

DEVELOPMENTS OF ION EXCHANGE MEMBRANES FOR THE THERMOCHEMICAL HYDROGEN PRODUCTION I-S PROCESS

Takehide Kodaira¹, Kotone Oura¹, Ayumi Ikeda¹, Mikihiro Nomura^{*1}

Yasuhito Naka¹, Shin-ichirou Imabayashi¹

Shin-ichi Sawada², Tetsuya Yamaki²

Nobuyuki Tanaka³, Shinji Kubo³

¹Department of Applied Chemistry, Shibaura Institute of Technology

²Quantum Beam Science Center, Japan Atomic Energy Agency

³Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency

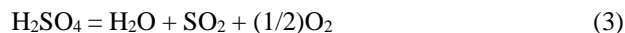
*Lscathy@shibaura-it.ac.jp

ABSTRACT

Thermochemical water splitting IS process is one of promising hydrogen production processes for large-scale applications. Hydrogen and oxygen are obtained from water by combining chemical reactions of iodine and sulfur compounds in Bunsen reaction ($I_2 + SO_2 + H_2O \rightarrow 2HI + H_2SO_4$). However, the amount of recycling I_2 needs to be reduced to improve the total thermal efficiency. In order to reduce I_2 in the Bunsen reaction, the reaction was conducted by using a cation exchange membrane (Electrochemical Bunsen reaction). Membranes were produced by a radiation grafting polymerization method to introduce poly-styrenesulfonicacid (grafted membrane) provide electrolyte membranes had ion exchange capacity (IEC) of 0.46–3.1 mmol g⁻¹. Water flux value evaluated by pervaporation (PV) method, grafted membrane showed under 55 % when compared to Nafion with same water uptake of 38 %. Besides about membrane performance indicators; reaction overpotential, grafted membrane showed 0.234 V and Nafion showed 0.240 V. From the point of water flux and overpotential, grafted membrane was developed as more suitable for Electrochemical Bunsen reaction than Nafion.

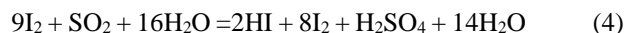
1. INTRODUCTION

A lot of attention of thermochemical water-splitting IS process (S. Kasahara et al., 2003) has been paid because it can use in large-scale and no CO₂ emission to produce hydrogen by introducing solar energy. Over 4000 processes have offered from 1970s, among them, IS process has been studied extensively for more than 30 years. The basic chemical reactions of IS process are as follows:



Reaction (1) is known as the Bunsen reaction to produces HI and H₂SO₄. HI and H₂SO₄ were produced as two phases because of difference in specific gravity between HIx and H₂SO₄ solution; HIx phase (HI-I₂-H₂O) and H₂SO₄ phase (H₂SO₄-H₂O). H₂ and O₂ are produced by reaction (2) and (3) respectively with recycling I₂ and SO₂ which are reactant for the process.

To separating HI and H₂SO₄ after Bunsen reaction, liquid-liquid phase separation are used with I₂ oversupply (M. Nomura et al., 2004). Then the equation of Bunsen reaction which added the excess I₂ is described below.



HI phase and H₂SO₄ phase separate (2HI-8I₂-10H₂O) and (H₂SO₄-4H₂O) respectively. At reaction (2) and (3), these solution will be evaporated and decomposed by using heat. However these vapor include a lot of water, thus large quantities of energy is required for evaporating and concentrating these liquid.

Carrying out Bunsen reaction without excess I₂, one of expected methods are Electrochemical Bunsen reaction which is using polymer electrolyte membrane for proceeding Bunsen reaction as an electrical reaction (M. Nomura et al., 2004). Fig. 1 shows the simplified schematic of Electrochemical Bunsen reaction. The reactions are as follows:



Cathode side: $I_2 + 2H^+ + 2e^- = 2HI$

Both of HI and H_2SO_4 solution is obtained separately into different cells compartmentalized by cation exchange membrane. Nomura et al (M. Nomura et al., 2004) reported that the excess amount of I_2 will be reduced by 93 % by Electrochemical Bunsen reaction. This means large quantities of H_2O which is used in Bunsen reaction by excess I_2 will be reduced. Then finally it connect to reduce increased energy consumption for evaporating and concentrating HI and H_2SO_4 solution. Many research groups have reported about Electrochemical Bunsen reaction, especially the efficiency of operating condition, such as reaction temperature, concentration of solution, for cell voltage and energy consumption with using Nafion as cation exchange membrane (V. Immanuel et al., 2012). However to solve problems such as lowering reaction voltage, suitable membranes for Electrochemical Bunsen reaction have to be developed by feedback membrane performance evaluation.

In this work, Nafion212 as reference membrane, and the membrane which was prepared by a radiation-graft polymerization technique were used for reaction experiments to determine their performances, over potential, proton transport number (t_+), to optimize process conditions in membrane making.

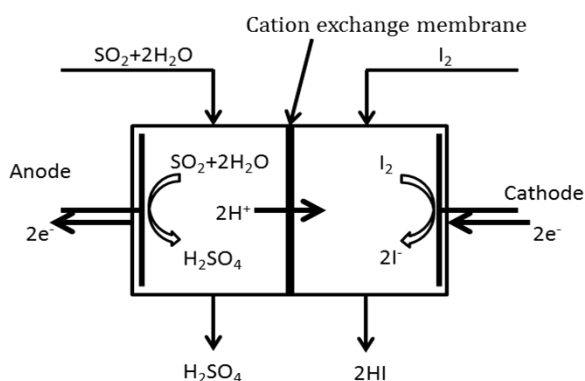


Fig. 1 Concept of Electrochemical Bunsen reaction.

2. EXPERIMENTAL

2.1 Membrane preparation

Cation exchange membranes were prepared by the radiation-induced grafting of styrene and divinylbenzene (DVB) into poly(ethylene-co-tetrafluoroethylene) (ETFE) films and subsequent sulfonation (T. Yamaki et al., 2010). A 50- μ m thick ETFE film was irradiated with γ -rays in Ar gas at the dose of 15 kGy. The irradiated film was immersed in a monomer solution containing styrene and DVB at 60 °C for 1-10 h. After grafting reaction, excess styrene was removed by toluene and drying under reduced pressure.

For sulfonation, the grafted film was immersed in a 0.2 M chlorosulfonic acid/1,2-dichloroethane mixture at 60 °C for 6 h. Finally, the sulfonated membrane was immersed in pure water for hydrolysis at 60 °C for 12 h.

2.2 Pervaporation (PV) test

The permeation properties of water thorough Nafion and obtained membranes were evaluated by using pure water PV test at room temperature. Fig. 2 shows a pervaporation apparatus. Before starting PV test, water fed continuously 30 min under vacuum to confirm steady state. Water fluxes were calculated by the weight of trapped water.

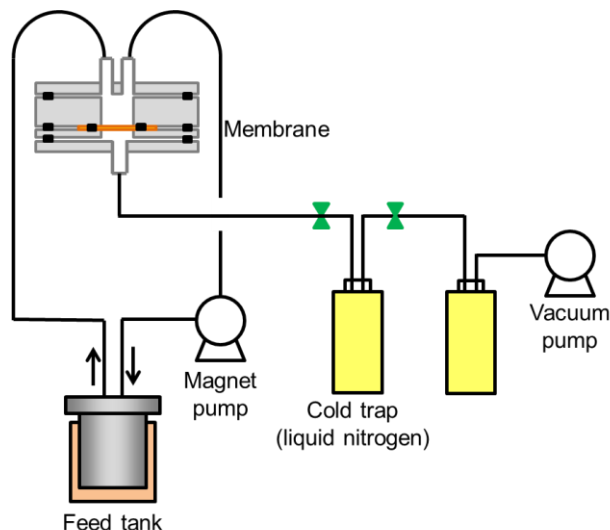


Fig. 2 The schematic of PV apparatus.

2.3 Electrochemical Bunsen reaction

Anolyte and catholyte of the redox type reactor were divided by a cation exchange membrane which is a filter-press type Electrochemical Bunsen reaction cell connecting with 2 glass reservoirs. The effective membrane area was 5 cm². 300 g of anolyte and catholyte with concentrations of H_2SO_4 (9 mol kg⁻¹) saturated with SO_2 gas and HI_x ($HI=10$ mol kg⁻¹, $I_2=10$ mol kg⁻¹), respectively. The test was carried out at room temperature for 3 h using 200 mA cm⁻² current density was by galvanostatic mode. Both anolyte and catholyte were sampled whenever someone choose for measuring the concentration of the solutions. Concentrations of the solution were evaluated by using an automatic potentiometric titrator of NaOH (0.1 mol L⁻¹) for H^+ and of $Na_2S_2O_3$ (0.1 mol L⁻¹) for I_2 .

The t_+ was calculated from the concentration profile of HI in catholyte (N. Tanaka et al., 2010).

$$t_+ = \frac{F \Delta A_{HI}^{Cathode}}{I \cdot t}$$

$\Delta A_i^{Cathode}$ is molality change of a component i in catholyte. I, t and F are electric current (A), electrolyte time (s) and Faraday constant (96485 C mol⁻¹), respectively.

The reaction resistance was introduced from the difference between the intercept of cell voltage-current curve and the voltage at 1 A of the current.

3. RESULTS AND DISCUSSION

3.1 Water permeation

About water permeation property, the relationships between water flux and water uptake was shown in Fig. 3. In the case of same water uptake about 40 %, radiation grafting membranes show small water flux comparing to Nafion especially crosslinked membrane. previous study (S. Kasahara et al., 2003) reported, performance of membrane was decreased by removal of water in the membrane. With the object of this point, radiation grafting membranes are superior to previous membranes. Besides, radiation grafting membranes have over twice ion exchange capacity (IEC) than Nafion. This indicates that smaller reaction overpotential will be expected because of high proton conductivity. Fig. 4 shows the activation energy of water permeation on same water uptake. The activation energy increased 5.59 kJ mol⁻¹ to 16.3 kJ mol⁻¹ by crosslinking. Therefore it was quantitatively estimated that crosslinking can make flow path inside of membrane narrow.

3.2 Proton transport number and reaction over potential

Fig. 5 shows the cell voltage-current curve. The reaction resistance of Nafion and grafting membrane at 1 A of the current were 0.240 V and 0.234 V respectively. This low value of the obtained membrane must be due to high proton conductivity of the membrane. Besides both of Nafion and the grafting membrane show 1 of t_+ . This means the grafting membrane has possibility to be used as the membrane with low reaction resistance and high t_+ .

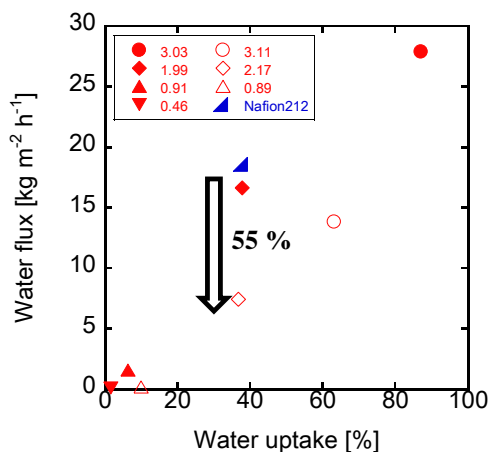


Fig. 3 The relationships between water flux and water uptake. Closed: non-crosslinking. Open: Crosslinked. Caption: IEC.

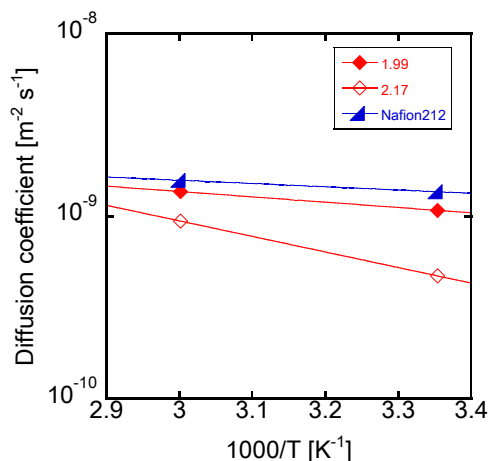


Fig. 4 The derivation of activation energy on 40 % of water uptake. Closed: non-crosslinking. Open: crosslinked. Caption: IEC

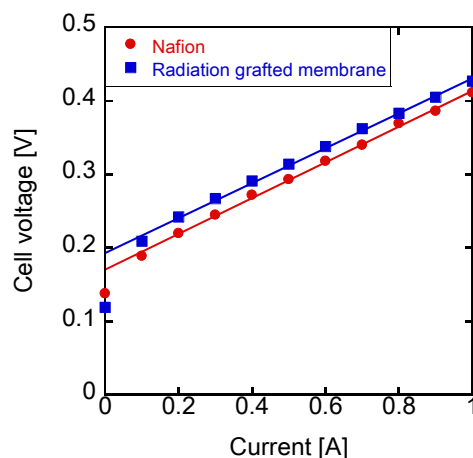


Fig. 5 Cell voltage-current curve.

CONCLUSION

The membrane which show low reaction overpotential and same extent of t_+ comparing to Nafion was developed by radiation grafting polymerization method. In the future, membrane performances will be evaluated moreover, and developed the membrane is optimized to Electrochemical Bunsen reaction.

ACKNOWLEDGEMENT

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “energy carrier” (Funding agency: JST).

REFERENCES

Kasahara Seiji, Hwang Gab-Jin, Nakajima Hayato, Choi Ho-Sang, Onuki Kaoru and Nomura Mikihiro, Effects of Process Parameters of the IS Process on Total Thermal Efficiency to Produce Hydrogen from Water, *J. Chem. Eng. Jpn.*, 36(7), 887-899, 2003.

Nomura Mikihiro, Nakao Shin-ichi, Okuda Hiroyuki, Fujiwara Seiji, Kasahara Seiji, Ikenoya Kazuhiro, Kubo Shinji, Onuki Kaoru, Development of an Electrochemical Cell for Efficient Hydrogen Production thorough the IS Process, *AIChE J.*, 50(8), 1991-1998, 2004.

Nomura Mikihiro, Fujiwara Seiji, Ikenoya Kazuhiro, Kasahara Seiji, Nakajima Hayato, Kubo Shinji, Hwang Gab-Jin, Choi Ho-Sang, Onuki Kaoru, Application of an electrochemical membrane reactor to the thermochemical water splitting IS process for hydrogen production, *J. Membr. Sci.*, 240, 221-226, 2004.

Immanuel V., Shukla A., Effects of operating variables on performance of membrane electrolysis cell for carrying out Bunsen reaction of I-S cycle, *Int. J. HYD. E.*, 37, 4829-4842, 2012.

Yamaki Tetsuya, Quantum-beam technology: A versatile tool for developing polymer electrolyte fuel-cell membranes, *J. Power Sources*, 195, 5848-5855, 2010.

Tanaka N., Yamaki T., Asano M., Maeawa Y., Onuki K., Electro-electrodialysis of HI-I₂-H₂O mixture using radiation-grafted polymer electrolyte membranes, *J. Membr. Sci.*, 346, 136-142, 2010.



Takehide Kodaira received the B.E. (2013), degrees in Applied Chemistry from Shibaura Institute of Technology. He is a master course student, Department of Applied Chemistry, Shibaura Institute of Technology.



Kotone Oura received the B.E. (2014) degrees in Applied Chemistry from Shibaura Institute of Technology. She is a master course student, Department of Applied Chemistry, Shibaura Institute of Technology.



Ayumi Ikeda received the B.E. (2012), M.E. (2014) degrees in Applied Chemistry from Shibaura Institute of Technology. She is a doctor course student, Department of Applied Chemistry, Shibaura Institute of Technology.



Mikihiro Nomura received the B.E. (1990), M.E. (1992) degrees Chemical Engineering from the University of Tokyo. He received the D.E. (1998) degrees Chemical System Engineering from the University of Tokyo. He is a Professor, Department of Applied Chemistry, Shibaura Institute of Technology. His Current interest is membrane separation.



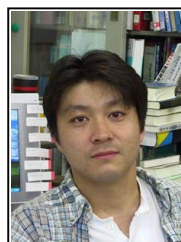
Yasuhito Naka received the B.E. (2013), degrees in Applied Chemistry from Shibaura Institute of Technology. He is a master course student, Department of Applied Chemistry, Shibaura Institute of Technology.



Shin-ichiro Imabayashi received the B.E. (1981) in Materials Chemistry (Yokohama National Univ.), and the M.Sc. (1983) and Ph.D. (1988) in Electronic Chemistry (Tokyo Inst. of Tech.). He is now a Professor in the Dept. of Applied Chemistry at Shibaura Inst. of Tech.



Shin-ichi Sawada received the B.E. (2003), M.E. (2005), and Ph.D. (2009) in Nuclear Engineering from the University of Tokyo. He is a scientist in Japan Atomic Energy Agency (JAEA).



Tetsuya Yamaki received the B.E. (1994) in Applied Chemistry from Waseda University, and the M.E. (1996) and Ph.D. (1999) in Nuclear Engineering from the University of Tokyo. He is a group leader in JAEA.



Nobuyuki Tanaka received the B.E. (2002) and the M.E. (2004) in Chemical System Engineering, and Ph.D. (2013) in Nuclear Engineering from the University of Tokyo. He is a scientist in JAEA.



Shinji Kubo received the B.E. (1991) and the M.E. (1993) in Mechanical Engineering from Utsunomiya University. He is a group leader in JAEA.