Studies of Hydrogen-Chlorine Fuel Cell. I.

Basic Studies of the Hydrogen-Chlorine Fuel Cell at Low Temperature*

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Hydrochloric acid is produced by the reaction of hydrogen and chlorine in chloro-soda industry. Electric power can be generated by the electrochemical reaction of hydrogen and chlorine in the following cell :

The hydrogen-chlorine fuel cell at low temperature was studied because fuel cells of this type were not yet investigated in detail, and also the merits of this process were discussed.

The ionization of hydrogen took place on the porous carbon electrode impregnated with platinum or palladium as a catalyst, but not without catalyst. It was also found that the ionization of hydrogen easily took place on the ferro-silicon electrode. The ionization of chlorine easily took place on the porous carbon electrode without catalyst. The overpotential associated with the ionization of both hydrogen and chlorine and also the electric resistance of the electrolyte, HCl solution, gave minimum values at concentrations around 5 to 8 N. The ionization overpotential decreased with the increase of the temperature of the electrolyte. Therefore it is favourable to operate the cell with the solution containing 5 to 8 N of HCl and at the temperature as high as possible.

The overpotential of the hydrogen electrode was greater than that of the chlorine electrode at high current densities.

The energy efficiencies based on ΔF and ΔH at current density of 4 A/dm², were evaluated 51% and 41% respectively.

Introduction

Hydrochloric acid is produced by the reaction of hydrogen and chlorine in chloro-soda industry, but this method usually accompanies a large loss of heat energy. Therefore, the following hydrogen-chlorine fuel cell

has been studied.

If reaction $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2 \text{HCl}$ takes place in the cell, electric power can be generated with the production of hydrochloric acid. Studies of the fuel cell of this type have been carried out by a few authors^{1,2,3}. However, their data are not satisfied in detail and seem to be those of the discharge at low current density. In order to study the hydrogen-chlorine fuel cell at low temperature, the polarization characteristics of both hydrogen and chlorine electrodes and the merits of this process were studied, respectively.

Experimental Method

The electrode materials are restricted to carbon, graphite and/or metals of platinum group, because the corrosive chemicals i.e. HCl and Cl₂ are used. The gas electrode of the diffusion type² is the most favourable. The electrodes (effective surface area of 5 cm², thickness of 1.3 cm) were prepared with porous carbon impregnated with metals of platinum group as a catalyst. The porous carbons*¹ as shown in Table 1 were employed in this study.

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The cylindrical graphite*² (Fig. 1 (a)), at the end of which was equipped with porous carbon, was employed as the supporting material of hydrogen or chlorine electrode*³.

By the use of the circuit shown in Fig. 1(b), the polarization characteristics at the discharge with constant current on hydrogen or chlorine electrodes were measured under various conditions. Graphite rod was employed as opposite electrode and porcelain diaphragm was inserted between electrodes. Electrode potential was measured by the Luggin capillary method, in reference to the Hg/Hg₂Cl₂/3.3 N KCl/3.3 NHCl electrode. The ohmic drop between the electrode and the Luggin capillary and the liquid

junction potential were eliminated*⁴ by calculations.

Table 1 Physical Characteristics of Porous Carbon Used at This Experiment

Porous carbon No.	Porosity (%)	Mean radius of pores (μ)	Surface area of electrode (cm ²)	Thickness of electrode (cm)
P 170	50	20	5	1.3
P 150	50	45	5	1.3
P 140	50	60	5	1.3

a : porous carbon gas electrode, b : cylindrical impervious graphite, c : opposite electrode (graphite rod), d : porcelain diaphragm, e : Luggin capillary, f : electrolyte (various concentrations of HCl), g : pinhole, h : 3.3 N HCl, i : reference electrode (Hg/Hg₂Cl₂/3.3 N KCl), j : vacuum-tube voltmeter, k : lead acid battery

Fig. 1 (a) Schema of gas electrode used at this experiment
(b) Schema of experimental apparatus

Results and Discussions

1) **Equilibrium potential** The porous carbon and graphite as hydrogen electrode did not show equilibrium potential, but the porous carbon impregnated with platinum or palladium, platinated platinum and ferrosilicon (15% Si, 4% Mo) showed the hydrogen equilibrium potential within 20 min after the hydrogen was

a : sintered plate of ferrosilicon, b : cast ferrosilicon, c : platinated platinum, d : platinum plate, e : porous carbon, f : graphite, g : porous carbon impregnated with palladium, h : equilibrium potential of hydrogen electrode.
Electrolyte; 13°C, 1 N HCl

Fig. 2 The relations between the hydrogen electrode potential and time for various electrode materials.

*1 No influences of mean radius of the pore of the porous carbon electrode on the chlorine ionization overpotential were observed, if the same flux of gas was adopted. While the ionization overpotential of the hydrogen electrode (P 140) impregnated with platinum under the same conditions showed ill reproducibility and fairly dispersed values, as shown in Fig. 3. Therefore, in the case of hydrogen overpotential, the influences of mean radius of the pore of the porous carbon electrode were not to be confirmed. In this paper, the measured value of the electrode prepared with P 140 porous carbon were adopted as typical one.

*2 The surface of the cylindrical graphite was coated by polystyrene. The electric resistance of the electrode between A and B (Fig. 1 (a)), was about 0.02 ohm, so the ohmic drop in the electrode was negligible.

*3 No water-proof treatment was done in this study. To prevent the porous carbon electrode from wetting by the electrolyte, the measurement of the polarization was carried out bubbling the hydrogen or chlorine gas in the electrolyte under pressure. With the decrease of the flux of hydrogen or chlorine gas, the electrode, due to the wetting by the electrolyte, showed rapid increase of the polarization.

*4 The liquid junction potentials of +3.3 N KCl/3.3 N HCl/x N HCl- cell were calculated by the following equation⁴.

$$E = (2n_H + 1) \frac{RT}{F} \ln \frac{a_{\pm}(\text{HCl})_{xN}}{a_{\pm}(\text{HCl})_{3.3N}} + \frac{RT}{F} \ln \frac{A_{(\text{HCl})_{3.3N}}}{A_{(\text{KCl})_{3.3N}}} = \frac{RT}{F} \left\{ (2n_H + 1) \ln \frac{a_{\pm}(\text{HCl})_{xN}}{a_{\pm}(\text{KCl})_{3.3N}} + \ln \frac{A_{(\text{HCl})_{3.3N}}}{A_{(\text{KCl})_{3.3N}}} \right\}$$

where,

n : transport number, A : equivalent conductivity and a_± : mean activity (suffix shows each substance)

supplied to the electrode surface immersed in 1 N HCl, as shown in Fig. 2. Ferrosilicon was corroded by hydrochloric acid during several hours.

The porous carbon as chlorine electrode showed the equilibrium potential as soon as the chlorine was supplied to the electrode surface.

The equilibrium electrode potentials of hydrogen on the platinated porous carbon and of chlorine on the porous carbon were measured in various concentrations of hydrochloric acid. The experimental data obtained from the difference of the potential between both electrodes agreed with the theoretical values which were evaluated from the thermodynamical data⁵⁾ as shown in Table 2.

Table 2 Equilibrium Potential at 30°C

Concentrations of hydrochloric acid (N)	Equilibrium potential (V)			
	1/2 Cl ₂ +e $\rightleftharpoons$ Cl ⁻		1/2 H ₂ $\rightleftharpoons$ H ⁺ +e	
	measured value*	measured value*	measured value*	theoretical value
0.1	1.10	-0.28	1.38	1.42
1.0	1.12	-0.23	1.35	1.36
5.0	1.05	-0.16	1.21	1.29

*referred to Hg/Hg₂Cl₂/3.3 N KCl

The equilibrium potential for the formation of hydrochloric acid decreases with the increase of the concentration of hydrochloric acid. The cell supplies, e.g. in 1 N HCl at 30°C, the direct electric power of 377 kWh for the production of 1 ton of the 38% hydrochloric acid, when the potential loss due to the polarization and cell resistance is negligible.

2) Hydrogen electrode The relation between current density and electrode potential on the porous carbon electrode impregnated with platinum or palladium at constant discharge current is shown in Fig. 3⁵⁾. In the case of the electrode impregnated with platinated platinum (curve a, b, c), the hydrogen ionization overpotentials showed the gradual decrease with the increase of the volume of platinated platinum from curves a to c. When the current density increased, the hydrogen ionization overpotentials showed the rapid increase. The electrode for the curve d was prepared as follows: after dipping a porous carbon electrode in chloroplatinic acid solution (ca 10°C, 1 g Pt/10 cc solution) under atmospheric pressure for 24 hr, chloroplatinic acid remained in the electrode was thermally decomposed (650°C, 3 hr) in a sealed carbon vessel. At the use of the electrode of this type, the rapid increase of overpotential was not observed below the current density of 10 A/dm². The difference between these characteristics of electrodes may be explained as follows: the former is of two-dimensional distribution of platinated platinum on electrode surface, while the

- a: platinated electrode* (electroplated at 8 A/dm² for 10 min)
- b: platinated electrode* (electroplated at 16 A/dm² for 10 min)
- c: platinated electrode* (electroplated at 16 A/dm² for 30 min)
- d: electrode impregnated with platinum** (resulting in the decomposition of chloroplatinic acid solution)
- e: electrode impregnated with palladium** (resulting in the decomposition of palladium nitrate solution)

* Plating conditions: bath compositions; H₂PtCl₆·6 H₂O 10 g, (CH₃COO)₂Pb 0.02 g, distilled water 100 g, bath temp.; 10°C, Porous carbon electrode was wholly immersed in the bath and electroplated with alternating change of the direction of current every 30 sec, using platinum plate as an opposite electrode, in the beaker.

** ||| part shows the dispersion of the measured value due to electrode samples.

Electrolyte; 30°C 1 N HCl, Flux of hydrogen gas; 90 cc/cm/min

Fig. 3 Ionization overpotential of hydrogen on the various materials

⁵⁾ The relation between electrode potential and current density was fairly dispersive, as shown in Fig. 3. This is due to the difficulty of the identical impregnation of porous carbon electrode with platinum or palladium as a catalyst. Such dispersion of polarization values was observed with the change of the electrode, while the fairly good reproducibility was observed with the same electrode. So in this paper, the measured value of the electrode which showed the nearly middle value in Fig. 3 was adopted as typical one.

latter is three-dimensional distribution of platinum in the electrode. The electrode for curve e, impregnated with palladium was prepared by the following method. After dipping a porous carbon electrode in palladium nitrate solution (ca 10°C, 1 g Pd/10cc solution) under atmospheric pressure for 24 hr, palladium nitrate remained in the electrode was thermally decomposed (650°C, 3 hr) in a sealed carbon vessel. This electrode showed higher overpotential than that of curve d. Therefore, in the following experiment, the porous carbon electrode impregnated with platinum (curve d) which showed the lowest overpotential, was adopted.

Fig. 4 shows the changes of the electrode potential with time at constant current density of 2 A/dm². The electrode potential changes with time and shows unstable value at low flow flux of the hydrogen gas, however the potential is stabilized over certain values of flow flux, and on further increase, the potential remained unchanged. Namely, there is some optimum condition of the flux of hydrogen gas to stabilize the electrode potential.

Fig. 5 shows the relation between electrode potential and discharge current density under various conditions of concentration of hydrochloric acid and of the operating temperature. The equilibrium potential takes more positive value with the increase of temperature, while the ionization overpotential decreasing tendency. For example, the electrode potential of hydrogen ionization at 50°C was more negative than at 7°C at the current density over 0.8 A/dm². Therefore it is concluded that high operating temperature is desirable for high rate discharge of this fuel cell because of low overpotential. The equilibrium electrode potential takes more positive value with high concentration of hydrochloric acid. Comparing the case of 1 N HCl with that of 5 N HCl, the overpotential of the latter was lower, so with current density above 2 A/dm², the latter was more favourable.

Fig. 6 shows the influence of the concentration of hydrochloric acid on the overpotential. The minimum values of the overpotentials at con-

Fig. 4 The relations between the electrode potential and time

Fig. 5 The relations between electrode potential and discharge current density

Fig. 6 The influences of the concentration of hydrochloric acid on the overpotential

stant current densities exist on overpotential vs. concentration diagram as shown in Fig. 6. That means there is an optimum concentration for the ionization of the hydrogen gas.

Fig. 7 shows the influence of the dilution of hydrogen with nitrogen on the relations between electrode potential and discharge current density. With the increase of proportion of nitrogen, the ionization overpotential showed a remarkable increase.

3) The chlorine electrode As the chlorine electrode consisting of porous carbon without any catalyst was proved to attain rapidly the equilibrium potential, this electrode was adopted in the following experiment.

Fig. 8 shows the changes of the electrode potential with time at constant current density of 2 A/dm² under various flux of the chlorine gas. The chlorine electrode potential, as the hydrogen one, showed unstable values with smaller flux of the gas. Stable values were obtained at moderate increase of the flux and further increase of flux caused no variation at all.

Fig. 9 shows the influences of concentration and temperature of hydrochloric acid on the chlorine electrode potentials. These phenomena indicate that high temperature is favourable*6 at the high current discharge as in the hydrogen electrode. Concerning the hydrochloric acid concentration, the minimum ionization overpotentials were ob-

Fig. 9 The influences of concentrations and temperatures of hydrochloric acid on the chlorine electrode potential

Fig. 7 The influences due to the dilution of hydrogen with nitrogen on the electrode potential

Fig. 8 The relations between the electrode potential and time

served in the solution containing 5 N HCl.

Fig. 10 shows the influence of the concentration of hydrochloric acid on the ionization overpotentials. The overpotential shows minimum values at about 5 N HCl, but the overpotential increases little even in the solution almost saturated with hydrochloric acid.

4) Hydrogen-chlorine fuel cell

Fig. 11 shows the influence of concentration of hydrochloric acid on the ionization overpotentials on both hydrogen and chlorine electrodes and the formation potential, which is evaluated from a sum of

*6 The chlorine reacts with water to produce chlorine hydrate (Cl₂·8H₂O, decomp. temp. 9.6°C) and this compound covers the electrode surface at the electrolyte temperature below 7°C, making the passage of chlorine gas impossible.

hydrogen and chlorine electrode potentials, at the current density of 1 A/dm². The formation potential shows minimum value at concentration of about 5 to 8 NHCl. Moreover, the changes of the electric conductivity with the concentration are shown in Fig. 11 by a dashed line. The ohmic drop between electrodes shows minimum value at 6 NHCl because of the highest conductivity. After all, from the standpoints of both overpotential and ohmic drop, to operate the fuel cell using about 6 NHCl is the most favourable. While

Fig. 11 The influences of the concentration of hydrochloric acid on the overpotential and conductivity

the equilibrium potential of hydrogen-chlorine fuel cell decreases with the increase of concentration of hydrochloric acid, the changes of the ionization potential at high current densities are much greater than those of equilibrium potential, thus the influence of the latter can be negligible.

Fig. 12 shows the relation between the electrode potential and discharge current density of both hydrogen and chlorine electrodes at 50°C in 5 NHCl. Assuming the distance between electrodes to be zero, the difference of potentials between both polarization curves shows the terminal voltage of the cell. The polarization curves for each electrode are of different form and at high current density region, the overpotential on hydrogen electrode is much greater than that of chlorine electrode. At the current density above 7 A/dm², the fuel cell operates without utilizable terminal voltage. As the overpotentials on the hydrogen electrode show remarkably great values at high current densities, it is favourable to prepare the hydrogen electrodes with larger effective surface than that of chlorine electrode for the cell of high current discharge.

Fig. 10 The influences of the concentrations of hydrochloric acid on the chlorine electrode potential

Fig. 12 The relations between current density and electrode potential for hydrogen-chlorine fuel cell

Table 3 shows the relation between discharge current density and energy efficiency calculated from the data of Fig. 12, assuming the distance between electrodes to be 1 cm. The energy efficiencies based on ΔF and ΔH are calculated. The utilization ratios*⁷ of hydrogen and chlorine at discharge current density of 6 A/dm² are 5.7% and 33.3% respectively.

Summary

(1) The ionization of hydrogen takes place on the porous carbon electrode impregnated with platinum or palladium as a catalyst, but not without catalysts. Ferrosilicon electrode shows fairly good ionization characteristics, but suffers corrosion in hydrochloric acid with ease. The porous carbon electrode impregnated with thermally-decomposed platinum shows the best ionization characteristics.

(2) The ionization of chlorine easily takes place on the porous carbon electrode without any catalyst.

(3) The equilibrium potential of hydrogen-chlorine fuel cell decreases with the increase of concentration of hydrochloric acid and temperature of electrolyte.

(4) The ionization overpotentials on both hydrogen and chlorine electrodes show minimum values at about 5 to 8 N HCl. Moreover, the electric conductivity of hydrochloric acid shows maximum value at the region of this concentration of hydrochloric acid. The ionization overpotential decreases with the increase of the temperature of electrolyte.

(5) The changes of ionization overpotential, depending upon the concentration of hydrochloric acid and the temperature of electrolyte, are much greater than those of corresponding equilibrium potential. Therefore, for the purpose of high current discharge, it is favourable to operate the cell in 5~8 N HCl and at as high a temperature of electrolyte as possible.

(6) As the overpotentials on hydrogen electrode show much greater values than those on the chlorine electrode at high current densities, it is favourable to prepare the hydrogen electrode with larger effective surface than that of chlorine electrode.

(7) The energy efficiencies based on ΔF and ΔH were evaluated 51% and 41% at current density of 4 A/dm² respectively.

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*⁷ For the experimental convenience' sake, single porosity electrode was adopted, but with the adoption of the double porosity electrode, better utilization ratios for each gas will be gained.

Table 3 Energy Efficiency of Hydrogen-chlorine Fuel Cell

Current density (A/dm ²)	Energy efficiency* (%)	
	Based on ΔF	Based on ΔH
2	81	65
4	51	41
6	17	14

* Conditions : Temp. of electrolyte; 50°C, Concentration of hydrochloric acid; 5 N, Distance between electrodes; 1 cm