Electrochemical hydrogen production from thermochemical cycles using a proton exchange membrane electrolyzer

PremKumar Sivasubramaniana, Ramaraja P. Ramasamyb, Francisco J. Freireb, Charles E. Hollanda, John W. Weidnera,∗

aCenter for Electrochemical Engineering, Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA
bChlorine Recycle Consultants, Miami Beach, FL 33140, USA

Available online 9 August 2006

Abstract

The electrochemical step in two thermochemical cycles for hydrogen production is reported. One cycle involves the electrochemical oxidation of sulfur dioxide to sulfuric acid (both water and SO2 are reactants). The other cycle involves the oxidation of anhydrous hydrogen bromide to bromine (anhydrous HBr is the only reactant). In both cycles, protons are reduced at the cathode to produce hydrogen. The novelty of this work is that both anode reactions are carried out in the gas phase of a proton exchange membrane (PEM) electrolyzer, which enhances the transport rate of reactants to the electrode surface. The HBr process achieved 2.0 A/cm2 at 1.91 V. The SO2 process reached 0.4 A/cm2, but behind this current density the cell experienced mass transfer limitations of water across the membrane. However, the voltage required to achieve 0.4 A/cm2 was 0.835 V, compared to 1.025 V for the HBr process at this current density.

Keywords: Hydrogen; Nuclear hydrogen; Thermochemical

1. Introduction

Recent advances in fuel cell technology and an increasing demand for hydrogen are driving the need for the development of more efficient methods to produce hydrogen. The main methods for hydrogen production include reforming of hydrocarbons such as natural gas, coal gasification, biological processes, water electrolysis, and thermo-chemical cycles using a high temperature thermal source (e.g., nuclear or solar energy) [1–6]. Thermochemical cycles produce hydrogen through a series of chemical reactions that result in the splitting of water at much lower temperatures (~800–1000 °C) than direct thermal dissociation (> 2500 °C) [1,2]. All other chemical species in these reactions are recycled resulting in the consumption of only heat and water to produce hydrogen and oxygen. Since water rather than hydrocarbons are used as the source of hydrogen, no carbon dioxide emissions are produced and the hydrogen produced is highly pure.

Although there are hundreds of possible thermochemical cycles that can produce hydrogen from water, the two leading candidates are the sulfur-based cycles and the calcium–bromide-based cycles [4–6]. The sulfur-based processes all have the common oxygen generating, high-temperature step, which is the decomposition of sulfuric acid to sulfur dioxide and oxygen at temperatures in the 850–1000 °C range. In the sulfur–iodine (S–I) cycle, the SO2 is converted back to H2SO4 and hydrogen is produced via a two-step process involving iodine. The distillation of HI from solution and concurrent decomposition to iodine is the most difficult process issue for the iodine containing portion of the cycle [5,6].

In the 1970s, Westinghouse Electric Corporation developed the hybrid sulfur process, which eliminated the use of iodine completely [7,8]. They electrochemically oxidized SO2 to H2SO4 from a liquid-phase anode stream. The schematic of the hybrid-sulfur process is shown in Fig. 1. Westinghouse demonstrated this process on a scale of 150 l/h of hydrogen in 1976, and a conceptual plant design was developed. However, improved performance of the electrolytic cell is needed to improve the overall efficiency of this promising cycle.
O2
SO2
H2O
H2
Electrolysis
H2SO4
Decomposition
850˚ C
Heat
Fig. 1. A schematic of the hybrid sulfur cycle, developed by Westinghouse. The H2SO4 is decomposed to SO2 at high temperature, and the SO2 is converted back to H2SO4 in the PEM electrolyzer at 80°C. Overall only water and energy is consumed, and H2 and O2 are produced.

CaBr2
H2
Electrolysis
Br2
H2O
CaO
O2
HBr
550˚ C
Heat
730˚ C
Heat
Fig. 2. A schematic of the modified Ca–Br cycle. The CaO and CaBr2 are recycled in a high temperature, solid-gas, fixed bed reactors, and the HBr is converted to Br2 in the PEM electrolyzer at 80°C. Overall only water and energy are consumed, and H2 and O2 are produced.

The calcium–bromide-based cycles also have the potential of high efficiencies but with lower temperature requirements (~750°C) than the sulfur-based cycles. The common step in these cycles is the conversion of CaO and Br2 to CaBr2 and O2 at approximately 550°C, and the conversion of CaBr2 back to CaO and HBr at 730°C. The second recycle step, converting HBr to Br2 and generating hydrogen, can be done thermally in a solid-gas, fixed bed reactor of iron oxide, which in turn needs to be regenerated [5,6]. The iron reaction beds can be eliminated in the modified Ca–Br cycle by converting HBr directly to Br2 and H2 in a single step (see the schematic in Fig. 2). This direct conversion can be performed electrochemically [9–11] or in a plasma process [12].

Aqueous-phase electrolysis of HBr suffers from (1) low current densities due to liquid-phase mass-transfer limitations and (2) difficult product separation due to dissolution of Br2 in solution [9]. Gas-phase electrolysis has been attempted in phosphoric acid [9,10] and molten-salt cells [11] to address these limitations. Although Br2 dissolution was avoided in these cells, cell performance was poor.

The objective of this work is to demonstrate the operation of a proton exchange membrane (PEM) electrolyzer for the conversion of: (1) SO2 to H2SO4 and H2; and (2) HBr to Br2 and H2. Our hypothesis is that, carrying out the anode reactions in the gas phase of a PEM electrolyzer will significantly improve the electrochemical step in these two important thermochemical cycles. A similar cell was used for the conversion of anhydrous HCl to Cl2, which produced superior performance to one with an aqueous HCl feed [13].

2. Experimental procedure

2.1. MEA preparation: SO2 electrolyzer

The membrane electrode assembly (MEA) was prepared by the catalyst spraying/hot-pressing method [14]. Carbon cloth, gas diffusion layers (GDLs) (ELAT-R® from ETEK) were used on both the anode and the cathode. The ink consisted of 40 wt% Pt on carbon and Nafion dissolved in isopropanol. The Nafion and carbon were in a 1:1 mass ratio. A mask with a square opening of 40 cm² was placed on the micro-porous carbon layer, and the ink was uniformly sprayed onto the GDL until a desired loading was achieved. The anode and cathode platinum loadings were 0.66 and 0.70 mg/cm², respectively.

A poly[perfluorosulfonic] acid membrane (Nafion 115 from DuPont) was placed between the catalyst-coated GDLs and hot-pressed at 2000 psia and 130°C in a Carver hot press (Model #3851-0). Prior to its use, the Nafion 115 membrane was boiled in 1N H2SO4 solution for 90 min and rinsed thoroughly with de-ionized water for 10 min.

2.2. MEA preparation: HBr electrolyzer

The MEAs were prepared with carbon cloth GDLs containing 2.0 mg/cm² of RuO2 (ELAT-S® from ETEK) as the catalyst for both the anode and cathode. The 50 cm² cloths were taped at the edges with Teflon tape (3M Corporation, serial 5190) to give an active area of 40 cm². A poly[perfluorosulfonic] acid membrane (Nafion 105® from DuPont) was placed between the catalyst-coated GDLs and hot-pressed at 2000 psia and 130°C in a Carver hot press (Model #3851-0). Prior to its use, the Nafion 115 membrane was boiled in 1N H2SO4 solution for 90 min and rinsed thoroughly with de-ionized water for 10 min.

2.3. PEM electrolyzer

The electrolyzer for both processes used two back plates that contained 80 wt% graphite and 20 wt% fluoro inert polymer composite (Diabond® F100). The back plates were followed by copper current collectors and stainless steel end plates on both sides. Flow fields made out of 3.385 mm thick carbon paper (SpectraCorp 2050-A) were place inside a 3.385 mm deep well
machined into the diabond back plates. Two Viton ‘O’ rings fit into grooves machined into the diabond plates and served to seal the cell. The MEA was placed between the two flow fields, and the cell assembly was bolted together with twelve bolts by the application of a uniform torque of 60 in-lbs. A schematic of the cell assembly is shown in Fig. 3. The only difference between the anode and cathode sides of the cell was that the latter contained carbon paper with 21 machined flow channels. Each channel was 1.4 mm deep, 1.5 mm wide and ran in the direction of flow. These channels were away from the membrane and they served to facilitate the removal of hydrogen gas bubbles and allow free flow of water. A schematic of these flow fields is shown in Fig. 4.

The cell temperature was maintained at 80 °C with the aid of heating cartridges and thermocouples on the anode and cathode sides. Preheated (80 °C) de-ionized water was sent to the cathode side of the electrolyzer at a fixed rate of 130 cm³/min using a FMI model QV pump. The flow of water helped to maintain the desired cell temperature and to prevent hydrogen bubbles from accumulating in the cathode. The anode feed gas was set according to the current to maintain the desired percent conversion of HBr or SO₂. Pressure was maintained at 1.0 atm (absolute) on both sides of the cell using back pressure regulator valves. The current to the electrolyzer was controlled using a HP model 6031A power supply.

3. Results and discussion


On the anode side of the electrolyzer, the sulfur dioxide combines with water to produce sulfuric acid via the reaction

\[
\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \quad E^\circ = 0.17 \text{ V vs. SHE.} \quad (1)
\]

Protons pass through the membrane and recombine at the cathode to produce hydrogen via the reaction

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E^\circ = 0.0 \text{ V vs. SHE.} \quad (2)
\]

Thus the overall reaction in the electrolyzer is

\[
\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad (3)
\]

We hypothesized that the water needed in reaction (1) could be provided by transport across the membrane from the cathode. This was based on our earlier work that measured the flux of water across a Nafion 115 membrane as a function of current density with anhydrous HCl as the anode feed [15,16]. These data are plotted in Fig. 5 (symbols) along with the stoichiometric amount of water needed in reaction (1) (dashed line). The flux of water across the membrane decreases with increasing current density because electro-osmotic drag pulls water from
the anode to the cathode to counter the diffusion of water from the cathode to the anode. Although SO2 in place of HCl will alter the amount of water transported across the membrane, the results in Fig. 5 suggest that no additional water needs to be fed with the SO2 at current densities below 0.7 A/cm².

Fig. 6 shows the current–voltage response of the PEM electrolyzer for the oxidation of SO2 to H2SO4 and the reduction of protons to H2. Our data (▲) was collected at 80 °C, 1.0 atm, and 5% conversion of SO2. Although this conversion is low, the voltage varied by less than 30 mV for conversions between 5 and 40%, which is less than the size of the symbols. Our results indicated that water transported across the membrane is sufficient to sustain reaction (1) up to current densities of 0.4 A/cm². A mass-transfer limiting current density is observed beyond this point. It is most likely that the limiting reactant in reaction (1) is water and not SO2. Therefore, it is not possible to increase the rate of reaction (1) by increasing the voltage or the SO2 flow rate. Rather, the reaction rate is limited by the rate of water transport across the membrane. It should be possible to extend the limiting current by using thinner membranes or by humidifying the SO2 before it enters the electrolyzer.

Fig. 6 also shows the best data from [7] (gray line) obtained at 50 °C and 1.0 atm. The catholyte was dilute H2SO4 and the anolyte was 50 wt% H2SO4 pre-saturated with SO2. The anode and cathode compartments were separated by a rubber diaphragm, and the platinum loadings were 7 and 10 mg/cm² on the anode and cathode, respectively. The dotted line in Fig. 6 is the targeted cell performance given by Lu et al. [7] for 100 °C, 5–20 atm, and 50–60 wt% sulfuric acid, which was not achieved. A cell performance of 0.5 A/cm² at 0.6 V in the hybrid sulfur process was estimated to provide greater overall efficiency and lower production cost than direct electrolysis of water [17].

Our data at 0.4 A/cm² shows an improvement of over 150 mV in cell voltage at 1/10th the Pt loadings. Although our temperature was 30 °C higher, the PEM electrolyzer shows promise as a means of carrying out this reaction. This improvement is most likely due to improved gas-phase mass transfer and high membrane conductivity.

The concentration of H2SO4 produced by the oxidation of SO2 is crucial in determining the overall operating efficiency of the hybrid-sulfur cycle [17]. The lesser the amount of water (i.e., higher H2SO4 concentration) sent to the decomposition reactor, the lesser energy needed to vaporize this stream. Therefore, to determine the concentration of sulfuric acid exiting our electrolyzer, the outlet liquid stream was collected at the bottom of a knock-out vessel. This solution was titrated against 1.0 N sodium hydroxide using Phenol Red as an indicator. At 0.1 and 0.4 A/cm², the reactor produced 13 and 46 wt% H2SO4, respectively. Consistent with Fig. 5, less water ends up in the sulfuric acid at higher current density since more water is consumed in the reaction and less water is transported across the membrane.

3.2. Current–voltage response: HBr electrolyzer

On the anode side of the electrolyzer, the HBr is converted to Br2 via the reaction

$$2\text{HBr} \rightarrow \text{Br}_2 + 2\text{H}^+ + 2\text{e}^- , \quad E^\circ = 0.58 \text{V} \text{ vs. SHE}. \quad (4)$$

Protons pass through the membrane and recombine at the cathode to produce hydrogen via the reaction

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 , \quad E^\circ = 0.0 \text{V} \text{ vs. SHE}. \quad (5)$$
Fig. 7. The current–voltage response for SO\(_2\) (▲) and HBr (♦) electrolysis in a PEM electrolyzer. The results for the SO\(_2\) electrolysis are the same as that given in Fig. 5 but with a wider voltage scale. The HBr electrolyzer was operated at 80°C, 1.0 atm, and 50% conversion with a RuO\(_2\) loading on the anode and cathode of 2.0 mg/cm\(^2\).

Thus the overall reaction in the electrolyzer is

\[2\text{HBr} \rightarrow \text{Br}_2 + \text{H}_2. \quad (6)\]

Unlike reaction (3), no water is consumed in reaction (6). The purpose of adding water to the cathode side of the HBr electrolyzer is to keep the membrane wet and hence conductive, to help maintain the desired operating temperature, and to remove the hydrogen produced at the catalyst surface. Fig. 7 shows the current-voltage response of the PEM electrolyzer for the oxidation of HBr to Br\(_2\) and the reduction of protons to H\(_2\). Our data (♦) was collected at 80°C, 1.0 atm and 50% conversion of HBr. For comparison purposes, the results from Fig. 5 are replotted on this figure. The main difference between the HBr and SO\(_2\) electrolysis is that the former can be run at significantly higher current densities. This supports our argument that water and not SO\(_2\) is the limiting reactant in reaction (1).

Another difference between the V–I performance curves for these two reactions is the overpotentials required to carry out the reactions. For HBr electrolysis, a small activation barrier is needed to produce Br\(_2\) and H\(_2\), as evidenced from a cell voltage of 0.66 V at 0.2 A/cm\(^2\), which is 80 mV above the equilibrium voltage of 0.58 V. In contrast, SO\(_2\) electrolysis at 0.2 A/cm\(^2\) requires 530 mV above the equilibrium voltage of 0.17 V. Therefore, SO\(_2\) rather than HBr oxidation would benefit from improved catalyst performance. For both reactions, the linear relationship between current and voltage above 0.2 A/cm\(^2\) is characteristic of the ohmic resistance of the membrane. Thinner membranes should result in a lower slope in the V–I curve.

The larger current range for HBr electrolysis provides great flexibility in operating this step in the process. For example, if operating efficiency (i.e., electric power consumed for a given hydrogen production rate) is the key constraint than the cell can be run at low current densities and hence low cell voltage (i.e., high efficiency). However, if capital cost is the key constraint then the cell can be run at higher current densities, resulting in a smaller cell for given hydrogen production rate.

Kondo et al. [9] used a phosphoric acid electrolyzer to perform electrolysis of HBr. They impregnated Pt onto carbon cloth with a loading of 5.3 mg/cm\(^2\). They were able to achieve 0.1 A/cm\(^2\) at a voltage of 0.73 V, a pressure of 0.45 atm, and temperature of 150°C. Shimizu et al. [10] tried to improve upon the performance of the above experiments and used PTFE bonded carbon electrodes in the same electrolyzers at the same temperature. At a Pt loading of 2.5 mg/cm\(^2\) they achieved a current density of 0.1 A/cm\(^2\) at 0.575 V. However their cell also showed signs of mass transfer limitations at current densities greater than 0.1 A/cm\(^2\).

Wauters and Winnick [11] constructed a cell with gas diffusion electrodes made of reticulated vitreous carbon or graphite felt with a Zirconia matrix holding a molten salt electrolyte. At temperature of 300°C, they observed a cell voltage of 3.5 and 9 V at 0.1 and 0.4 A/cm\(^2\), respectively.

4. Conclusions

A proton exchange membrane (PEM) electrolyzer was used for the electrochemical conversion of: (1) SO\(_2\) to H\(_2\)SO\(_4\) and H\(_2\); and (2) HBr to Br\(_2\) and H\(_2\). We showed that carrying out the anode reactions in the gas phase of a PEM electrolyzer significantly improves the electrochemical step in both the hybrid sulfur and modified Ca–Br thermochemical cycles. Both of these cycles are being strongly considered as alternative processes to direct water electrolysis for large-scale production of hydrogen for the hydrogen economy.
In the PEM electrolyzer, SO₂ oxidation in the gas phase reduced the cell voltage by over 150 mV at 0.4 A/cm² compared to SO₂ oxidation in the liquid phase. This improvement was achieved with one tenth the Pt loading. The process started to become mass-transfer limited at 0.4 A/cm² due to limitations in transporting water across the membrane above these currents. Further improvements maybe be possible by using thinner membranes, a humidified SO₂ feed stream, and elevated pressures. The activation barrier for SO₂ oxidation is also large, suggesting that reductions in cell voltage could be obtained with more active catalysts.

In the HBr electrolyzer, dramatic improvements in current densities were achieved over previous gas-phase HBr electrolysis. Current densities were increased by over an order of magnitude (0.15–2.0 A/cm²) with no evidence of mass-transfer limitations. Future decreases in voltage while maintaining high current densities may be possible by using thinner membranes to minimize ohmic resistance.

Acknowledgements

We would like to thank E. I. Du Pont de Nemours and Company for patent donations covering halogen electrolysis (US Patent RE 37,042) and the Department of Energy (Contract No. DE-FC36-04GO14232) for financial support of this work.

References