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Improvement of the Catalytic Properties of Porous Nickel Hydrogen Electrodes for Alkaline Fuel Cell

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알칼리형 연료전지용 다공성 니켈수소극의 촉매특성개선

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Abstract: Nickel was used as a catalyst for the hydrogen electrode in alkaline fuel cell. The optimum electrolyte concentration and recommendable operating temperature identified from polarization curves were 6N KOH and 80℃, respectively. Comparing the conductivity, apparent porosity and current density at porous hydrogen electrode manufactured with various PTFE additions, the proper content of PTFE was 10wt%. Chemisorption was carried out to define the appropriate surface area. The electrode produced with 10wt% of PTFE and sintered at 340℃ showed more than 200mA/㎠ of current density. The morphology of electrode surface was investigated with SEM. Cold pressing, hot pressing, rolling and calendering methods were carried out for manufacturing the electrode, and eletrochemical characteristics for each method was studied.

요 약: 알칼리형 연료전지의 수소극을 제작하기 위해 니켈을 사용하였다. 분극곡선을 측정한 결과 최적의 전해질 농도와 운전온도 조건은 6N KOH와 80℃였다. 다양한 양의 PTFE현탁액을 첨가하여 제조한 수소극에서의 전도도와 겉보기기공도 및 전류밀도를 비교한 결과 10wt%의 PTFE를 첨가하는 경우가 가장 적당함을 알았다. CO화학흡착량으로부터 표면적을 구했으며 10wt%의 PTFE를 침적시키고 340℃에서 소결시켜 제조한 수소극의 경우 200mA/㎠이상의 전류밀도를 나타내었다. 전극의 표면구조를 SEM으로 관찰하였고 cold pressing, hot pressing, rolling 및 calendering방법 등의 전극제작방법에 따른 전기화학적 특성을 고찰하였다.

1. INTRODUCTION

After the energy crisis, world-wide interest in fuel cell has been increased and developed. Environmental strains resulted from combustion of fossil fuels have demanded the development of new energy system. Fuel cell which can continuously convert the chemical energy of fuel into the electrical energy has several advantages; favorable higher conversion efficiency of fuel, use of the exhaust heat, noiseless conversion, lower production of pollutants and minimal siting restriction.

First successful H_2-O_2 alkaline fuel cell was started in 1932 by Bacon and culminated in a 5-kW system in 1955 which was used 30% KOH as an electrolyte and was operated at 200℃[1]. Alkaline fuel cell(AFC) technology was developed in the early 1960's for the NASA Space Program for terrestrials uses. AFC has several advantages over phosphoric acid fuel cell(PAFC)[2, 3]; (A) potentially higher energy efficiency caused from the higher rates of oxygen reduction, (B) low operation temperature and better material tolerance and (C) better performances. The economic factor such as the cost of catalyst is important for the commercial application because most of catalysts used in electrode is noble metal such as platinum. But in AFC, Raney nickel and carbonyl nickel powder are employed as catalysts for the hydrogen elect-

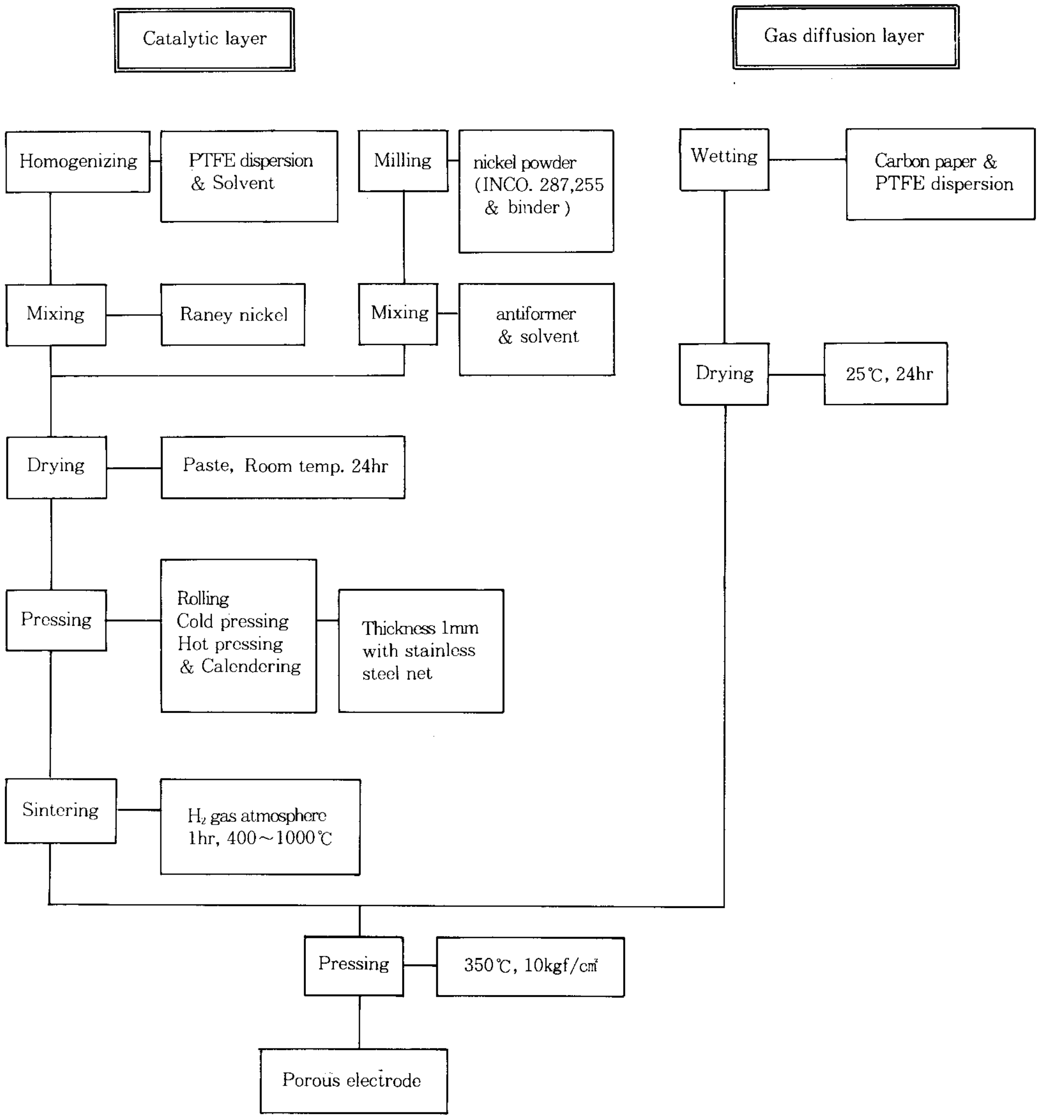


Fig. 1. Fabrication process of porous electrode.

rode because of their low corrosion rates in alkaline solution[4-9].

The effectiveness of the electrode could be governed with physical and chemical factors such as wetting property, teflon content[10], electrode structure[11], surface area[12] and activation method[13]. In this study, nickel powder(INCO. 287) was selected as catalyst. The effects of sintering temperature, amount of PTFE content and others on the electrochemical characteristics of the porous hydrogen electrode were investigated.

2. EXPERIMENTAL

2. 1. Meterials

INCO. 287(International Nickel Co. Ltd, United States) was used without further purification for the catalyst, and PTFE of Teflon 30J(Du Pont) was used as binder. Carbon paper for the gas diffusion layer was purchased from Toray Co. of Japan (TGP-H-60, 73% of porosity, 0.17mm of thickness). Deionized water after triple distillation was also used and the other reagents were obtained from Aldrich Chem. Co..

2. 2. Preparation of Electrode

The porous hydrogen electrode consisted of the catalytic layer and gas diffusion layer. The fabrication process is shown in Fig. 1. For the catalytic layer, polytetrafluoroethylene (PTFE) dispersion was homogenizing with an ultrasonic generator (US-300T, Japan) in small amount of water and then mixed with INCO. 287. After homogenizing again, it was dried overnight at room temprature until it became a paste. The content of PTFE added in catalytic layer or gas diffusion layer was calculated by percent in weight against the dry powder.

The obtained paste was pelleted by pressing, calendering or rolling method with isopropyl alcohol on 60 mesh stainless steel net for mechanical support and by sintering at 300 ℃~1000℃ in N_2 atmosphere for 1 hr. The heating rate was 2℃/min.

The gas diffusion layers were prepared with carbon paper containing 40wt% of PTFE dispersion and dried in room temperature. They were attached to the catalytic layer with hot

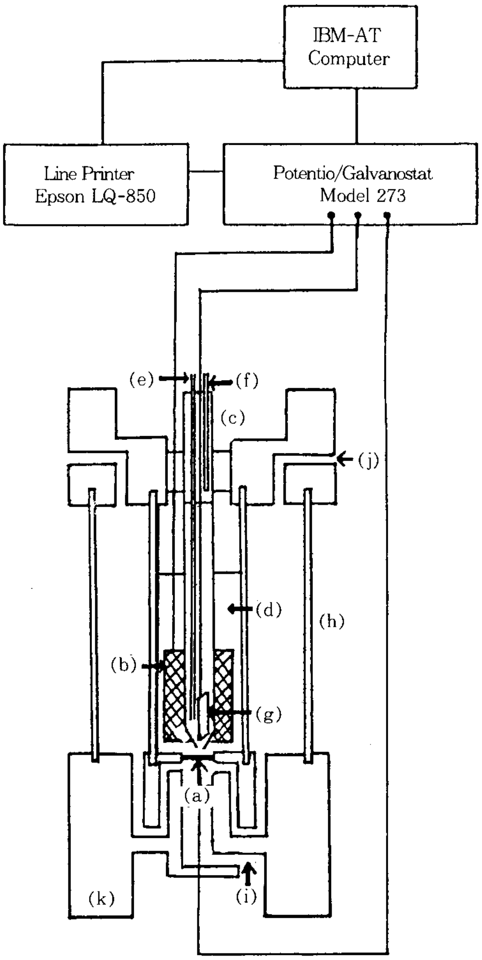


Fig. 2. Scheme of half cell.

(a) working electrode
(b) counter electrode
(c) reference electrode
(d) electrolyte
(e) H_2 gas inlet
(f) H_2 gas outlet
(g) platinum sheet
(h) pyrex dual tude
(i) fuel gas inlet
(j) fuel gas outlet
(k) teflon

press at 300℃, activated for 1hr in H_2 gas atmosphere, and stored in vacuum prior to electrochemical investigation, an additional activation was done in the same way.

2. 3. Method of Measurement

Fig. 2 shows the apparatus for measuring the electrochemical characteristics. Potentiostat/Galvanostat(EG & G PARC Model 173) connected with IBM computer system was used for this experiment. The counter electrode was Pt gauze and the reference electrode was NHE. The IR drop was reduced by making close the reference electrode through the luggin capillary to the working porous electrode. The whole cell assembly was sealed to prevent from the precipitation of potassium bicarbonate and/or carbonate.

For calculating the conductivity, four-probe method with the instrument manufactured in our laboratory was performed. Investigtation of morphology was carried out with SEM(JSM 350, JEOL).

Surface areas were measured with CO adsorption method. The apparent porosity of the electrode was determined from the weight difference between dry electrode and wet electrode with known density of the catalyst.

3. RESULT AND DISCUSSION

3. 1. Influence of Temperature and Concentration of Electrolyte

The changes of current density according to the electrolyte concentration and operation temperature of electrolyte were measured at the nickel plate electrode and the porous hydrogen electrode with a catalyst of 0.3g/㎠ and shown in Fig. 3 and Fig. 4. As shown there, the electrochemical characteristics of the nickel plate and the porous hydrogen electrode was improved linearly with the increase of temperature. Considering the vaporization of water and decrease of the ionic conductivity of electrolyte with the increase of temperture, the following experiment was carried out at 80℃.

They were also influenced considerably by the concentration of electrolyte. Over 6N KOH it showed almost similar tendency but high concentration of KOH caused the increase of the solubility of Raney-Ag used[14] for cathode catalyst and the decrease of O_2-reduction

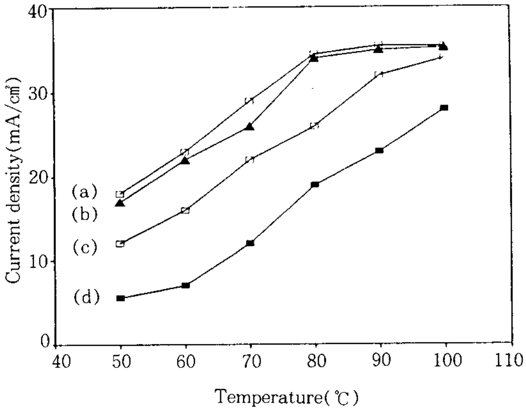


Fig. 3. Plots of current density vs. temp. in various KOH electrolyte concentrations at nickel plate electrode.
(a) 7N, (b) 6N, (c) 5N and (d) 4N.

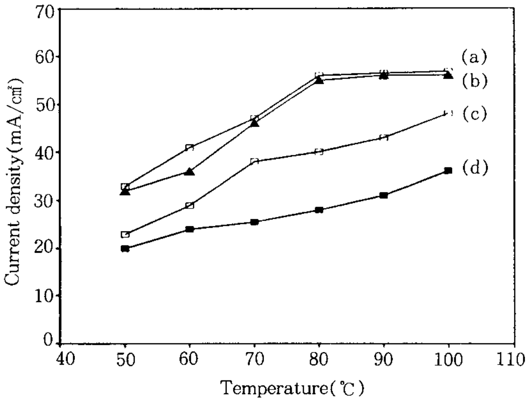


Fig. 4. Plots of current density vs. temp. in various KOH electrolyte concentrations at 30wt% PTFE bonded hydrogen electrode.
(a) 7N, (b) 6N, (c) 5N and (d) 4N.

rate. So 6N was selected as the optimum concentration of KOH electrolyte.

3. 2. Effect of Electrode Thickness

The dependence of current density according to the various catalyst loading amount and thickness of the active layer at porous hydrogen electrode sintered at 340℃ with 10wt% of PTFE has been studied and the results are presented in Fig. 5. The loading amount of catalyst at catalytic layer was varied between 0.2 and 0.4g/cm^2. Before 0.29g/cm^2 of catalyst loading, the polarization characterictics was increased with the increase of catalyst loading amount but showed the tendency of decreasing after loaded more than 0.3g/cm^2.

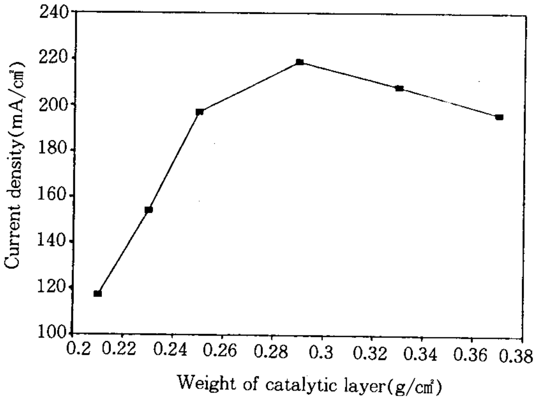


Fig. 5. Influence of catalyst loading of the active layer on the polarization charaterictics.

These results indicated that thickness of the catalytic layer had a profound influence on the electrochemical performance. Below 0.9mm of catalytic layer thickness, the current density of the electrode was increased while above of this thickness the electrode showed a little decay of current density.

It could be explained with the electrolyte film model that catalyst loading is proportional to the thickness and the polarization resistance ω is expressed as the fuction of catalytic layer thickness d.

$$\omega = \sqrt{\rho K} \coth \sqrt{\frac{\rho \cdot d^2}{K}}$$

where ρ is the electrolyte resistivity in the catalytic layer and K is the polarization resistance of the catalyst.

For obtaining the accurate data, calibration in each experiment is needed from the different catalyst loading and thickness, Fig. 5 was provided as the parameter for the next experimental run.

3. 3. Effect of PTFE Contents in Catalytic Layer

In general, micropores of the catalytic layer are filled with electrolyte and the fuel gas stream into via macropores[15]. Thus the control of porosity and structure of electrode is an important factor for the increase of electrode performance. The electrochemical characteristics and properties of the hydrogen porous electrode with various PTFE contents which was used as binder and wet-proof agent were examined.

In Fig. 6 the conductivity and apparent porosity of active layer produced with different PTFE contents from 5wt% to 50wt% were calculated. With the absence of PTFE, it was

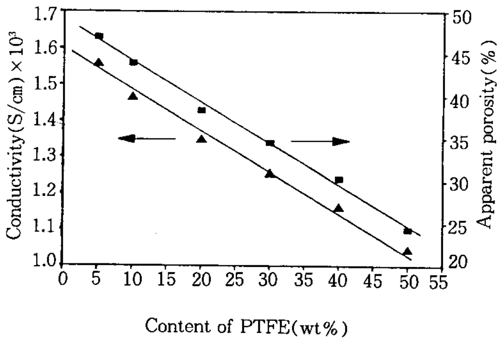


Fig. 6. Plots of conductivity and apparent porosity vs. PTFE content of porous hydrogen electrode (sintered at 340℃).

difficult to produce the electrode which had mechanical endurance. As the PTFE content was increased, it showed the tendency of diminishing the conductivity and apparent porosity. In the case of mixing with 5wt% PTFE, it is expected to have the best result in electrochemical characteristics.

But as shown in Fig. 7, a rapid increase of current density with the increase of PTFE content was observed and a sharp decrease current density was occured with the further adding of the PTFE. The maximum current density was appeared when 10wt% of PTFE was contained in the electrode. It could be illustrated that the role of binder was not sufficient at the electrodes in the case of mixing with 5wt% PTFE. When 10wt% of PTFE was mixed, the uniformity of pore size and prevent of gas leak could be reached as a well-dispersed electrode and high activity of electrode was accomplished with the catalysts which had a large surface area.

The polarization resistance ω and Tafel slope showed the same result caused the loss of surface area due to the excess PTFE coverage at the surface of catalyst as shown in Fig. 8 and Fig. 9. This was concurred with the result of chemisorption shown in Fig. 10. In the case of active layer containing 10wt% PTFE had maximum surface area of 75m^2/g. From the SEM photographs in Fig. 11, the changes of morphology were confirmed that the distribution of nickel particles became sparse with the increase of the amount of PTFE.

3. 4. Effect of Sintering Temperature

In Fig. 12, TGA curves of PTFE and PTFE mixed with nickel powder were shown. The decomposition temperature of PTFE was 536℃ and shifted to the right when nickel powder was mixed. For obtaining the suitable sintering temperature, the investigation of electrochemi-

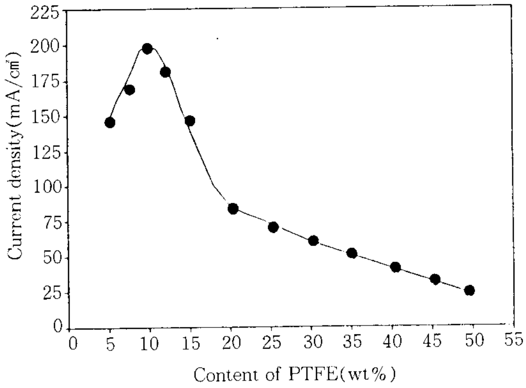


Fig. 7. Plot of current density vs. PTFE content of porous electrode (6N KOH, 80℃).

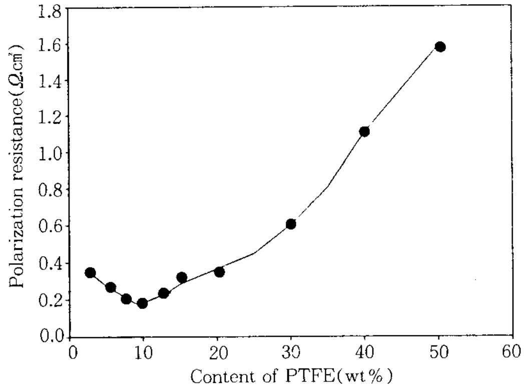


Fig. 8. Effect of PTFE content on the polarization resistance (6N KOH, 80℃ and catalyst loading 0.3g/cm²).

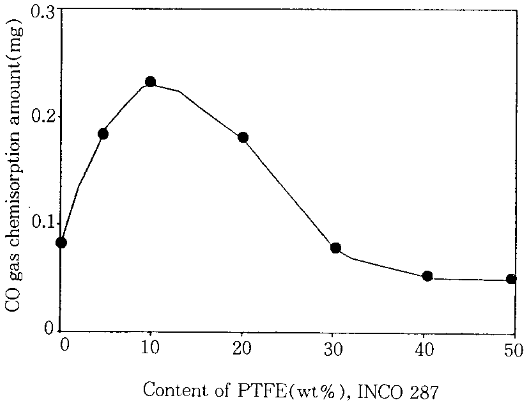


Fig. 9. Plot of CO chemisorption vs. various PTFE contents.

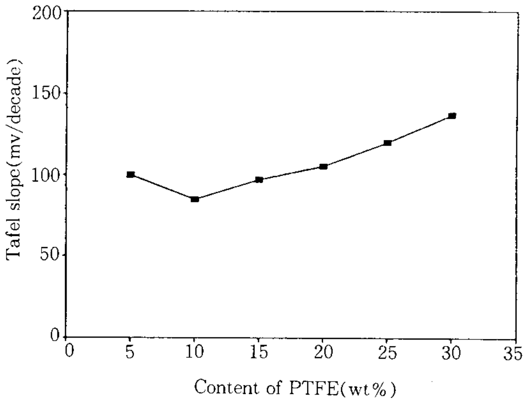
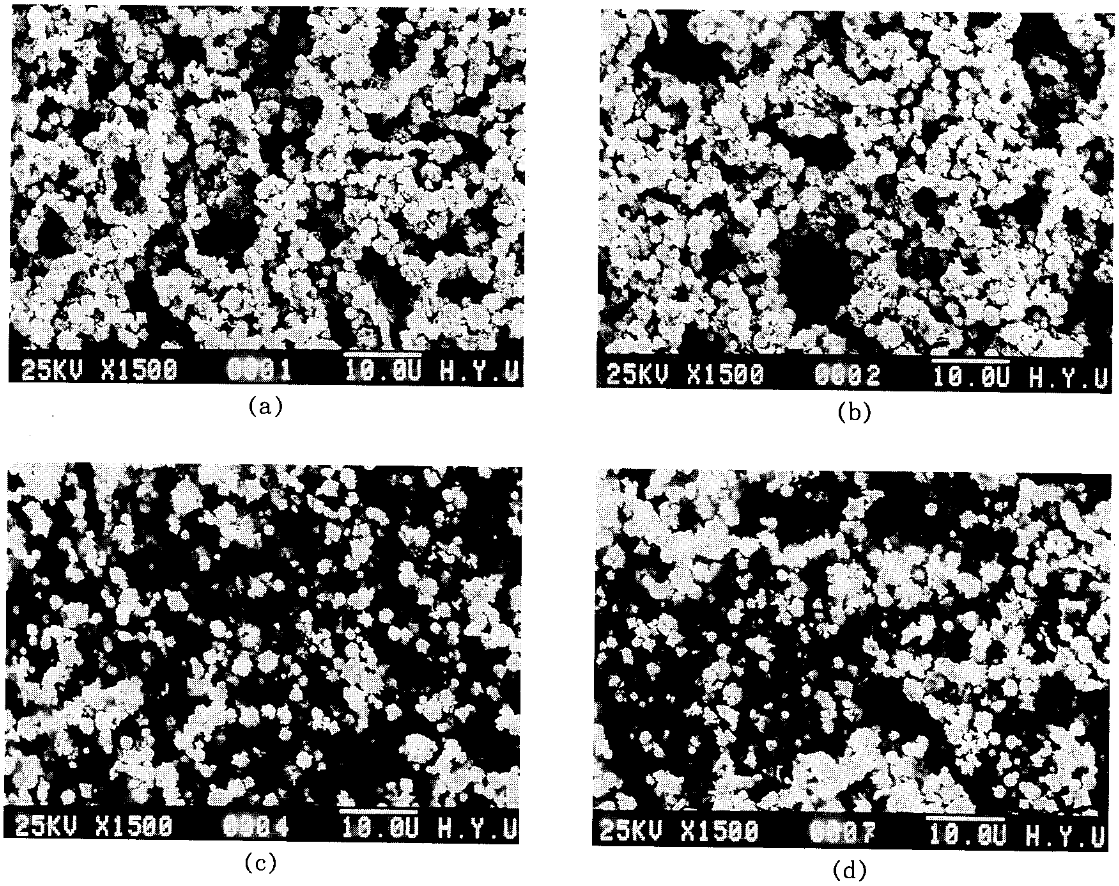


Fig. 10. Change of Tafel slope according to various PTFE contents in catalytic layer.

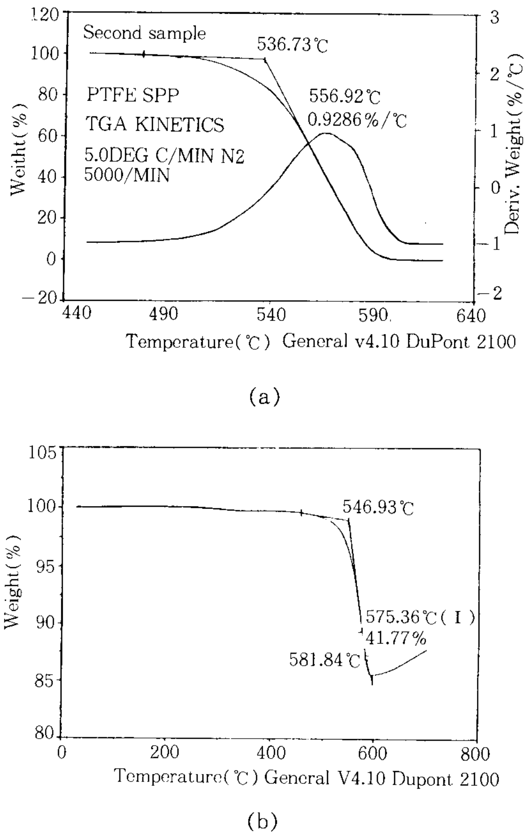
cal performances with the electrode prepared at different sintering conditions was carried out.

Under the given experimental condition, Fig. 12 illustrated that 340℃ was the most appropriate temperature for the optimal electrochemical behavior of the hydrogen electrode; the temperature of 340℃ means the melting point of PTFE and provides the good dispersion on the electrode. For the comparison of the structure of nickel powder sintered at 400 ℃ or 1000℃, SEM photographs were shown in Fig. 13.



(a) (b) (c) (d)

Fig. 11. SEM photographs of porous hydrogen electrode containing PTFE sintered at 340℃. (a) 5wt% of PTFE, (b) 10wt% of PTFE, (c) 15wt% PTEE and (d) 20wt% PTEE.



(a)

(b)

Fig. 12. TGA curve of PTFE.
(a) PTFE only
(b) PTFE + Ni powder mixture

Skeleton structure was found when sintered at 1000℃ and not obtained when sintered below 400℃. With those two electrodes containing the catalyst which had different structures, the almost similar current density of 210mA/㎠ was obtained. For the simplification of the electrode manufacturing process, sintering at 340℃ could be recommended.

3. 5. Different Manufacturing Processes of Hydrogen Electrode

Effects of different processes for manufacturing the hydrogen electrodes with the above mentioned condition were investigated and the results are reported in Table. 1.

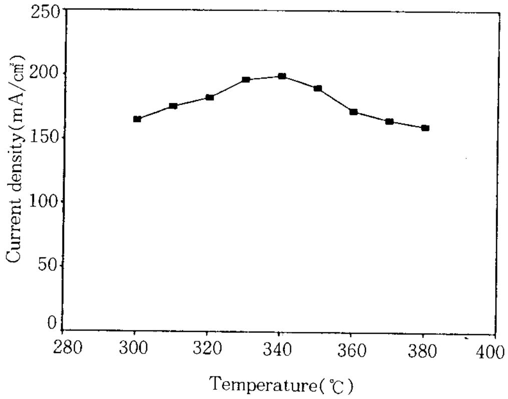
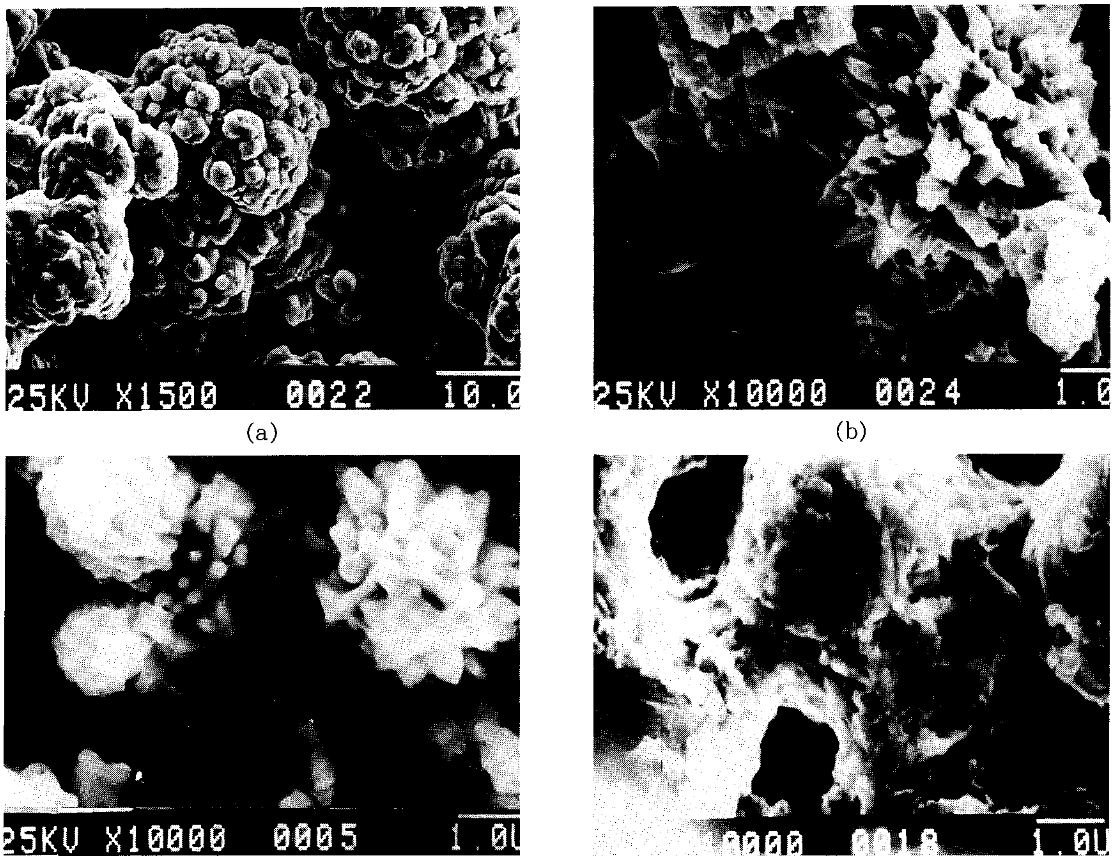


Fig. 13. Plot of current density va sintering temperature(6N KOH, 80℃, 10wt% of PTFE and catalyst loading 0.29g/㎠).

Table 1. Effect of Different Process on Properties of Ni Hydrogen Electrode (10wt% of PTFE, catalyst loading 0.25 g /㎠)

process	apparent porosity	current density(mA/㎠)
cold pressing	33.66	170
hot pressing	30.12	200
rolling	41.25	156
calendering (1)	63.31	160
calendering (2)	38.72	205

The electrode obtained from hot pressing method showed good current density due to the good adhesion of catalytic layer and gas diffusion layer compared with cold pressing or rolling method. The apparent porosity of each electrode showed in the range from 30.1% to 41.2%. In the case of calendering method, 160mA/㎠ of current density was improved to 205mA/㎠ when the apparent porosity of electrodes droped from 63.3% to 38.7 % due to the uniform pore size and to the prevent of gas leak. As controlled the apparent porosity arounds 40%, the maintenance of uniform pore size and prevent of gas leak was accomplished.



(a) (b)

(c) (d)

Fig. 14. SEM photographs of nickel particle.
(a) nickel powder
(b) INCO. 287
(c) sintered at 400℃ containing 30wt% of PTFE
(d) sintered at 1000℃ containing 30wt% of methyl cellulose

4. CONCLUSIONS

From these results, the following conclusions can be drawn;

1. It suggested that the optimum condition of electrolyte concentration and operating temperature was 6N KOH and 80℃, respec tively.
2. The maximum thickness of active layer was 0.9mm and proper catalyst loading amount of nickel was below 0.3g/cm².
3. The electrode mixed with 10wt% of PTFE in nickel powder showed well-dispersed characteristics and highest electrode performance.
4. Sintering the electrode around the melting point of PTFE showed good electrochemical characteristics and there was no difference whether sintered at 340℃ or at 1000℃.
5. For the large-scale production calendering

method is recommended.

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