POLYANILINE COMPOSITE MEMBRANES FOR HYDROGEN PRODUCTION IN Cu-Cl THERMOCHEMICAL CYCLE

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1 ABSTRACT

The dissociation of water by a thermochemical cycle is a promising green method of producing hydrogen on a large scale. A thermochemical cycle is comprising a closed loop of chemical reactions that ultimately leads to the decomposition of water to hydrogen and oxygen. The Cu-Cl cycle is a promising hybrid cycle which has many potential advantages. First, it has relatively low operating temperatures (500-600 °C). Second, it can have high energy efficiency by utilizing low-grade waste heat. One step in the Cu-Cl cycle employs an electrochemical process where Cu(I) is converted to Cu(II) and hydrogen is generated from an acidic solution. The electrochemical cell used is similar to a water electrolysis cell and employs a membrane electrode assembly (MEA) that utilizes a proton exchange membrane (PEM). The most widely used PEM, Nafion, is permeable to cations and neutral species. Because of this, Cu can permeate the membrane and enter the cathode where it is readily deposited on Pt catalytic sites. This drastically reduces cathode efficiency as well as the whole cell.

In this study, we have examined several alternative membranes, including Nafion/polypyrrole and Nafion/polyaniline composite membranes. Ex situ permeation experiments were performed along with impedance spectroscopy to investigate the rate of the copper crossover and the conductivity of the composite membranes, respectively. A full electrolytic cell was used to understand how these factors influence the performance and the hydrogen production efficiency.

2 INTRODUCTION

The most common method of producing hydrogen on a large scale is steam methane reforming, which employs fossil fuels. Over usage of fossil fuels causes devastating effects on the environment such as air pollution. As an alternative, thermochemical cycles can be used to produce hydrogen from water. A thermochemical cycle combines heat and chemical reactions to split water into hydrogen and oxygen. All chemicals used in this cycle are continuously regenerated. Hybrid thermochemical cycles utilize at least one electrochemical reaction in the cycle. The Copper-Chloride (Cu-Cl) cycle is one of the most promising thermochemical cycles due to lower operating temperatures, and high overall efficiency.

The Cu-Cl thermochemical cycle is a hybrid cycle which consists of three reactions. Two of these reaction are thermally driven at temperatures above 400 °C, while the third reaction is electrochemical. The electrochemical reaction occurs at temperatures below 100 °C with Cu(I) being oxidized to Cu(II) at the anode, and hydrogen evolved from acid at the cathode. The cell is operated in essentially the same manner as a proton exchange membrane (PEM) electrolyzer. Nafion is the PEM of choice due to its high chemical and mechanical stability as well as high proton conductivity (S. Slade et al., 2002). However, Cu ions can permeate from the anolyte through Nafion and enter the cathode compartment, which poisoning the Pt sites on the cathode. This process is referred to as copper crossover and it severely decreases cell performance and the efficiency of the entire cycle.

Copper crossover is similar to the phenomena of methanol crossover in direct methanol fuel cells (DMFC’s). Thus, we have hypothesized that strategies that have led to reductions in methanol crossover could also mitigate Cu crossover. To investigate this further, we have prepared Nafion/conducting polymer composite membranes by in situ polymerization with some promising monomers such as aniline. Because of the stability and high conductivity of the formed polymer, polyaniline (PANI) was used in many applications in various fields (Bhattacharya et al., 1996; Gospodinova et al., 1998). The strategy of reducing the methanol crossover depends on reducing the porosity of the Nafion membrane to prevent or reduce the permeation of methanol. Nafion/PANI composites have been shown to reduce the rate of methanol crossover in DMFC (Jia et al., 2000; Neburchilov et al., 2007; Wang et al., 2009).
Our focus in this paper is to study Nafion/PANI composite membranes prepared with Nafion membranes of different thickness and compare them with pristine Nafion membranes. The physical properties of the modified composite membranes, such as the water uptake, ion exchange capacity (IEC) and proton conductivity ($\sigma$) were studied. Furthermore, the Cu diffusion was investigated using an ex situ diffusion cell. In addition, the efficiency of these composite membranes in eliminating the copper crossover were assessed in a full cell Cu-Cl electrolyzer. Eventually, the Faradic current efficiency was determined for the membranes.

3 EXPERIMENTAL

3.1 Preparation of Polyaniline Composite Membranes

All membranes were cleaned prior to examination using a common literature procedure (De Almeida et al., 2010). The composite membranes of Nafion-PANI were prepared by in situ chemical polymerization of aniline within Nafion membranes. Composite membranes were prepared using different polymerization times at ambient temperature and different oxidizing agents. The method of synthesis was based on several reports in the literature (Choi et al., 2008; Schwenzer et al., 2011; Wang et al., 2009). A solution of aniline dissolved in 1.0 M HCl was used to impregnate the cleaned Nafion membranes for 30 min on each side in a glass covered petri dish, after which they were rinsed with deionized (DI) water. The membrane was then immersed in one of the following solutions of oxidizing agents for polymerization; 30% $\text{H}_2\text{O}_2$, 0.2 M ferric chloride in 1.0 M HCl or 0.2 M aqueous solution of ammonium persulfate (APS). The polymerization was allowed to proceed for either 1, 5 or 24 h independently. The membrane was then washed with DI water and coated by dipping it for few seconds in 5% Nafion solution, and hung to dry in a fume hood for ca. 3 hours. The coated membrane was washed with 1.0 M aqueous solution of sulfuric acid and stored in DI water for at least 24 h.

The membranes were tested with standard electrode materials in our CuCl/HCl electrolyzer system, which is described in detail elsewhere (Edge et al., 2013). For selected experiment, $\text{H}_2$ production efficiency measurements were performed. Similar efficiency tests were implemented by Lvov et al. (Balashov et al., 2011). To do this, modification was made on the catholyte container in order to collect the produced $\text{H}_2$. A glass container filled with deionized water was carefully connected to the catholyte container through a short rubber tube above water level. Inside this container, a glass tube was inserted to the bottom of the container. The upper part of the glass tube was connected to a rubber tube into a 500 mL graduated measuring cylinder. Therefore, the produced $\text{H}_2$ that reached the catholyte container transferred to the water container and displaced the same volume of water to the measuring cylinder. To check the hydrogen production performance setup, water electrolysis was performed using $\text{H}_2\text{SO}_4$ 0.5 M solution as electrolyte for both the catholyte and anolyte. N115 was employed as a membrane and Pt/C was utilized as an electrode for both the cathode and anode. In our study, we initially performed conventional water electrolysis and collected the produced $\text{H}_2$ to validate our apparatus and methodology. These replicates showed 99.7 % and 98.6 % current efficiency which supports the efficiency of the system.

4 CHARACTERIZATION

4.1 UV-Vis Characterization

The UV-Vis spectroscopy was used to identify the formation of PANI and its different oxidation forms. As can be seen from Fig. 1, there are three oxidation forms for the PANI; fully reduced-Leucomeraldine, 50% oxidized-Emeraldine and fully oxidized-Pernigraniline. Many literature reports investigated the characteristic UV-Vis spectra of the PANI and its different oxidation states (Bhadra et al., 2007; Choi et al., 2008; Pan et al., 2006; Ram et al., 1997; Sapurina et al., 2009). Fig. 2 shows the spectra of N115 PANI APS, N115 PANI $\text{H}_2\text{O}_2$, and N115 PANI $\text{FeCl}_3$. Peaks appeared in the ranges 380-390 nm and 720-830 nm. The peak at ca. 380-390 nm can be attributed to the $\pi-\pi^*$ transition in the benzene rings. The peaks at around 720-830 nm ascribed to $\pi$-polaron transition formed at the nitrogen oxidized atoms of PANI. Both N115 PANI $\text{H}_2\text{O}_2$, and N115 PANI $\text{FeCl}_3$ membranes showed higher wavelength bands (800-830 nm) compared to N115 PANI APS (730 nm) which means lower energy bands for both N115 PANI $\text{H}_2\text{O}_2$, and N115 PANI $\text{FeCl}_3$. This lower energy bands could represent higher conductivity which support the formation of 50% oxidized-Emeraldine structure. On the contrary, N115 PANI APS showed a peak at around 720 nm which has higher energy and lower conductivity than other two composite membranes. It can be concluded that N115 PANI APS has a reduced form of PANI as Leucomeraldine.
4.2 TGA Measurements

TGA and DTG measurements were employed to investigate the thermal stability and thermal properties of N115-PANI composite membranes and compare them with the pristine N115. Measurements were taken under two different environments; air and argon. Small amount of composite membranes was heated up from room temperature to 1000 °C at a rate of 10 °C/min. Fig. 3 (a,b,c,d) shows the TGA and DTG of N115, N115-PANI APS, N115-PANI $\text{H}_2\text{O}_2$, and N115-PANI FeCl$_3$ under both air and argon, respectively. Fig. 3 (a) shows that the degradation pattern of the PANI composite membranes has more stability than the pristine N115. The DTG curves in Fig. 3 (b) show the degradation stages according to the literature (de Almeida et al., 1999; Nagarale et al., 2004; Tan et al., 2005a; Yang et al., 2009). The peak at ca. 340 °C is ascribed to the desulfonation of the hydrophilic part of the membrane which evolved as SO$_2$ gas. This peak is large for the composite membranes in comparison to the pristine N115 which could be due to the degradation of the organic part of the PANI composite membranes. The same observation has been reported by Jinyan et al. (Yang et al., 2009). The peaks in the range of 425-450 °C are attributed to the decomposition of the backbone of the Nafion membrane. The pristine and two composite membranes displayed two steps decomposition while the N115-PANI FeCl$_3$ showed one step decomposition. In addition it showed a small degradation peak which could be attributed to the iron cation atoms confined in the hydrophilic channels of the membrane. Moreover, Fig. 3 (c) shows the degradation of PANI composite membranes and pristine N115 under a flow of argon, and it shows the same trend of degradation under air with the exception of ca. 10-15 % mass residue which is thermostable up to 1000 °C for N115-PANI FeCl$_3$ membrane. Additionally, Fig. 3 (d) shows the DTG under argon with the same range of degradation peaks at 330 °C and 490-500 °C. It is generally noticeable that the decomposition peak of the backbone of the polymer in air occurred at lower temperatures compared to the same peak under argon. From the thermograms, it is clear that the PANI composite membranes have different degradation patterns which are more stable than the pristine Nafion.

4.3 SEM Characterization

SEM images were captured to characterize the properties of the formed PANI within the composite membranes. Different SEM micrographs were taken for different PANI composite membranes prepared by different oxidizing agents. Aniline was oxidized and polymerized by a cationic oxidizing agent such as Fe(III), anion APS or $\text{H}_2\text{O}_2$. The SEM images in Fig. 4 show significant changes in the morphology of the membranes. As can be seen in Fig. 4 (a), the morphology of the surface of the pristine membrane shows clear porosity with no particles on the surface, which is in contrast to the composite prepared with FeCl$_3$, which shows a smooth surface covered with the PANI polymer, as shown in Fig. 4 (b). Polymerization with APS is likely to occur on the surface of the Nafion membrane, as shown in Fig. 4 (c). It is believed that the negative charge on the
persulfate makes repulsion with the negative charge of the sulfonic acid groups inside the channels of the membranes, limiting the polymerization to the outer surface. Whereas polymerization by hydrogen peroxide occurs inside the channels of the membrane because of the neutral charge of the oxidizing agent. This can be seen in Fig. 4(d) as dispersed particles on the pores of the membrane.

Fig. 3: Thermal gravimetric profile TGA and DTG obtained for PANI composite membranes compared to N115 under flowing (a,b) air and (c,d) argon gas TGA. All tests have been done from room temperature to 1000 °C with rate 10 °C/min.

4.4 Water Uptake Results

The water uptake was measured for the pristine and composite membranes by measuring the mass difference of the totally hydrated and vacuum dried membranes according to Eq. (1). The mass of the hydrated membrane and the vacuum dried membrane were represented by $m_{wet}$ and $m_{dry}$, respectively. Initially, the water from the fully hydrated membrane was carefully blotted by Kim wipe tissues. Then dried in a vacuum oven at 60 °C for 24 h.

$$\text{water uptake(\%)} = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \%$$  \hspace{1cm} Eq. (1)

Table 1: Physical properties of some PANI composite membranes and pristine Nafions.

<table>
<thead>
<tr>
<th>membrane</th>
<th>% Water uptake</th>
<th>IEC(meq/g)</th>
<th>Conductivity S/cm</th>
<th>Permeability cm²/s</th>
<th>Selectivity S.s/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>N115</td>
<td>26.8</td>
<td>0.854</td>
<td>9.78E-02</td>
<td>6.86E-07</td>
<td>1.43E+05</td>
</tr>
<tr>
<td>N115-0.2M PANI FeCl₃</td>
<td>13.7</td>
<td>0.579</td>
<td>2.35E-02</td>
<td>4.20E-07</td>
<td>5.60E+04</td>
</tr>
<tr>
<td>N115-0.5M PANI FeCl₃</td>
<td>17.1</td>
<td>0.543</td>
<td>2.37E-02</td>
<td>3.76E-07</td>
<td>6.29E+04</td>
</tr>
<tr>
<td>N117</td>
<td>31.4</td>
<td>0.847</td>
<td>1.19E-01</td>
<td>1.05E-06</td>
<td>1.13E+05</td>
</tr>
<tr>
<td>N117-0.2M PANI FeCl₃</td>
<td>20.4</td>
<td>0.573</td>
<td>3.53E-02</td>
<td>4.94E-07</td>
<td>7.14E+04</td>
</tr>
<tr>
<td>N117-0.5M PANI FeCl₃</td>
<td>20.1</td>
<td>0.560</td>
<td>2.77E-02</td>
<td>4.78E-07</td>
<td>5.80E+04</td>
</tr>
</tbody>
</table>
The water uptake values are 31.4 and 26.8 % for pristine N117 and 115 membranes, respectively. This is in general agreement with other reports in the literature of pristine Nafion (Choi et al., 2008; Tan and Bélanger, 2005a; Tan et al., 2005b). The water uptake of N115 decreased to 13.7 and 17.1 % for N115-0.2M PANI FeCl₃ 24 c and N115-0.5M PANI FeCl₃ 24 c, respectively. Furthermore, the water uptake of N117 membrane decreased to 20.4 and 20.1 % for N117-0.2M PANI FeCl₃ 24 c and N117-0.5M PANI FeCl₃ 24 c, respectively. This reduction in the water uptake is most likely because of the pores filled with PANI chains which replacing the water molecules in the channels of the membrane.

Fig. 4: Scanning electron micrographs of the surface of the (a) pristine N115 membrane (b) N115 PANI FeCl₃ (c) N115 PANI APS (d) N115 PANI H₂O₂.
4.5 Ion Exchange Capacity (IEC)

The ion-exchange capacity (IEC) of the membranes was measured by titration. A specific mass of vacuum dried membranes was soaked in a 3.0 M NaCl aqueous solution for 24 h at an ambient temperature with occasional shaking. The solution was then titrated against a 0.005 M NaOH solution to neutralize the exchanged protons (H\(^+\)) using a phenolphthalein pH indicator. The IEC was calculated using Eq. (2):

\[
IEC = \frac{\Delta V_{NaOH} \cdot C_{NaOH}}{m_s} \quad \text{(mol g}^{-1}\text{)} \quad \text{Eq. (2)}
\]

where \(\Delta V_{NaOH}\) is the consumed volume of the NaOH solution, \(C_{NaOH}\) is the exact concentration of the NaOH standard solution, and \(m_s\) is the mass of the membrane sample in g.

Since IEC represents the exchangeable cationic species such as protons (H\(^+\)) which interact with the sulfonic groups, the IEC results obtained are used to determine the relative quantity of PANI in the composite membranes. From Eq. 2, the calculated IEC values for N115 and N117 pristine membranes are 0.854 and 0.847 meq/g, respectively which is in good agreement with the literature values (Compañ et al., 2008). As we modified the membranes with PANI, the IEC values noticeably decreased to ca. 0.5 meq/g, as listed in Table 1. This reduction, which is in the range of ca. 32-36%, reflects the amount of PANI interacting with the sulfonic groups in the membranes. As expected, when PANI chains replaced the H\(^+\) and interacted with the sulfonic groups, the IEC value decreased as less protons were available for replacement. These results are supported by Sophie et al. (Tan et al., 2003). Both PANI composite membranes of N115 and N117 showed almost the same reduction trend of the IEC values. Furthermore, changing the concentration of aniline from 0.2 M to 0.5 M has very minimal effect on the value of IEC. In addition, comparing the values of IEC of the PANI composite membranes with the Ppy composite membranes, we found that Ppy composite membranes have lower IEC values indicating larger quantity of Ppy in the membrane.

4.6 Proton Conductivity and Diffusion

The proton conductivity (\(\sigma\)) was evaluated via electrochemical impedance spectroscopy (EIS). Moreover, the membrane ionic resistance, \(R_m\) can be estimated from the semi-circle Nyquist plot (Bhadra et al., 2007; Nam et al., 2008; Peckham et al., 2008) and the proton conductivity (\(\sigma\)) can be calculated from \(R_m\) using the following equation:

\[
\sigma = \frac{L}{R_m W h} \quad \text{Eq. (3)}
\]

where L, W and h are the length, width and height of the membrane samples, respectively.

Almost all PANI composite membranes that were prepared failed to pass the selectivity and/or the full cell Cu-Cl electrolyzer tests due to low selectivity or high resistivity. Eventually, a membrane which can maintain its conductivity and show a noticeable copper permeability reduction is required. From previous experiments, PANI composite membranes that used an aniline concentration of 0.2-0.5 M showed suitable properties. In addition using FeCl\(_3\) as oxidant resulted acceptable proper conductivity. Table 1 summarizes the conductivity, Cu permeability and selectivity of N115 PANI and N117 PANI polymerized by FeCl\(_3\) for 24 hours and coated with 5% Nafion solution. N115 0.2M PANI FeCl\(_3\) 24 h c and N115 0.5M PANI FeCl\(_3\) 24 h c showed almost the same conductivity ca. 0.024 S/cm, whereas N115 0.5M PANI FeCl\(_3\) 24 h c showed lower permeability than N115 0.2M PANI FeCl\(_3\) 24 h c. Therefore, the measured selectivity was 5.60X10\(^4\) and 6.29X10\(^4\) S/cm\(^3\) for N115 0.2M PANI FeCl\(_3\) 24 h c and N115 0.5M PANI FeCl\(_3\) 24 h c, respectively. Additionally, N117 0.5M PANI FeCl\(_3\) 24 h c showed lower conductivity than N117 0.2M PANI FeCl\(_3\) 24 h c which is expected as larger amount of PANI chains replaced protons that are important for conductivity. In comparison, their conductivity were little higher than N115 PANI composite membranes but their copper permeability were lower than the N115 PANI composite membranes. Therefore, the selectivity of both N115 and N117 PANI composite membranes resulted with almost similar values.

5 FULL CELL ELECTROCHEMICAL CHARACTERIZATION

5.1 Cu-Cl Electrolysis

Fig. 5 illustrates full cell H\(_2\) CV for pure Nafion N115 membrane and other composite membranes after 3 working days (abbreviated d). This test was used to detect any copper species deposited from the copper crossover during regular electrolysis cell operation. It was conducted at the beginning of each day before
starting other tests. Therefore, the first day of the CV measurement, for all membranes, does not show any traces of copper deposition. Previously prepared Ppy composite membranes were used for comparison. The CV measurement of N115/Ppy c membranes for the 3 days did not display any oxidation or reduction peaks at ca. 0.4-0.5 V, as can be seen in Fig. 5 (a), which could be a positive sign of absence of any copper crossover. Fig. 5 (b) illustrates the CV measurements of N115 pristine membrane. It is clearly showing the oxidation and reduction peaks on second and third testing days, whereas these peaks were absent on the first day. These peaks are attributed to the oxidation and reduction of copper accumulated as a result of crossover. The CV measurements obtained for N117/Ppy c and N1170.2M PANI FeCl3 24 h c are shown in Fig. 5 (c) and (d), respectively. The CV measurements of N117/Ppy c membrane did not show any oxidation or reduction peaks for the first and second day. An oxidation peak was appeared at ca. 0.3 V without any clear reduction peak. Most probably this peak does not related to copper crossover as it does not match the ca. 0.4-0.5 V value. The CV measurements of N117-0.2M PANI FeCl3 24 h c membrane showed small oxidation reduction peaks, as illustrated in Fig. 5 (d). These small peaks prove that there was some copper deposition. Compared to N115, it is clear that N115/Ppy c performance is the best amongst other tested membranes.

5.2 Hydrogen Collection

The Faradic current efficiency of different MEAs can be calculated from Eq. (4)

\[ \eta_c = \frac{H_2 \text{ (exp)}}{H_2 \text{ (theor)}} \times 100 \]

Eq. (4)

Fig. 5: Full cell H\textsubscript{2} CV for pure Nafion N115 membrane and other composite membranes after certain working days (abbreviated d). (a) N115/Ppy c (b) N115 (c) N117/Ppy c (d) N117-0.2M PANI FeCl\textsubscript{3} 24 h c. Measurements were taken at a sweep rate of 50 mV s\textsuperscript{-1} at 25 °C with 2.0 M HCl flowing in the left side of the cell at 60 mL min\textsuperscript{-1} and H\textsubscript{2} flowing in the right side at 25 mL min\textsuperscript{-1}.  

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The current efficiency for pristine Nafion in the Cu-Cl electrolysis was 98% based on a 5-hour electrolysis as determined by Lvov et al. (Balashov et al., 2011). Furthermore, longer electrolysis experiment was proposed to discover the influence of long term copper permeation on efficiency. In this work, to confirm the efficiency of the system, conventional water electrolysis was performed and the H₂ produced showed ca. 100% current efficiency. Later, the MEAs tested in the Cu-Cl electrolysis for 6 h each day for three days and the H₂ was collected to calculate the current efficiency. The Faradic efficiency values of N115 that calculated from H₂ collection were only ca. 79 % and 18 % for day 1 and 3, respectively. In contrast, N117-0.2M PANI FeCl₃ 24 h c shows a superior high H₂ production with current efficiency 97.1 and 90.0 % for day 1 and 3, respectively, as detailed in Table 2 and illustrated in Fig. 6. These illustrate how N117-0.2M PANI FeCl₃ 24 h c improves the cell performance over the pristine Nafion membranes.

Table 2: The percentage of hydrogen efficiency of pure Nafion membrane N115 and N117-0.2M PANI FeCl₃ 24 h c composite membrane during 6 h of fixed current of 0.5 A at 25 °C for certain working days. Anolyte is 0.2 M CuCl in 2.0 M HCl and catholyte is water, both flow at rate 60 mL min⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>N115</th>
<th>N117 PANI FeCl₃ 24 h c</th>
</tr>
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<tbody>
<tr>
<td>day1</td>
<td>79.3</td>
<td>97.1</td>
</tr>
<tr>
<td>day3</td>
<td>18.3</td>
<td>90.0</td>
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</table>
6 CONCLUSIONS

The modification of Nafion membranes by in situ chemical polymerization with aniline was investigated for CuCl/HCl electrolysis. These modified membranes were characterized by UV-Vis spectroscopy and TGA to confirm the formation of the PANI polymer. UV-Vis data demonstrated that using APS as an oxidizing agent formed leucomeraldine, a reduced form of PANI, which had high resistivity. On the contrary, using either H₂O₂ or FeCl₃ formed the 50% oxidation form emeraldine. It is believed that the polymerization of Nafion by APS mostly occurs on the outer membrane surface because of the repulsion of negative charge of persulfate with the negative charge of the sulfonic acid groups within the pores. While the polymerization by FeCl₃ occurs inside the pores of the membrane as the negative sulfonate groups attract the cationic iron oxidant. As the polymerization needs acidic medium to occur, the polymerization by the neutral H₂O₂ oxidizing agent occurs inside the pores of the Nafion membrane where the sulfonic acid groups are available. These conclusions were supported by the data obtained from SEM.

Testing of N115-PANI FeCl₃ 24 h c and N117-PANI FeCl₃ 24 h c showed significant Cu reduction accompanied with a reduction in conductivity. The electrochemical investigation by full cell Cu-Cl electrolyzer showed excellent performance compared to the pristine Nafion membranes, with sustained higher current efficiencies over the course of 3 days of testing.

7 REFERENCES


