© 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2504—2508 (1983) [Vol. 56, No. 8

Decomposition of Hydrogen Bromide or Iodide by Gas Phase Electrolysis

Wakichi KONDO,* Susumu MIZUTA, Yoshinao OOSAWA, Toshiya KUMAGAI, and Kinjiro FUJII
Energy Chemistry Division, National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki, 305

(Received December 10, 1982)

Gas phase electrolysis of HBr or HI was studied by using a fuel-cell-type electrolyzer provided with graphite gas diffusion electrodes and liquid film electrolyte of H_3PO_4. Current efficiency 100% may be achieved at decomposition voltages of 0.73 V (at 100 mA cm^{-2} and 150 °C) for HBr and 0.28 V (at 100 mA cm^{-2} and 145 °C) for HI. Both bromine and iodine produced may smoothly be evolved out of the anode in the gas or liquid form without being dissolved into the electrolyte H_3PO_4, causing no trouble on the separation of products. This electrolytic method may be incorporated in the bromine or iodine cycles for thermochemical hydrogen production to constitute an effective hybrid system.

The hydrogen production by a thermochemical cycle was extensively studied in 1970's. On the other hand, the hybrid system consisting of thermochemical and electrochemical processes began to be investigated when the pure thermochemical system was concluded to be extremely difficult. For the bromine and the iodine cycles,[1—6)] much effort has been concentrated on the electrochemical decomposition of hydrogen bromide and iodide[4—12)] since the decomposition of hydrogen halides was found to play a vital role in the cycle.

Below are listed some thermochemical values[13)] associated with the decomposition of HBr and HI:

$$2HBr(g) \longrightarrow H_2(g) + Br_2(g) \qquad (1)$$

$$\Delta H^\circ_{298} = 24.8\ \text{kcal mol}^{-1}\ (1\ \text{cal}=4.184\ \text{J})$$

$$\Delta S^\circ_{298} = -5.2\ \text{cal mol}^{-1}\,\text{K}^{-1}$$

$$\Delta G^\circ_{298} = 26.2\ \text{kcal mol}^{-1}$$

$$\Delta G^\circ_{700} = 28.0\ \text{kcal mol}^{-1},$$

$$2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad (2)$$

$$\Delta H^\circ_{298} = 2.3\ \text{kcal mol}^{-1}$$

$$\Delta S^\circ_{298} = -5.3\ \text{cal mol}^{-1}\,\text{K}^{-1}$$

$$\Delta G^\circ_{298} = 3.9\ \text{kcal mol}^{-1}$$

$$\Delta G^\circ_{700} = 5.6\ \text{kcal mol}^{-1}.$$

From these values one can easily understand that the thermochemical decomposition of HBr is fairly difficult[6,14,15)] because of its too high a ΔG° (over 25 kcal mol^{-1}). The electrochemical decomposition of HBr in the aqueous state has extensively been studied by several investigators; according to Schuetz,[5)] an HBr electrolysis, using graphite electrodes, at a cell voltage of 0.75—0.8 V and a current density of 200 mA cm^{-2} proceeds with a highly concentrated (47 wt%) HBr aqueous solution at 353—373 K and atmospheric pressure.

On the other hand, the decomposition of HI seems at first sight much easier because of its low ΔG° (5.6 kcal mol^{-1} at 700 K), but has been found more troublesome than expected since the mixed gas (H_2, I_2, HI, and H_2O) formed by direct pyrolysis requires a severe separation processing; some separation processes have been proposed[16—20)] but their improvement is still required. As for the HI electrolysis no reports with detailed experimental descriptions have been published to the best of the present authors' knowledge.

The present authors have noted that the gas phase electrolysis is superior to the aqueous electrolysis in the following three respects:

1) As shown in Table 1, the theoretical decomposition voltages for the HX gases (0.58 V for HBr and 0.065 V for HI) are by far lower than those (1.08 and 0.54 V, respectively) for the aqueous HX. This is because the HX molecule in the gas phase is at a higher energy level than the one in the aqueous state ($a=1$) by the amount of free energy of hydration. For aqueous electrolyses at sufficiently low cell voltages (*e.g.*, 0.6—0.8 V for HBr) are to be achieved, an extremely concentrated HX solution is required as previously reported.[8,9,12)]

2) In the case of aqueous electrolysis, it is necessary to separate product X_2 from HX solution because Br_2 or I_2 immediately dissolves into aqueous HBr or HI solution by forming polyions such as Br_3^-, Br_5^-, I_3^-, and I_5^-. Such a separation process for the aqueous products is regarded as a great burden on the whole cycle from both the viewpoints of the circulation of materials along the cycle and the suppression of excessive overvoltage. On the other hand, the gas phase electrolysis has a possibility to be provided with some proper electrolyte in which Br_2 or I_2 is insoluble.

3) In the case of actual thermochemical cycles where HBr or HI is produced mostly in the gas phase, the direct participation of HX in electrolysis with no condensation

TABLE 1. FREE ENERGY CHANGES AND THEORETICAL DECOMPOSITION VOLTAGES FOR THE DECOMPOSITION OF HBr AND HI

Reaction	Temp K	ΔG° kcal mol^{-1}	E° V
$2HBr(aq\ a=1) \longrightarrow H_2(g)+Br_2(l)$	298	49.7	1.08
$2HBr(g) \longrightarrow H_2(g)+Br_2(g)$	400	26.8	0.58
$2HI(aq\ a=1) \longrightarrow H_2(g)+I_2(c)$	298	24.7	0.54
$2HI(g) \longrightarrow H_2(g)+I_2(l)$	400	3.0	0.065

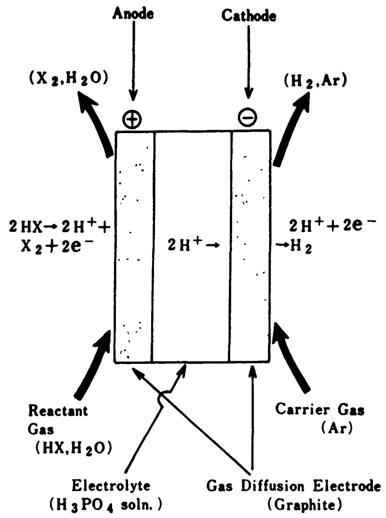

Fig. 1. Principle of the gas phase electrolysis for HX.

process is efficient and favorable.

In view of the above advantages a new process of gas phase electrolysis for hydrogen bromide or iodide has been devised and experimentally studied which makes use of a fuel-cell-type electrolyzer with electrolyte H_3PO_4 and graphite gas-diffusion electrodes.

Principle

The principle of this method is illustrated in Fig. 1. When reactant gas HX (=HBr or HI) containing some amount of water vapor is supplied into the gas diffusion type anode, the following electrochemical reaction takes place at contact points among the three phases of gas, electrolyte, and electrode:

$$2HX \longrightarrow 2H^+ + X_2 + 2e^-. \qquad (3)$$

Product X_2 (=Br_2 or I_2) hardly dissolves into the electrolyte H_3PO_4 because of its intrinsic, extremely low solubility and is released from the anode in the gas or liquid form, whereas the H^+ migrates through the electrolyte to be reduced at the cathode according to the following reaction and removed by a carrier gas of Ar:

$$2H^+ + 2e^- \longrightarrow H_2. \qquad (4)$$

These electrochemical processes require no cation exchanger membranes since the dissolution of HBr or HI gas into H_3PO_4 and their subsequent diffusion toward the cathode are negligible; the electrolyte H_3PO_4 is taken to serve as an ion separator.

The water vapor contained in the reactant gas does not interfere with the electrochemical reactions but has a favorable effect for the suppression of water evaporation from the electrolyte H_3PO_4.

Experimental

The fuel-cell-type electrolyzer used is illustrated in Fig. 2. The cell consists of the following parts: two stainless steel flanges of 140×120×5 t mm; two graphite holders of 95×110×22 t mm, each of which is provided with 26 ditches of 2×50×1 d mm to allow the reaction gas to pass from the inlet to outlet and with a lead terminal made of tantalum; two gas-diffusion-type graphite-cloth electrodes of 18×45×0.5 t mm, on both of which platinum was loaded by impregnation of hexachloroplatinic(IV) acid followed by H_2 reduction; four PTFE spacers 0.3—0.5 mm thick; an electrolyte-bearing matrix of 35×55×0.5 t mm, made of tantalum(V) oxide cloth with a porosity of *ca.* 90%. No trouble was experienced throughout the experiment up to temperatures as high as 170 °C. The electric resistance of the cell was about 0.12±0.02 Ω for 85% H_3PO_4 electrolyte.

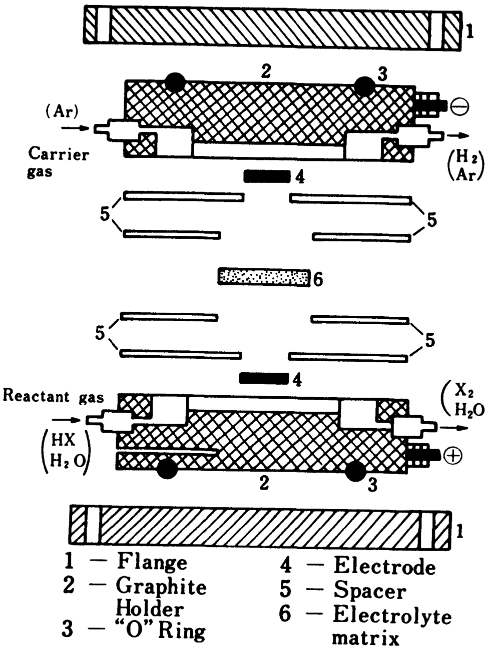

Fig. 2. Fuel-cell-type electrolyzer for HX gas.

A reactant gas, prepared by mixing a commercially available anhydrous cylinder HBr or HI gas (Matheson, purity >99%) and a vaporized hydrobromic acid (aqueous HBr, 47.5 wt%) or hydriodic acid (aqueous HI, 57 wt%), respectively, was introduced into the anode side at a rate of 250 cm³ min⁻¹. An argon carrier gas was supplied into the cathode side at a rate of about 80 cm³ min⁻¹. The current efficiency was calculated on the basis of the hydrogen concentration in the argon as determined by gas chromatography.

To examine qualitatively the dissolution of bromine or iodine into phosphoric acid, a mixture of bromine or iodine with 85 wt% H_3PO_4 solution was heated to 150 °C, and subjected to a visual check for coloration; such a slight color change was observed that we might regard the dissolution as negligible.

Results and Discussion

Gas Phase Electrolysis for Hydrogen Bromide. The following four findings have been derived from the current-voltage results in Fig. 3 and the current efficiency results in Table 2.

(i) Current efficiency 100% is always obtained at electrolysis temperatures above 150 °C, in contrast to 75—95% at 118 °C (see Table 2). This low current efficiency at a lower temperature is possibly due to dissolution of bromine into the electrolyte H_3PO_4 followed by diffusion to the cathode. It is evident that there is no problem with respect to current efficiency above 150 °C (compare runs 1, 3, 7, and 8 with runs

TABLE 2. CELL VOLTAGES AND CURRENT EFFICIENCIES WITH RUNNING CONDITIONS FOR HBr GAS ELECTROLYSIS

Run no.	Amount of catalyst mg-Pt cm^{-2}	Temp °C	Reactant gas constituent atm ($HBr/H_2O/Br_2/N_2$)	Cell voltage (at 100 mA cm^{-2}) V	Current efficiency %
1	0.75	118	0.45/0.45/0/0.1	0.80	≈75
2	0.75	135	0.45/0.45/0/0.1	0.84	≈100
3	5.3	118	0.45/0.45/0/0.1	0.74	≈95
4	5.3	135	0.45/0.45/0/0.1	0.73	≈100
5	5.3	150	0.45/0.45/0/0.1	0.73	≈100
6	5.3	165	0.45/0.45/0/0.1	0.73	≈100
7	5.3	118	0.2/0.2/0/0.6	0.80	≈95
8	5.3	118	0.2/0.2/0.2/0.4	0.79	≈80
9	5.3	135	0.2/0.2/0.2/0.4	0.80	≈95
10	5.3	150	0.78/0.12/0/0.1	0.73	≈100
11	5.3	150	0.2/0.2/0/0.6	0.80	≈100
12	5.3	150	0.2/0.2/0.2/0.4	0.81	≈100

TABLE 3. CELL VOLTAGES AND CURRENT EFFICIENCIES WITH RUNNING CONDITIONS FOR HI GAS ELECTROLYSIS

Run no.	Amount of catalyst mg-Pt cm^{-2}	Temp °C	Reactant gas constituent atm ($HI/H_2O/I_2/N_2$)	Cell voltages (at 100 mA cm^{-2}) V	Current efficiency %
1	0.75	118	0.45/0.45/0/0.1	0.26_5	≈20
2	0.75	135	0.45/0.45/0/0.1	0.44	≈100
3	0.75	145	0.45/0.45/0/0.1	0.43	≈100
4	0.75	155	0.45/0.45/0/0.1	0.42	≈100
5	3.5	145	0.45/0.45/0/0.1	0.35	≈100
6	5.3	145	0.45/0.45/0/0.1	0.28	≈100
7	3.5	145	0.66/0.28/0/0.06	0.31_5	≈100
8	3.5	145	0.86/0.06/0/0.08	0.37	≈100
9	3.5	155	0.14/0.74/0/0.12	(0.54)$^{a)}$	≈100
10	3.5	155	0.12/0.65/0.12/0.11	(0.57)$^{a)}$	≈100

a) Extrapolated.

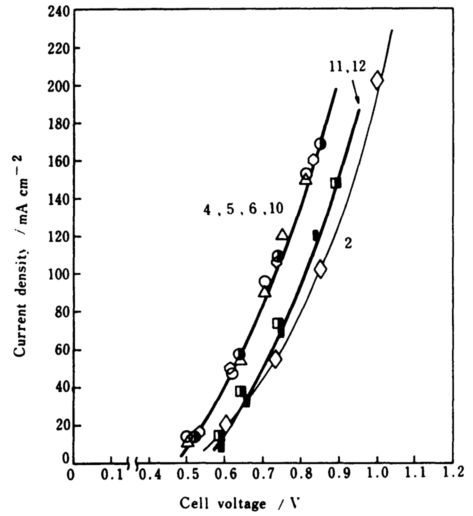

Fig. 3. Current-voltage Curves for HBr gas electrolysis.

5, 6, 10, 11, and 12).

(ii) When the reactant gas composition and the electrolysis temperature are kept $HBr/H_2O/Br_2/N_2$= 0.45/0.45/0/0.1 and 135 °C, respectively, the decomposition voltage at a current density of 100 mA cm^{-2} lowers (0.84→0.73 V) with increasing amount of the Pt catalyst loaded on the graphite electrodes (0.75→5.3 mg-Pt cm^{-2}) (compare run 2 with run 4).

Decomposition voltage 0.73 V obtained in runs 4, 5, and 6 may be considered to be low enough to be comparable with the values 0.75—0.8 V (at 200 mA cm^{-2} and 80—100 °C with 47.5 wt% HBr soln.) reported by Schuetz.[5)]

(iii) When the amount of catalyst and the electrolysis temperature are kept 5.3 mg-Pt cm^{-2} and 150 °C, the decomposition voltage rises (0.73→0.80 V) with decrease in the HBr partial pressure P_{HBr} (0.78→0.2 atm) (see runs 5, 10, and 11).

(iv) Inclusion of bromine in the reactant gas decreases the current efficiency at 118 and 135 °C (runs 7, 8, and 9), and at 150 °C it causes no change in current efficiency from 100% and increases the decomposition voltage a little (0.80→0.81 V) (runs 11 and 12).

Gas Phase Electrolysis for Hydrogen Iodide. The following four findings have been derived similarly to the case of hydrogen bromide, from the current-voltage results in Figs. 4 and 5 and the current efficiency results in Table 3.

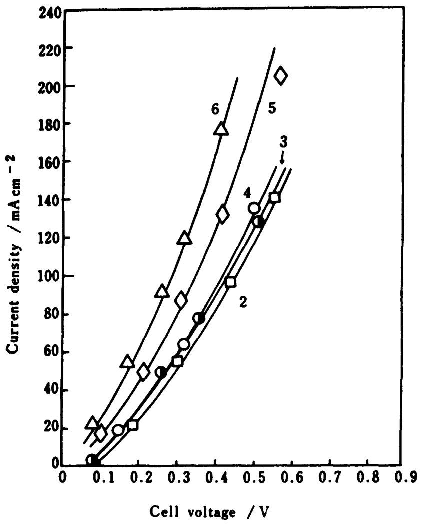

Fig. 4. Current-voltage curves for HI gas electrolysis with reactant gas constituent ($HI/H_2O/I_2/N_2=0.45/0.45/0/0.10$).

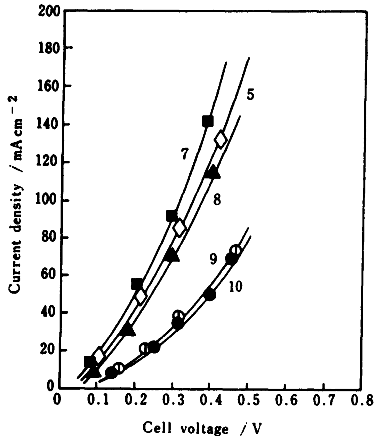

Fig. 5. Current-voltage curves for HI gas electrolysis with amount of catalyst 3.5 mg Pt/cm^2.

(i) Current efficiency 100% is successfully obtainable except at 118 °C (Table 3). The current efficiency drop at 118 °C is attributable to the dissolution of iodine into the electrolyte H_3PO_4 followed by the diffusion to the cathode. Above 135 °C, however, there is no trouble with the magnitude of current efficiency (compare run 1 with runs 2, 3, and 4).

(ii) When the reactant gas composition and the electrolysis temperature are kept $HI/H_2O/I_2/N_2=0.45/0.45/0/0.10$ and 145 °C, respectively, the decomposition voltage at a current density of 100 mA cm^{-2} lowers (0.43→0.35→0.28 V) with increasing amount of the Pt catalyst loaded on the graphite electrodes (0.75→3.5→5.3 mg cm^{-2}) (see runs 3, 5, and 6).

Decomposition voltage 0.28 V obtained in run 6 may be regarded practically as sufficiently low.

(iii) When the amount of catalyst and the electrolysis temperature are fixed at 3.5 mg-Pt cm^{-2} and 145 °C, respectively, the decomposition voltage lowers (0.35→0.315 V) with increasing HI partial pressure P_{HI} (0.45→0.66 atm) (see runs 5 and 7). A similar lowering occurs at 155 °C (see runs 4 and 9). However, in the case of extremely low H_2O partial pressures (P_{H_2O}) such as 0.06 atm as in run 8, the decomposition voltage even rises up to 0.37 V in spite of the high P_{HI} (0.86 atm). Thus, some amount of P_{H_2O}, together with high P_{HI}, is supposed to be important for the electrochemical reaction at the anode.

(iv) Inclusion of I_2 in the reactant gas does not interfere with the electrolysis or the separation of products, although it causes the decomposition voltage to increase a little (0.54→0.57 V) (see runs 9 and 10).

No change in H_3PO_4 concentration was observed throughout the experiments and a negligible evaporation of water was observed from the cathode. No adhesion of liquid I_2 onto the anode causing an increase in overvoltage was found.

Summary. The findings described above lead us to conclude that the present gas phase electrolysis can be operated with 100% in current efficiency at a favorable decomposition voltage as low as that in the conventional electrolyses, if the electrolysis temperature, electrode catalyst, P_{HX}, and P_{H_2O} are suitably selected; for example, operating voltages available are 0.73 V at 100 mA cm^{-2}, 150 °C, 5.3 mg-Pt cm^{-2}, and 0.45 atm for HBr and 0.28 V at 100 mA cm^{-2}, 145 °C, 5.3 mg-Pt cm^{-2}, and 0.45 atm for HI.

An important advantage of the present method is the immediate separation of products Br_2 and I_2 from the electrolyte, which enables a long-term operation to run with a steady condition.

The authors would like to express their gratitude to Messrs. Kyo Fuchida, Chiaki Kawamura, and Hiroshi Yufu of Yuasa Battery Co., Ltd. for their cooperation in making the fuel-cell-type electrolyzer.

References

1) G. E. Besenbruch, K. H. McCorkle, J. H. Norman, D. R. O'Keefe, J. R. Shuster, and M. Yoshimoto, Proc. of the 3rd WHEC, Tokyo, 243 (1980).

2) H. Kameyama and K. Yoshida, Proc. of the 3rd WHEC, Tokyo, 1939 (1980).

3) S. Sato, S. Shimizu, H. Nakajima, K. Onuki, and Y. Ikezoe, Proc. of the 4th WHEC, California, USA, 533 (1982).

4) K. Fujii, W. Kondo, S. Mizuta, Y. Oosawa, and T. Kumagai, Proc. of the 4th WHEC, California, USA, 553 (1982).

5) G. H. Schuetz, Proc. of the 4th WHEC, California, USA, 493 (1982).

6) I. Uehara, E. Ishii, H. Ishikawa, and M. Nakane, Proc. of the 3rd WHEC, Tokyo, 477 (1980).

7) G. H. Schuetz, *Int. J. Hydrogen Energy*, **1**, 379 (1977).

8) G. H. Schuetz and P. J. Fiebelman, *Int. J. Hydrogen Energy*, **5**, 305 (1980).

9) D. V. Velzen and H. Langenkamp, Proc. of the 3rd WHEC, Tokyo, 423 (1980).

10) P. J. Fiebelman and G. H. Schuetz, Proc. of the 3rd WHEC. Tokyo, 1949 (1980).

11) I. Uehara, E. Ishii, H. Ishikawa, and M. Nakane, *Nippon Kagaku Kaishi*, **1981**, 221.

12) E. N. Balko, J. F. McElory, and A. B. LaConti, *Int. J. Hydrogen Energy*, **6**, 577 (1981).

13) I. Barin and O. Knacke, "Thermochemical Properties

of Inorganic Substances," Springer Verlag, Berlin, Heidelberg, New York (1973).

14) C. F. V. Mason, *Int. J. Hydrogen Energy*, **1**, 427 (1976).

15) P. Lessart, R. Benizri, and P. Courvoisier, Proc. of the 2nd WHEC, Zurich, 595 (1978).

16) Y. Shindo, K. Obata, T. Hakuta, H. Yoshitome, N. Todo, and J. Kato, Proc. of the 3rd WHEC, Tokyo, 325 (1980).

17) S. Mizuta and T. Kumagai, *Denki Kagaku*, **47**, 105 (1979).

18) Y. Oosawa, *Bull. Chem. Soc. Jpn.*, **54**, 2908 (1981).

19) D. R. O'Keefe and J. H. Nomran, Proc. of the 3rd WHEC, Tokyo, 277 (1980).

20) R. H. Wentorf, Jr., and R. E. Hanneman, *Science*, **185**, 311 (1974).