Electrochemical Generation of Hydrogen Via Gas Phase Oxidation of Sulfur Dioxide and Hydrogen Bromide

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Abstract

Hydrogen is abundant in nature but occurs primarily in stable compounds that require significant energy to produce hydrogen for use as a fuel. Therefore hydrogen is an energy carrier, much like electricity, that requires a primary energy source to produce. Domestic energy sources that do not generate greenhouse gases and have the potential to produce hydrogen at costs competitive with carbon based fuels will be essential components of the long term energy supply. Thermochemical cycles which produce hydrogen through a series of chemical reactions have the potential to produce pure hydrogen at high efficiencies. Two promising cycles which are of interest are based on the internal recycle of sulfuric acid and bromine. We present here an electrochemical process that produces pure hydrogen and recycles sulfuric acid and bromine via the electrochemical oxidation of SO_2 and HBr, respectively in the gas phase. Both of these electrochemical reactions take place in a proton exchange membrane (PEM) reactor, similar in construction to a PEM fuel cell. The reactants, either SO_2 or HBr, are fed to the anode and water is fed to cathode. Protons are formed at the anode, and transported across a Nafion membrane, which are then reduced at the cathode to form hydrogen. The performance of the reactor is studied at the optimal conditions of operation for the PEM reactor. The process details for the SO_2 oxidation are reported and it can be shown that there are two distinct reactions occurring during the electrolysis in both higher and lower current densities.

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 (~800-1000ºC) than direct thermal dissociation (>2500ºC).[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.[5-6] 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 850-1000ºC range. In the sulfur-iodine (S-I) cycle, the SO_2 is converted back to H_2SO_4 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 SO_2 to H_2SO_4 from a liquid-phase anode stream. The schematic of the hybrid-sulfur process is shown in Figure 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.

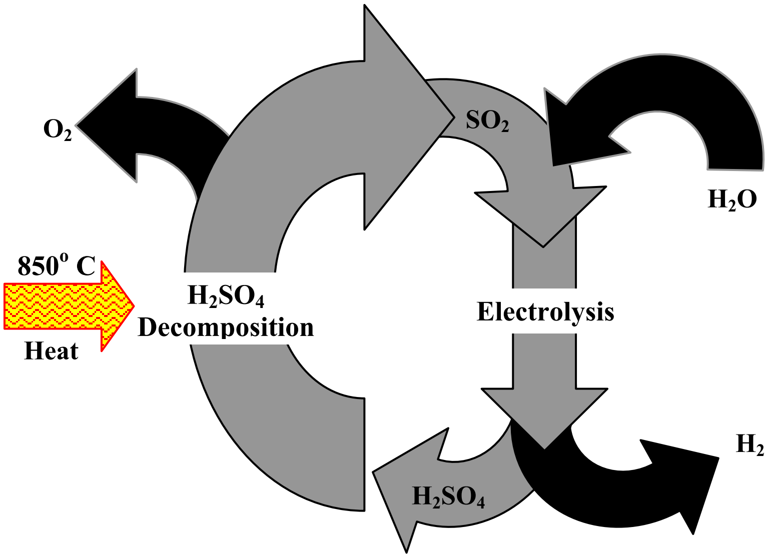

Figure 1: A schematic of the Hybrid Sulfur cycle, developed by Westinghouse. The H_2SO_4 is decomposed to SO_2 at high temperature, and the SO_2 is converted back to H_2SO_4 in the PEM electrolyzer at 80ºC. Overall only water and energy is consumed, and H_2 and O_2 are produced.

The calcium-bromide-based cycles also have the potential of high efficiencies but with lower temperature requirements (~750ºC) than the sulfur-based cycles. The common step in these cycles is the conversion of CaO and Br_2 to $CaBr_2$ and O_2 at approximately 550ºC, and the conversion of $CaBr_2$ back to CaO and HBr at 730ºC. The second recycle step, converting HBr to Br_2 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 Br_2 and H_2 in a single step (see the schematic in Figure 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 Br_2 in solution.[9] Gas-phase electrolysis has been attempted in phosphoric-acid[9,10] and molten-salt

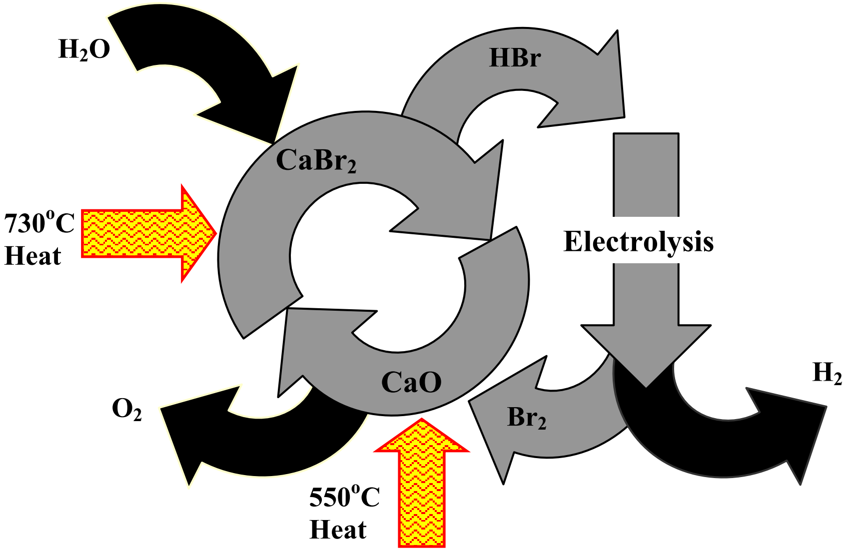

Figure 2: A schematic of the modified Ca-Br cycle. The CaO and $CaBr_2$ are recycled in a high temperature, solid-gas, fixed bed reactors, and the HBr is converted to Br_2 in the PEM electrolyzer at 80ºC. Overall only water and energy are consumed, and H_2 and O_2 are produced.

cells[11] to address these limitations. Although Br_2 dissolution was avoided in these cells, cell performance was poor.

In our previous work[13] we demonstrated the operation of a proton exchange membrane (PEM) electrolyzer for the conversion of: (1) SO_2 to H_2SO_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 improved the performance of electrochemical step in these two important thermochemical cycles. Here we show the results of increasing the current density and the platinum catalyst loading in the MEA.

Experimental Procedure

MEA Preparation: SO_2 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 cm^2 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 mg/cm^2 and 0.70 mg/cm^2, respectively. A poly[perfluorosulfonic] acid membrane (Nafion 115® from DuPont) was placed between the catalyst-coated GDLs and hot-pressed at 2000 psia and 130ºC in a Carver hot press (Model # 3851-0). Prior to its use, the Nafion 115 membrane was boiled in 1 N H_2SO_4 solution for 90 minutes and rinsed thoroughly with de-ionized water for 10 minutes.

MEA Preparation: HBr Electrolyzer

The MEAs were prepared with carbon cloth GDLs containing 2.0 mg/cm^2 of RuO_2 (ELAT-S® from ETEK) as the catalyst for both the anode and cathode. The 50 cm^2 cloths were taped at the edges with Teflon tape (3M Corporation, serial 5190) to give an active area of 40 cm^2. A poly[perfluorosulfonic] acid membrane (Nafion 105® from DuPont) was placed between the catalyst coated carbon cloths. No hot pressing was performed. Prior to use the Nafion membrane was boiled in 1 wt% HCl and rinsed and stored in D.I. water. Immediately before assembly the membrane was wiped dry.

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. 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 the free flow of water.

The cell temperature was maintained at 80 ºC with the aid of heating cartridges and thermocouples on the anode and cathode sides. Preheated (80 ºC) de-ionized water was sent to the cathode side of the electrolyzer at a fixed rate of 130 cm^3/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 SO_2. 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.

Results and Discussion

Current-Voltage Response: SO_2 Electrolyzer

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

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H^+ + 2e^- \qquad E^o= 0.17 \text{ V vs SHE.......[1]}$$

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

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^o = 0.0 \text{ V vs. SHE........[2]}$$

Thus the overall reaction in the electrolyzer is

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + H_2 \qquad \text{.................[3]}$$

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]

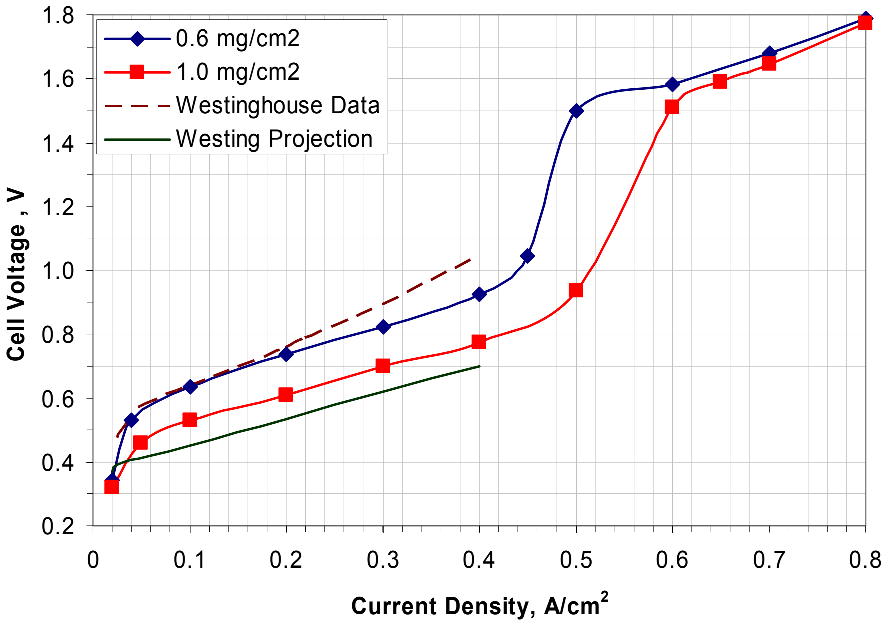

Figure 3: VI curves for the SO_2 oxidation reaction with two different loadings of Pt on carbon substrate. The data due to the experiments conducted by Westinghouse are also shown, they had a catalyst loading of 10 mg/cm^2.

Figure 3 shows the current-voltage response of the PEM electrolyzer for the oxidation of SO_2 to H_2SO_4 and the reduction of protons to H_2. Our data (♦ and ■) was collected at 80°C, 1.0 atm, and 5% conversion of SO_2. Although this conversion is low, the voltage varied by less than 30 mV for conversions between 5-40%, which is less than the size of the symbols. Two observations can be made from the figure. A higher loading of catalyst decreases the potential at which the reaction takes place. Furthermore we can see that there is a sharp rise in voltage at current densities higher than 0.45 A/cm^2. We hypothesize that the decrease in the amount of water crossing the membrane shifts the anode reaction from [1] to the following:

$$SO2 + H2O \longrightarrow SO3 + 2H+ + 2e- \qquad E^o = 0.82 \text{ V vs SHE........[4]}$$

Figure 3 also shows the best data from Lu *et al.*[7] (gray line) obtained at 50°C and 1.0 atm. The catholyte was dilute H_2SO_4 and the anolyte was 50 wt% H_2SO_4 pre-saturated with SO_2. The anode and cathode compartments were separated by a rubber diaphragm, and the platinum loadings were 7 mg/cm^2 and 10 mg/cm^2 on the anode and cathode, respectively. The dotted line in Figure 3 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/cm^2 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/cm^2 shows an improvement of nearly 300 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.

Current-Voltage Response: HBr Electrolyzer

On the anode side of the electrolyzer, the HBr is converted to Br_2 via the reaction

$$2HBr \longrightarrow Br_2 + 2H^+ + 2e^- \qquad E^o = 0.58 \text{ V vs. SHE........[5]}$$

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

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E^o = 0.0 \text{ V vs. SHE........[6]}$$

Thus the overall reaction in the electrolyzer is

$$2HBr \longrightarrow Br_2 + H_2 \qquad \text{...............[7]}$$

Unlike Reaction [3], no water is consumed in Reaction [7]. 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 the remove the hydrogen produced at the catalyst surface. Figure 4 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 Figure 3 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].

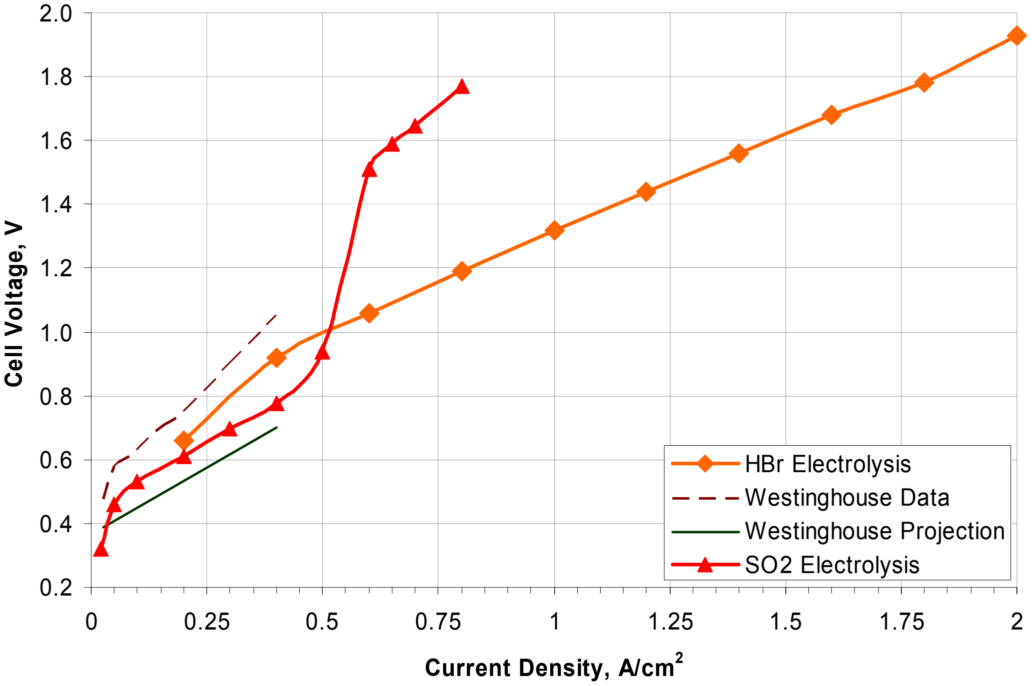

Figure 4: The current-voltage response for SO_2 (▲) and HBr (♦) electrolysis in a PEM electrolyzer. The results for the SO_2 electrolysis are the same as that given in Figure 3 but with a wider voltage scale. The HBr electrolyzer was operated at 80ºC, 1.0 atm, and 50% conversion with a RuO_2 loading on the anode and cathode of 2.0 mg/cm^2.

Another difference between the V-I performance curves for these two reactions is the overpotential 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 V and 9 V at 0.1 and 0.4 A/cm^2, respectively.

Conclusions

A proton exchange membrane (PEM) electrolyzer was used for the electrochemical conversion of: (1) SO_2 to H_2SO_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, SO_2 oxidation in the gas phase reduced the cell voltage by nearly 300 mV at 0.4 A/cm^2 compared to SO_2 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/cm^2 due to limitations in transporting water across the membrane above these currents. Further improvements maybe be possible by using thinner membranes, a humidified SO_2 feed stream, and elevated pressures. The activation barrier for SO_2 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 A/cm^2 to 2.0 A/cm^2) 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.

Acknowledgement

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.

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