5}$RNH$_2$ loading. This observation can be explained based on the relative surface area and enhanced transport of anionic Cu(I) within the CCE layer. The maximum current density achieved with the CCE layers that contained 22% and 36% SiO$_{1.5}$RNH$_2$ were very similar.
Fig. 5: CVs obtained for CCE-based electrodes with varying amount of SiO$_{1.5}$RNH$_2$. Also shown is the response of a bare CFP electrode.

Fig. 6. Cyclic voltammogram of CFP coated CCE: a) in 1.5M HCl and 1mM CuCl; b) in 1.5M HCl.
However the anodic peak current obtained for the CCE contains 22% SiO$_{1.5}$RNH$_2$ showed a CV-like peak and subsequently decayed before stabilizing at a lower value. This kind of peak and decay was not observed for the CCE layer containing 36% and 56% SiO$_{1.5}$RNH$_2$. Rather a sigmoidal wave shape with a plateau limiting current was observed. This may be due to enhanced anion conductivity imparted by the higher aminosilane loading. The maximum limiting current was achieved with a 36% SiO$_{1.5}$RNH$_2$ loading. A decrease in limiting current was observed when the amount of SiO$_{1.5}$RNH$_2$ was increased to 56%. This is likely due to the fact that there is a reduction in the available carbon surface area due to the high loading.

CONCLUSIONS

Amionsilane-based CCE electrodes have been prepared and investigated for use as anode materials in the CuCl electrolysis step of the Cu-Cl thermochemical cycle. Electrochemical results show that these CCE’s outperform bare CFP based electrodes. This in increased performance was attributed to the higher electrochemically active surface area and the enhanced transport of anionic Cu(I) species within the 3-dimensional electrode layer. Characterization of these CCE material showed that they have good thermal stability and can be used at high temperatures. Thus we believe that these CCE materials are very promising anode materials. However the efficiency of CCE at high concentration of CuCl is yet to be examined. Future experiments will focus on evaluating the efficiency of the CCE material under high concentration of CuCl and HCl.

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REFERENCES


