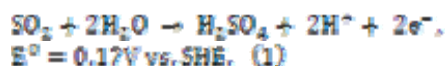


Nuclear Hydrogen Production by the SO₂ Depolarized Water Electrolysis Using PEMFC

Yong Hun Jung^{a*}, Byung Soo Shin^a, Yong Hoon Jeong^a
^aKAIST, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Korea
^{*}Corresponding author: moonrivery@kaist.ac.kr

1. Introduction

The sulfur-based thermochemical cycles are considered as the most promising methods to produce hydrogen. The Hybrid Sulfur (HyS) Cycle is a hybrid thermochemical cycle that utilizes the high temperature thermal decomposition of sulfuric acid to produce oxygen like S-I Cycle. However, HyS Cycle generates hydrogen in a water electrolyzer that is operated under conditions where dissolved sulfur dioxide depolarizes the anodic reaction, resulting in substantial voltage reduction. Sulfur dioxide is oxidized at the anode, producing sulfuric acid sent to the thermal decomposition part of the cycle. Eq. (1) and Eq. (2) are the anode and cathode side reaction each.



Thus the overall reaction in electrolyzer is Eq. (3).



In the 1970s, Westinghouse developed and demonstrated HyS Cycle [1]. Improved performance of the current electrolytic cell is expected to improve the overall efficiency of this promising cycle. This work focused on the improvement by the employment of the current commercial PEMFC (Proton Exchange Membrane Fuel Cell) and tested only electrolysis part of the HyS Cycle called once-through cycle compared to the closed cycle including the part of thermal decomposition of sulfuric acid.

2. Experiment

Schematic of electrolyzer equipment for this work is shown in Fig. 1. As you can see in this figure the equipment consisted of single PEMFC and two loops ; loop A(H₂SO₄-SO₂ or H₂O) and loop B(H₂O). Most of the loop B is made by Teflon to prevent chemical corrosion by sulfuric acid. Each loop has a reservoir chamber, pump and tube lines. H₂ chamber on loop B exists to measure the hydrogen production rate by using the ruler on the side of the H₂ chamber. The height of the H₂-water interface measured is multiplied for cross sectional area to give raw volume and then this is adjusted using measured pressure and temperature. Six thermocouples and four pressure transmitters are placed on the appropriate points.

The fuel cell hardware is EFC-25-01 model from Electrochem, Inc. and this consisted of 25cm² single

PEMFC with conditioned MEA, column flow pattern, attached heaters, fittings, gold plated current collectors, gaskets, voltage monitor banana plugs. The Membrane Electrode Assembly (MEA) using hydrophobic carbon paper as a backing layer with 1mg/cm² 20% Pt.catalyst loading and hot pressed into a Nafion™ membrane is the core component of a PEMFC.

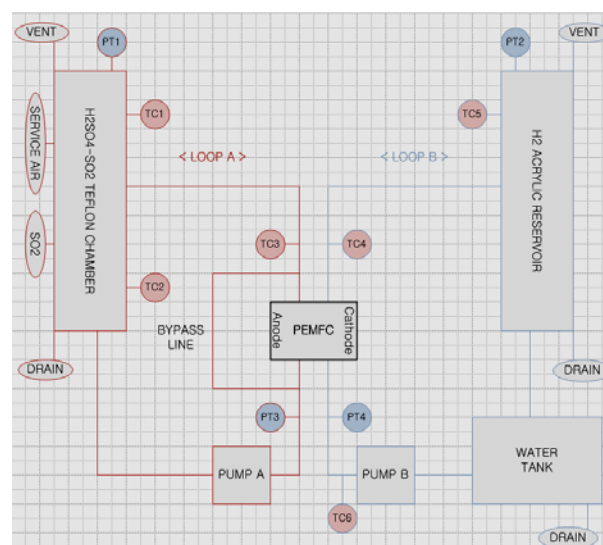


Fig. 1. Schematic of electrolyzer equipment.

3. Results and Discussion

Before using sulfur-based electrolysis, typical water electrolysis test was conducted to make sure the current commercial PEMFC is sufficiently efficient. In typical water electrolysis, water is oxidized at the anode to produce protons and oxygen. The minimum possible cell voltage for this typical water electrolysis is known as 1.23 V at 25°C. However, higher voltages ranging from 1.8 V to 2.6 V is typically needed for commercial water electrolysis [2].

Desirable results were accomplished. On all of the water electrolysis tests, hydrogen gas produced was visible to the naked eye on about 1.5 V and also the current as a result of water electrolysis was remained as a positive integer for the first time on voltages ranging from 2.0 V to 3.0 V according to the test conditions.

The following Fig. 2 and Fig. 3 show the results of the water electrolysis tests on the various conditions of flow rate and temperature.

As indicated in Fig. 2, the current density increases as the flow rate increases. The test beyond the range of 600mL/min couldn't be conducted due to the limitation coming from the characteristic of the pump and tube used on this work. However, results show us it would be saturated sooner.

Fig. 3 shows the current density increases with PEMFC cell temperature also. The optimized operating temperature of PEMFC is known as about 80°C. Both Fig. 2 and Fig. 3 show the results of the two test sets coming from use of the MEA rarely used and used for a long time period. This is due to the damage of MEA mainly caused by pressure imbalances within MEA for the long time use and seems to be much more severe than thought.

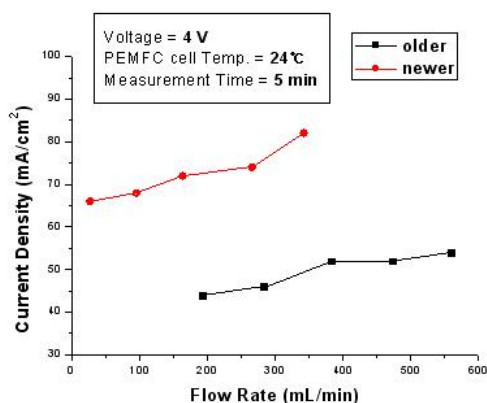


Fig. 2. The current density versus flow rate results of the typical water electrolysis tests.

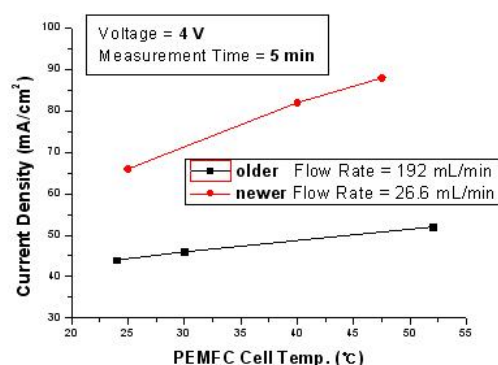


Fig. 3. The current density versus PEMFC cell temperature results of the typical water electrolysis tests.

Sulfur-based electrolysis test was conducted without any sulfuric acid on this work. Test with loop B filled with sulfur dioxide and about 1L water was conducted first and then filled with sulfur dioxide and little water which can barely wet the membrane was conducted after long time use of the same MEA. The first one was conducted in the condition of 200mL/min, 122mL/min on each loop A, B and 30°C of PEMFC cell temperature.

A slight positive pressure difference from the cathode side to anode side should be imposed to minimize sulfur dioxide crossover to the cathode. If this sulfur dioxide reacts with hydrogen gas produced, elemental sulfur can be formed [3].

On these tests hydrogen gas produced was observed clearly on about 0.8 V and also the current was maintained as a positive integer for the first time on voltages ranging from 0.5 V to 0.7 V. This is very

satisfactory results compared with the result from typical water electrolysis test.

After long time use of the same MEA, similar test was conducted with far less water on loop A. On this test, flow rate of each loop was kept as 150mL/min. Because loop A was filled with gas almost all, flow rate of loop A hardly affect the pressure imbalances within MEA. Therefore sulfur dioxide gas was injected continuously to keep a little bit less pressure to the anode side than the pressure to the cathode side resulted from flow rate of loop B water. It is known that carrying out the anode reactions in the gas significantly improves the efficiency because it enhances the transport rate of reactants to the electrode surface [4].

As a result, hydrogen gas was checked to the naked eye on about 0.9 V and also the current was maintained as a positive integer for the first time on voltages ranging from 0.5 V to 0.9 V. Considering this test was conducted after long time use of MEA, this is quite satisfactory result but it isn't when comparing with the current density result on 1.5 V and more than that. The first test set marked 116mA/cm² on 1.5 V but later test did only 44mA/cm² on 1.5 V.

4. Conclusions

An employment of the current commercial PEMFC and the use of sulfur-aided electrolysis could be a more efficient way to produce hydrogen. To keep getting advantage from increased flow rate, mass transfer limitation of MEA should be increased. Studies on the more efficient flow patterns in a PEMFC and membrane itself should be followed. Because of higher reaction rate and lower viscosity, sufficiently high temperature under consideration of the economical limitation and electrolyzer-based limitation would be favorable. Above all, it has developed that MEA is very weak at the mechanical damages especially at pressure imbalances. Further researches on the integrity of MEA by using new MEAs and on the optimization of the pressure balance in MEA would be carried out.

REFERENCES

- [1] Westinghouse Electric Corporation, 1980, "A Study on the Electrolysis of Sulfur Dioxide and Water for the Sulfur Cycle Hydrogen Production Process", AESD-TME-3043, July.
- [2] Kirk-Othmer, 1991, Encyclopedia of Chemical Technology, Fourth Edition, article on Hydrogen.
- [3] J. L. Steimke, T. J. Steeper, Characterization Testing and Analysis of Single Cell SO₂ Depolarized Electrolyzer, 2006.
- [4] P. Sivasubramanian et al., Electrochemical hydrogen production from thermochemical cycles using a proton exchange membrane electrolyzer, International Journal of Hydrogen Energy, 2006.