Application of Radiation-Grafted Polymer Electrolyte Membranes to the Bunsen Reaction

Nobuyuki Tanaka, Masaharu Asano, Kaoru Onuki and Yasunari Maekawa,
Japan Atomic Energy Agency

Abstract

Bunsen reaction was performed electrochemically using cation exchange membranes prepared by a radiation-induced grafting method for application to the iodine-sulfur thermochemical water-splitting cycle. The reaction experiments using sulfuric acid dissolving sulfur dioxide as the anolyte and hydriodic acid dissolving iodine as the catholyte verified the progress of the aimed reaction. Compared with Nafion 117, the radiation-grafted membranes showed lower electric resistance in the reaction condition, whereas they were less selective to proton permeation.

Introduction

Thermochemical water-splitting methods have been attracting a lot of interests because of its potential of efficient and economic hydrogen production, coupled with High Temperature Gas-Cooled Reactors (HTGR). Among many cycles proposed so far, those using iodine- and sulfur-compounds as process chemicals have been studied most intensively, the basic chemical reactions of which are as follows;

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4 \quad \text{[Bunsen reaction]} \qquad [1]$$

$$2HI = H_2 + I_2 \qquad [2]$$

$$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2 \qquad [3]$$

The reaction [1], known as Bunsen reaction, proceeds exothermically as SO_2 gas absorption reaction producing HI and H_2SO_4, and, then, decomposed endothermically at elevated temperatures producing H_2 and O_2, respectively. I_2 and SO_2 produced in the reactions [2] and [3], respectively, are reused in the Bunsen reaction. As the net result, H_2O is decomposed into H_2 and O_2. Here, the reaction [3] requires the highest temperature of over 800°C, which is well matched with the temperature range of HTGR.

Most of the present studies on the water-splitting process consider utilization of the liquid-liquid phase separation (LL separation) phenomenon for separating HI and H_2SO_4 produced by the Bunsen reaction, which was found by researchers of General Atomics (1). The LL separation occurs in the presence of excess amount of iodine and produces a heavier liquid phase containing mainly HI, I_2, H_2O and a lighter liquid phase containing mainly H_2SO_4 and H_2O. This method offers an easy and simple way of the separation. However, it requires large inventory and large circulation of iodine.

The present study concerns the Bunsen reaction using an electrochemical cell equipped with a cation exchange membrane. Fig. 1 shows the concept of the reaction system. The electrode reactions are as follows

Anode : $SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^-$ [4]
Cathode: $I_2 + 2H^+ + 2e^- = 2HI$ [5]
Total: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$ [Bunsen reaction] [1]

By using the separation membrane, an excess amount of iodine is not required for the separation. Dokiya et al. (2) first proposed the idea of using electrochemical cell and demonstrated the aimed separation. Recently, Nomura et al. (3) verified the production of sulfuric acid and hydriodic acid, whose concentrations were higher than those attainable by the spontaneous thermal reaction. However, in their experiments using Nafion, very high cell voltage was necessary for operating with the concentrated solutions, and sulfur formation was observed. In this paper, applicability of polymer electrolyte membranes prepared by a radiation-induced grafting method (4) was examined preliminarily.

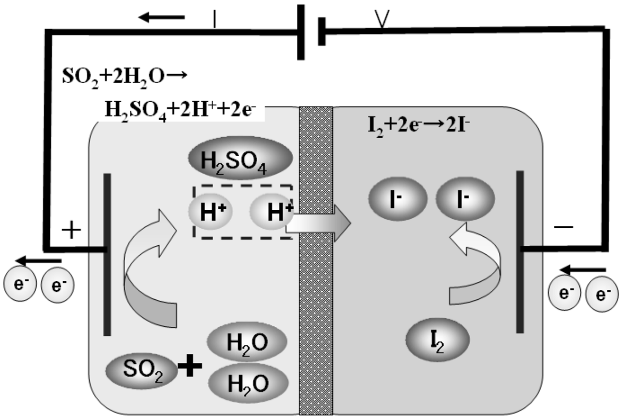

Fig. 1 Concept of electrochemical Bunsen reaction electrochemical cell

Experimental

Chemicals and membranes

Hydriodic acid (55-58wt%, Kanto Chemical Co., Inc.), iodine (>99.8wt%, Kanto Chemical Co., Inc.) and Sulfuric acid (97wt%, Wako Pure Chemical Industries, Ltd. and 47wt%, Kanto Chemical Co., Inc.) were used as received for prepared test solutions. SO_2 gas (>99.9%, Sumitomo Seika Chemicals Co., Ltd.) was used to prepare the anolyte solution by bubbling into sulfuric acid for one hour.

In the preparation of grafted membranes, poly-(ethylene-co-tetrafluoroethylene) (ETFE) film (thickness of 50 μm, kindly supplied from Asahi Glass Co.) was used as a base film for grafting. ,*P*-methlstyrene (MeSt, 99%, Sigma-Aldrich Japan K.K.) and *p-tert*-buthylstyrene (tBuSt, 93%, Sigma-Aldrich Japan K.K.) were used for grafting monomers. The sulfonic acid was introduced by the sulfonation reaction of the grafts in the membranes. Details of the membrane preparation and characterization were described elsewhere (4). Table 1 lists the properties of membranes used in this study. Nafion 117 (E.I.du Pont) was used as the reference membrane.

Table 1 Properties of the membranes prepared

ID	Monomer	IEC [mmol/g]	Conductivity [mS/cm]	Water uptake [wt%]
RG1	MeSt	1.4	71	39
RG2	MeSt/tBuSt(1:1)	1.4	82	44
RG3	tBuSt	1.0	22	22

0.1 mol/L sodium thiosulfate solution, 0.1mol/L sodium hydroxide, 0.5mol/L Iodine solution were purchased from Kanto Chemical Co., Inc. and used as received for the concentration analysis of test solutions.

Electrochemical Bunsen reaction

The experimental setup consisted of an electrochemical cell, two glass reservoirs for anolyte and catholyte solutions, two peristaltic pumps (RP-1000, Tokyo Rikakikai Co. Ltd.), and a DC power supply (HA-305, Hokuto Denko Corp.). The cell was a filter-press type one (FC-05-02, ElectroChem, Inc.) with two rubber gaskets made of Kalrez® (thickness of 0.5mm). Carbon felts (Toyobo Co. Ltd.) were used as the electrode by inserting in between membrane and carbon current collectors. The effective membrane area was 5cm^2. Rubber heaters were used to control the operation temperature. Glass reservoirs were connected with each compartment of the cell using Teflon® and Fluran® tubes.

In the experiment, 300g of a HIx solution with concentrations of [HI]=[I_2]=10 mol/kg was fed to the catholyte reservoir, and 300g of SO_2 gas saturated sulfuric acid with H_2SO_4 molality of 10 mol/kg was fed to the anolyte reservoir. The solutions were heated to 40℃ while circulating to the cell for about one hour. Then, direct current was supplied to the cell in a galvanostatic mode with current density of 200 mA/cm^2 for 3 hours. The catholyte and the anolyte solutions were sampled every 1 hour and the concentrations were measured by alkalimetry and iodometry.

Result and Discussion

Fig. 2 shows the changes of HI and I_2 molality in catholyte and H_2SO_4 molality in anolyte observed in the experiment using RG1 membrane. The change of SO_2 concentration is also shown in the same figure. As seen in the figure, in the course of operation, the HI molality in catholyte

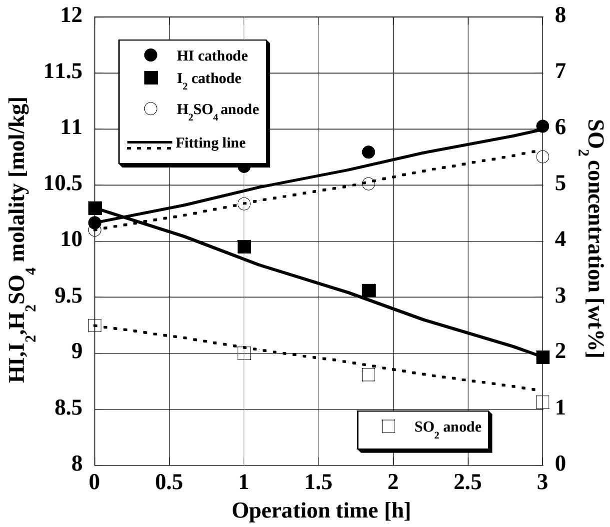

Fig.2 Concentration change in the electrochemical Bunsen reaction using RG1 membrane

Anolyte: SO_2 saturated sulfuric acid,

$[H_2SO_4]$=10mol/kg

Catholyte: HIx solution, $[HI]=[I_2]$=10mol/kg

Temperature: 40°C

Current Density: 200 mA/cm^2

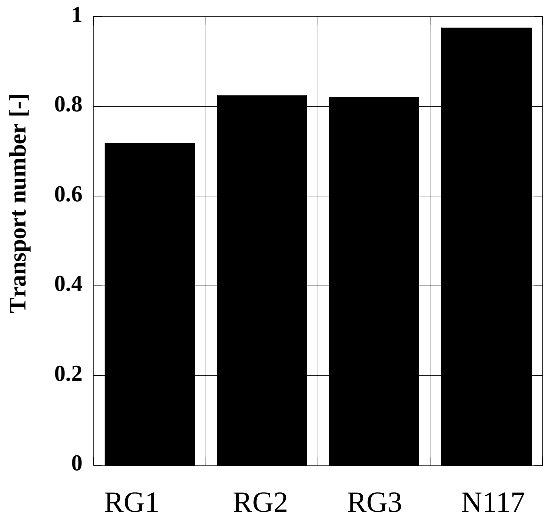

Fig. 3 Observed transport number

Experimental conditions are the same as in Fig.2

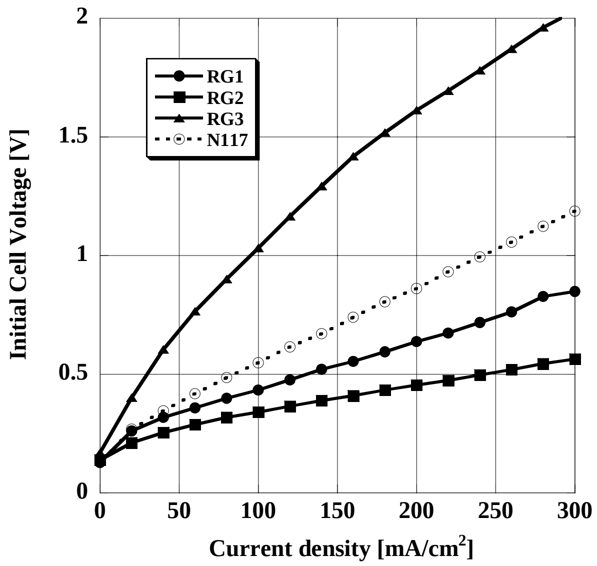

Fig. 4 Cell voltage vs current density

Experimental conditions are the same as in Fig.2

increased from 10.1 to 11.0mol/kg and the H_2SO_4 molality in anolyte increased from 10.1 to 10.7mol/kg, whereas the I_2 and the SO_2 concentrations decreased. These changes are qualitatively explained by assuming the reactions [4] and [5], indicating the progress of expected Bunsen reaction. At the same time, in the course of operation, the anolyte solution became yellow and the membrane surface faced to anolyte solution became white. It was presumed that precipitation of sulfur caused these phenomena.

In order to discuss the sulfur formation mechanism, transport number of proton (t_+) was estimated. It was defined as follows,

$$t_+ = \frac{F\Delta M_{HI}}{I \cdot t}$$

where, F, ΔM_{HI}, I, t denote Faraday constant, change of HI quantity in catholyte [mol], electric current supplied [A], operation time [s], respectively. The estimation of transport number was carried out by simulating the observed change of HI molality.

Fig. 3 shows the obtained transport numbers. The fitting line used this parameter was showed in Fig. 2. Nafion117 showed high value of 0.98, which was in accord with the reported one (3), whereas the radiation-grafted membranes showed lower value of 0.7 - 0.8. Also, it was observed that the lower the transport number was, the clearer the color changes were in anolyte and in membrane. These results suggest that iodide ion (I^-) permeated from catholyte to anolyte reacted with SO_2 to produce sulfur. The reaction equation might be "$SO_2 + 4HI = S + H_2O + 2I_2$" (3,5).

Fig. 4 shows the relationships between cell voltage and current density. The cell voltage was largest in the experiment using RG3 membrane, followed by RG1 and RG2 membranes. The cell voltages in the latter two cases were lower than that in the case of Nafion117.

It is interesting to note that RG2 membrane showed highest transport number and lowest electric resistance, as well, among the membranes prepared. Especially, the observed cell voltage was about half of that of Nafion. RG2 was prepared by graft co-polymerization of *p*-methylstylene and *t*-butylstylene, and exhibited the similar low electric resistivity as RG1 that featured *p*-methylstylene and the similar high ion selectivity as RG3 featuring *t*-butylstylene. The results suggest the possibility of further improvement of the membrane performance by optimizing membrane structure.

Conclusion

The radiation-grafted membranes were employed for the Bunsen reaction using an electrochemical cell equipped with carbon electrodes. The HIx solution with concentrations of $[HI]=[I_2]=10$ mol/kg in catholyte and SO_2 gas saturated sulfuric acid with H_2SO_4 molality of 10 mol/kg in anolyte were employed. The reaction was examined with current density of 200mA/cm^2 at 40℃. The results are summarized as follows.

1. The proton transport numbers of the radiation-grafted membranes (0.7-0.8) were lower than that of Nafion117 (0.98). Indication of sulfur formation due to the low ion selectivity was observed in anolyte.
2. Some radiation-grafted membranes showed lower electric resistance than Nafion117. The observed lowest cell voltage was about half of that of Nafion117.
3. A radiation-grafted membrane prepared by graft co-polymerizing *p*-methylstylene and *t*-butylstylene into ETFE film showed highest ion selectivity and lowest electric resistance among the membranes tested.

Improvement of the membrane performance is expected by optimizing the grafting conditions such as a base polymer and monomer structures, and a degree of grafting.

Acknowledgment

The authors express their gratitude to Mr. K. Ikenoya for the implementation of experiments. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1. J.L. Russell et al., (1976) "Water splitting – A progress report," *Proc. 1st World Hydrogen Energy Conf.*, Miami-Beach, Florida, USA, March 1-3, 1976, 1A105-1A124.
2. M. Dokiya et al., (1979) "Thermochemical Hydrogen Production – Part V. A feasibility study of the Sulfur Iodine Cycle," Int. J. Hydrogen Energy, 4, pp.267-277
3. M. Nomura et al., (2004), "Development of an Electrochemical Cell for Efficient Hydrogen Production through the IS process," *AIChE Journal*, 50, pp.1991- 1998.
4. J. Chen et al., (2006) "Preparation and characterization of chemically stable polymer electrolyte membranes by radiation-induced graft copolymerization of four monomers into ETFE films," *J. Membr. Sci.*, 269, pp.194-204.
5. M. Sakurai et al., (2000) "Experimental study on side-reaction occurrence condition in the iodine-sulfur thermochemical hydrogen production process," *Int. J. Hydrogen Energy*, 25, pp.613-619.