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Hydrogen Electrode Performance with PTFE Bonded Raney Nickel Catalyst for Alkaline Fuel Cell

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라니 니켈 촉매에 대한 알칼리형 연료전지용 수소극의 전극특성

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Abstract: Raney nickel was used as catalyst in the hydrogen electrode for an alkaline fuel cell. The hydrogen electrode manufactured with the Raney nickel catalyst which was sintered at 700℃ was found to have the highest electrode performance. Using the Raney nickel powder of average particle size 90Å for the electrode, the current density which had been measured was 450mA/cm^2 at 80℃ using 6N KOH solution as an electrolyte. The effects of PTFE addition were investigated with CO-chemisorption, polarization curves and Tafel slope. CO-chemisorption had shown the optimum value when the Raney nickel was mixed with 5wt% of PTFE, but from the current density and Tafel slope at porous Raney nickel electrode, the appropriate value of PTFE addition was 10wt%. Recommendable Ni and Al portion for Raney nickel was 60:40 and loading amount was 0.25g/cm^2. Also the influence of pressing pressure for manufacturing catalytic layer and for junction with gas diffusion layer was examined. The morphology of catalyst surface was investigated with SEM. The influence of reactivation time and heat-treatment temperature were also studied.

요 약: Raney nickel 촉매를 이용하여 알칼리형 연료전지의 수소극을 제작하였다. 700℃에서 소결한 Raney nickel로 제작한 수소극의 경우 가장 좋은 전극성능을 갖는 450mA/cm^{2}의 전류밀도를 나타냈으며 이때의 평균촉매입자 크기는 90Å이었다. CO-chemisorption 측정 및 분극곡선과 Tafel slope를 통하여 PTFE의 첨가량에 대한 전극의 전기화학적 성능을 고찰하였다. CO-chemisorption 측정 결과 5wt%의 PTFE가 첨가되었을 때 최고값을 갖는 것이 확인되었으나 전극에서의 전류밀도와 Tafel slope를 비교한 결과 10wt%의 PTFE를 첨가하는 경우가 가장 적당함을 알았다. Raney nickel제조시 nickel과 aluminum의 함량비는 60:40의 경우에 가장 좋은 전극 특성을 나타내었으며 담지량은 0.25g/cm^{2}의 경우가 적당하였다. 전극제조시 촉매층의 press압 및 촉매층과 기체확산층과의 접합시의 press압에 대한 영향도 검토하였다. 또한 촉매의 표면 구조를 SEM으로 관찰하였으며 활성화시간 및 열처리 온도 등 여러가지 조건에 대한 전극의 영향도 고찰하였다.

1. Introduction

From the successful H_2-O_2 alkaline fuel cell (AFC) demonstrated by Becon in 1932 and accomplished a 5 kW system in 1955 which was used 30% KOH as an electrolyte at 200℃[1], much inter-

est has been focused and developed the fuel cell. Alkaline fuel cell technology was developed in the early 1960's for the NASA Space Program for terrestrials used and 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. It is suitable in application where only quite small units are required such as aerospace, military purposes and electrical vehicles.

However the cost of catalyst is important factor for the commercial application because most of catalysts used in electrode is noble metal such as platinum and the hydrogen electrode in alkaline fuel cell, Pt impregnated on carbon black or Raney nickel is used as catalyst. The Raney nickel is usually employed as catalysts for the hydrogen electrode because of their low corrosion rates, large surface area and high activity in alkaline solution[4-16]. Therefore, AFC system could abandon noble metal as electrocatalyst.

The electrochemical characteristics 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 heat-treatment method[13]. In this study, Raney nickel was prepared at various sintering temperatures(500-800℃) using the mixture of different mass fraction of nickel and aluminum and the optimum condition was confirmed. Also the amount of PTFE content at the catalytic layer, heat treatment temperature and reactivation time of the electrode with governed the electrochemical characteristics of the porous electrode was studied.

2. Experimental

2. 1. Preparation of Raney nickel

The fabrication process of Raney nickel catalyst is followed. The various mass fraction of carbonyl nickel and aluminum powder was mixed in mortar for 1 hour thoroughly with water. The obtained mixture was pelleted by pressing at 200kg/cm^2 and sintered at 700℃ with the rising temperature of 2℃/min in hydrogen atmosphere and cooled in nitrogen atmosphere until it reached at room temperature. The alloy was grinded again in mortar and leached aluminum with 6N NaOH solution at 80℃ for 24 hours. Obtained as a black precipitate was washed with distilled deionized water, partially oxydized and stored in vacuum prior to the manufacturing of the electrode.

2. 2. Materials and manufacturing of the electrode

Materials for this experiment and manufacturing process of the porous electrode were used and prepared with already presented paper[8]. But soxhlet in acetone was carried out to remove residual surfactant which was originally mixed in PTFE dispersion.

2. 3. Methods of measurement

The electrochemical characteristics were measured with the Potentiostat/Galvanostat(EG&G PARC Model 273A) and same half cell system of prior paper was used[8]. The electrochemical performances of the porous electrode were measured in 6N KOH solution at 80℃ and the geometric area of electrode which contact with the electrolyte was 1cm^2.

Residual Al content was measured with direct current argon plasma emission spectrometer(DCP) or energy dispersive X-ray spectrometer(EDAX, Link sys. 560). CO-chemisorption was carried out with Cahn 2000 Micro-Balance and the flow of He and CO gas were controlled with Multiple-Dyne-Blender. Investigation of morphology and crystallinity were carried out with SEM(JSM 350. JEOL) and X-ray diffractometer(Rigaku Co.), respectively.

3. Results and discussion

3. 1. Effect of PTFE content in catalytic layer

In general, micropores of the catalytic layer are filled with electrolyte and the fuel gas stream into via macropores[17-18]. If the distribution of large

pore-size is exist in the catalytic layer at the hydrogen electrode, the fuel gas is leaked by the bubbling through the large pores and the total working area of catalytic layer is diminished. Thus the control of porosity and structure of electrode is an important factor for the increase of electrode performance.

CO-chemisorption of Raney nickel and nikel catalyst were carried out to compare the surface area containing various PTFE contents and shown in Fig. 1. Raney nickel catalyst had shown the highest value of CO-chemisorption amount when they were mixed with 5wt% of PTFE. With the increase of PTFE contents, the discrepancy of CO-chemisorption amount was appeared caused the excess of PTEF surrounded the surface of Raney nickel catalyst and blocked the pore entrance[9], therefore it diminished the CO-chemisorption site of catalyst and also interrupted the diffusion of fuel gas to the electrolyte-catalyst interface.

Higher chemisorption amount of Raney nickel than amount of Inco 255 or 287 only seemed to be due not only to the large effective surface area but also to the good catalytic activity of Raney nickel. With the result of Fig. 1, it could be estimated that

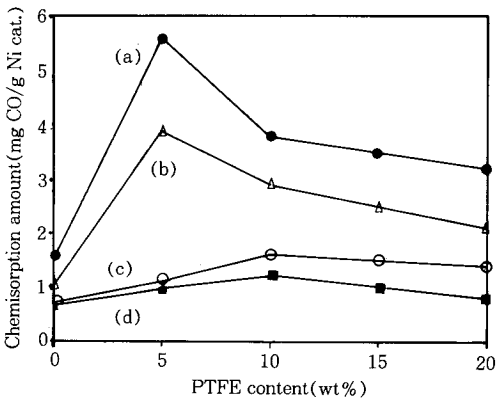

Fig. 1. Influence of PTFE content on CO-chemisoption amount of Raney nickel catalyst.
(a) produced with INCO. 255
(b) produced with INCO. 287
(c) INCO 255
(d) INCO 287

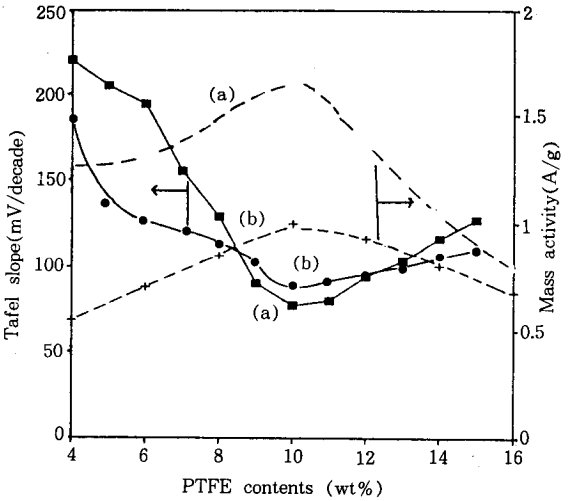

Fig. 2. Influence of PTFE content on mass activity and Tafel slope of porous hydrogen electrode.
(a) Raney nickel produced with INCO. 255
(b) INCO. 255

the hydrogen electrode manufactured with a Raney nickel catalyst containing 5wt% of PTFE will show the superior electrode performance. But as demonstrated in Fig. 2, the mass activity of hydrogen electrode which was prepared with the Raney nickel catalyst had the highest value of 1.65A/g when the catalytic layer was mixed with 10wt% of PTFE. This difference caused that less than 10wt% of PTFE was not sufficient to make well-dispersed state and to prevent the gas leak at the catalytic layer. The successful performance of the electrode reaction was described by the Tafel slope in Fig. 2. It was concurred with the tendency of mass activity and had the value of 77.5mV/decade when the electrode were manufactured with the Raney nickel catalyst containing 10wt % of PTFE.

The influence of PTFE content on current density and operating time dependence was illustrated in Fig. 3. When the electrode containing less than 8wt% of PTFE initially showed the high current density and shown the decrease according to the operating time. The electrolyte wetted rapidly because there were little amount of PTFE to control the macropores

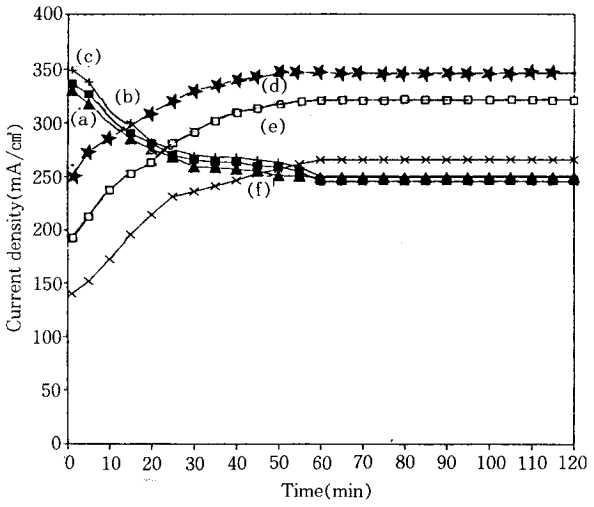

Fig. 3. Influence of PTFE contents on current density of porous hydrogen electrode containing Raney nickel catalyst with time dependence.
(a) 4wt%, (b) 6wt%, (c) 8wt%, (d) 10wt%, (e) 12wt%, and (f) 14wt%

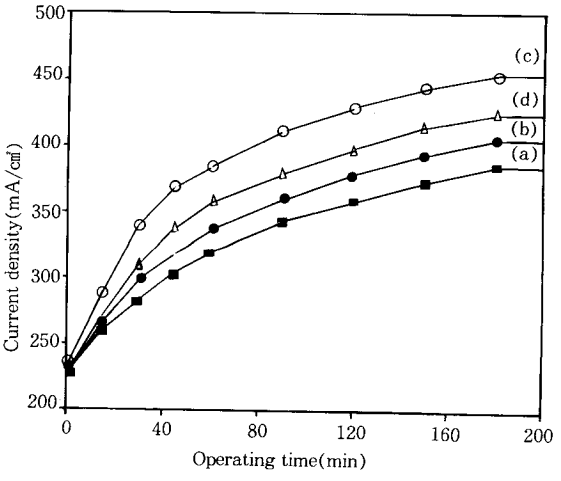

Fig. 4. Influence of current density of porous hydrogen electrode prepared from Raney nickel treated at various sintering temperature for Ni-Al alloy.
(a) 500℃, (b) 600℃, (c) 700℃, and (d) 800℃

and lead to show the high electrode performance immediately. But gradually the fuel gas was leaked and the electrode hold the bubbles of fuel gas on the surface layer. It prevented the penetration of electrolyte and the real surface area of catalytic layer was decreased. In the case of more than 10wt% of PTFE addition, the increase of current density was due to the fact that unreduced catalyst was activated during the passage of fuel gas. They almost had the saturated value after 60 minutes of operating time in this experiments.

3. 2. Optimum sintering temperature for Raney nickel catalyst

The influence of sintering temperature for the preparation of Raney nickel with the particle size and electrode performance was investigated. For obtaining the best condition of sintering temperature and confirming the relationship between particle size and electrode performance, the polarization characteristics of porous hydrogen electrodes containing these catalyst individually were studied and the results were shown in Fig. 4. The electrode perfomance were considerably influenced by the sintering temperature of Ni-Al alloy formation. The electrode containing Raney nickel catalyst prepared by sintering at 700℃ showed the highest current density. It could be explained with the two experimental results, change of particle size and various precursor formation with different alloy temperature.

To determinate the average particle size d(Å) of Raney nickel catalyst, the line broadening method from the XRD patterns with Scherrer equation was used[14]. The particle size of Raney nickel was increased linearly as the tempertature increased. It suggested that the diminish of the real surface area of catalyst with the increase of particle size as the sintering temperature increased and finally large particle size affected the electrode performance became worse.

The X-ray diffraction patterns of Ni-Al alloy sintered at various temperature(500-900℃) were represented in Fig. 5. At 500℃ and 600℃ of sintering temperature, there was a little evidence of Ni-Al alloy and higher than 700℃, characteristic peaks

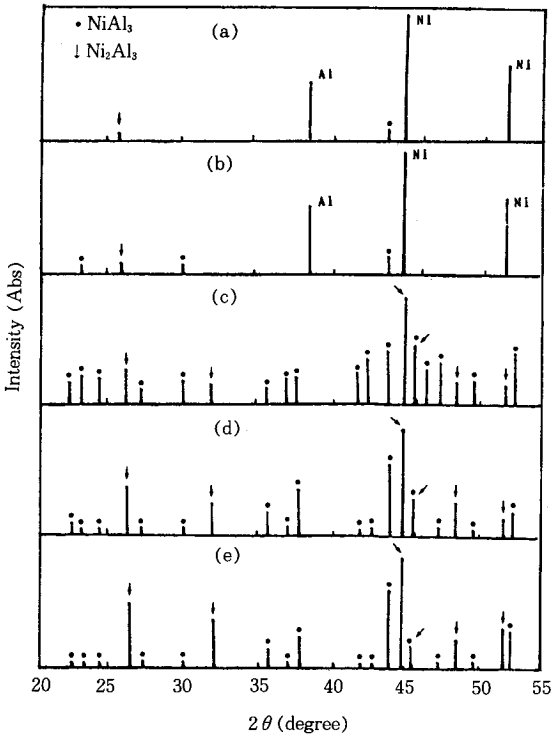

Fig. 5. X-ray diffraction patterns of Ni-Al alloy.
(a) sintered at 500℃, (b) sintered at 600℃
(c) sintered at 700℃, (d) sintered at 800℃
(e) sintered at 900℃

of Ni_2Al_3 and $NiAl_3$ which is needed for preparation of Raney nickel had been appeared. But higher than 800℃, though $NiAl_3$ peak was decreased and Ni_2Al_3 peak was increased, the liquid phase of $NiAl_3$ and Ni_2Al_3 could be exist and obtained high dense of alloy lead to decrease of surface area. Also it was hard to powdering the Ni-Al alloy which was produced at the sintering temperature higher than 800 ℃. This tendency was resulted as the difficulty of leaching the aluminum from the Ni-Al alloy.

3. 3. Effect on the different mass fraction of Ni and Al powder for Raney nickel

The Raney nickel was manufactured with various mass fraction of nickel and aluminum powder for Ni-Al alloy and compared the electrochemical characteristics of the electrode using these different catalysts.

As shown in Fig. 6, the current density of the electrode were considerably influenced by the portion of nickel and aluminum content. When the catalysts were prepared with 60wt% of nickel and 40wt% of aluminum and sintered at 700℃, the electrode shown the highest current density of 450mA/cm². From the binary phase diagram of Fig. 7[19], 40wt% of nickel content indicated the region of $NiAl_3$ and 60wt% in-

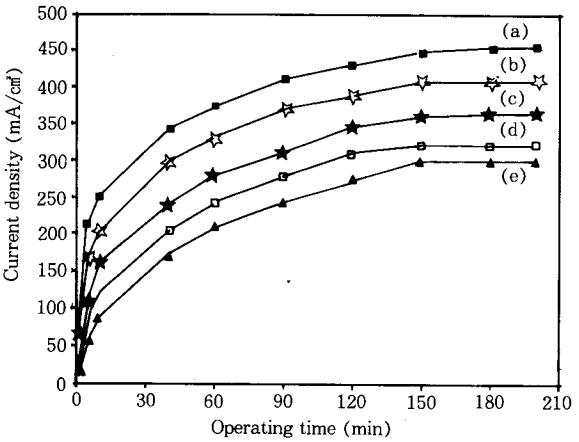

Fig. 6. Influence of current density at the hydrogen electrode produced with various portion of Ni and Al powder for Ni-Al alloy at 700℃.
(a) Ni 60wt% : Al 40wt%
(b) Ni 55wt% : Al 45wt%
(c) Ni 50wt% : Al 50wt%
(d) Ni 45wt% : Al 55wt%
(e) Ni 40wt% : Al 60wt%

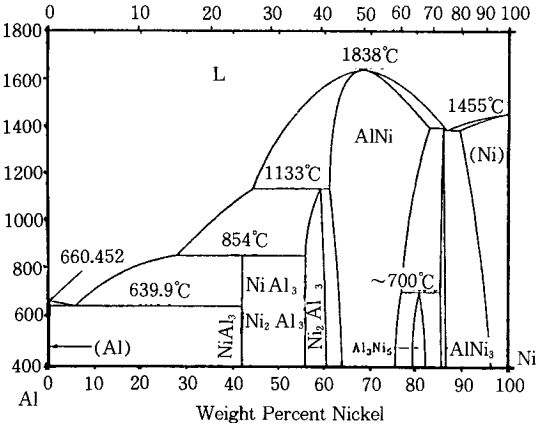

Fig. 7. Assessed Al-Ni phase diagram(reference 19).

dicated Ni_2Al_3. Though the phase diagram obtained from liquid phase and equilibrium state and it could not correspondent to the alloy from powder state, but similar tendency had been obtained. As illustrated in Fig. 8, with the increase of Ni content approach of Ni_2Al_3 region was founded and the intensity of characteristic XRD peak of $NiAl_3$ was diminished a little. With the respect of stoichiometry, almost 50:50 of Ni : Al could be produce equivalent ratio of Ni_2Al_3 : $NiAl_3$, $NiAl_3$ is more difficult for leaching the aluminum than Ni_2Al_3 and unleached $NiAl_3$ could exist and diminish the activity of catalyst. Actually residual aluminum amount was decreased from 7.7% to 3.4% obtained from DCP or EDAX data as nickel amount were increased from 40% to 60%. Therefore it was found that 700℃ of sintering temperature and 60:40 of Ni and Al portion was appropriate to obtain the high active Raney nickel catalyst and its surface area was $54m^2/g$.

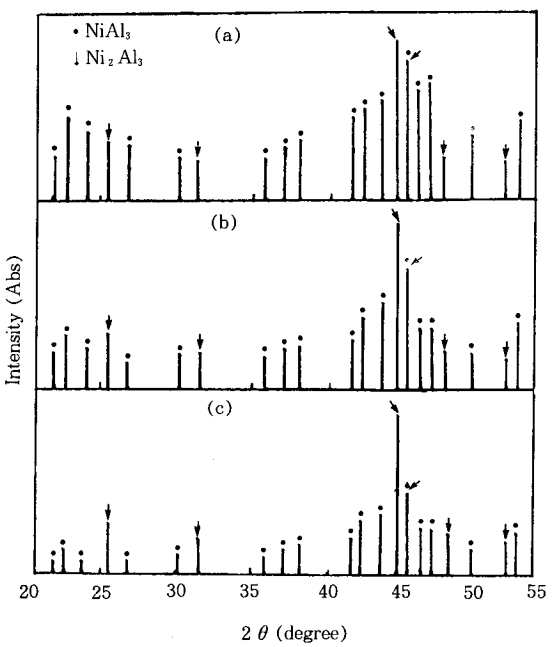

Fig. 8. X-ray diffraction patterns of Ni-Al alloy.
(a) Ni 40wt% : Al 60wt%
(b) Ni 50wt% : Al 50wt%
(c) Ni 60wt% : Al 40wt%

3. 4. Influence of pressure for manufacturing the electrode and catalyst loading amount

Because the pore distribution of catalytic layer is influenced by the manufacturing pressure, anodic current density of hydrogen electrode prepared by different pressure should be compared. Less than $100kg/cm^2$ of pressure, the electrode could not obtained and the increased of pressing pressure made the electrode performance worse caused the compact of pore distribution. The influence of current density and wettability at hydrogen electrode according to the various pressing pressure for catalytic layer was shown in Fig. 9. Rapid decrease of current density was appeared with the increase of pressure due to the penetrate of catalyst to the gas diffusion layer. It was confirmed with SEM photographs.

In hydrogen electrode with the Raney nickel catalyst, the active site was controlled by the loading amount of the catalyst. With the increase of catalyst amount, the electrode performance would be increased. But shown in Fig. 10, when the electrode with the loading of $0.25g/cm^2$ indicated the highest value of $450mA/cm^2$ and decrease as the increase of catalyst loading amount. With the increase of loading amount, the mass transfer was hindered

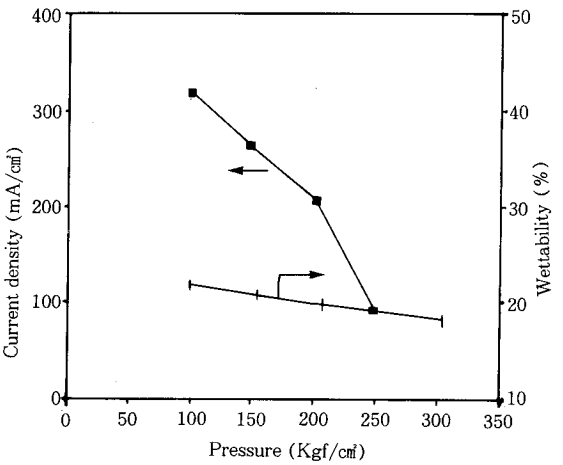

Fig. 9. Influence of current density and wettability at the hydrogen electrode according to the various pressing pressure for catalytic layer.

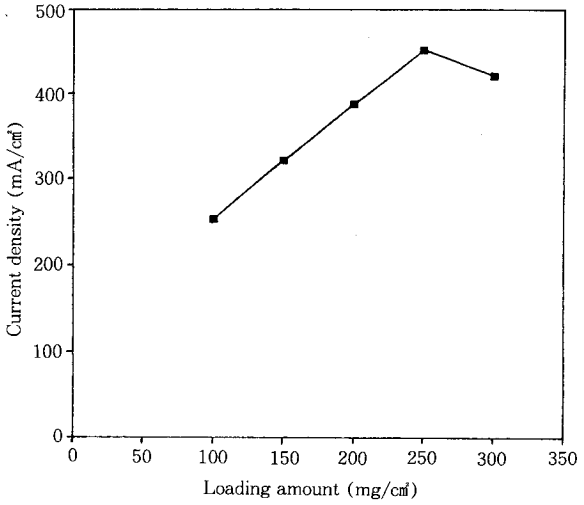

Fig. 10. Relation between current density at the hydrogen electrode and various loading amount of Raney nickel catalyst.

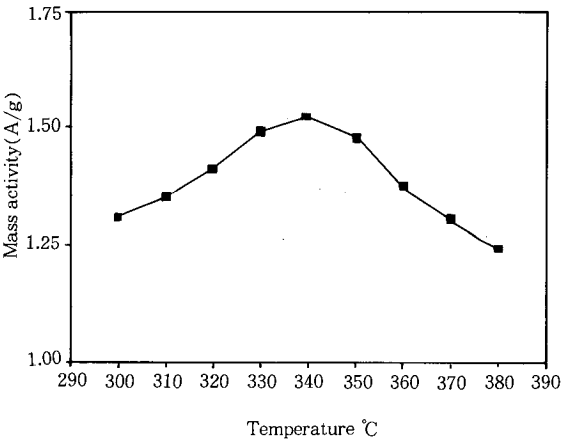

Fig. 11. Influence of heat treatment temperature on mass activity of porous hydrogen electrode.

cause the increase of thickness and the decrease of electrode performance could be assumed.

3. 5. Effect of heat treatment temperature and reactivation time in hydrogen electrode

The electrode was heat treated in a nitrogen atmosphere to sinter the PTFE particle and to remove the surfactant containing originally in the PTFE dispersion. The various temperature of heat treatment was carried out and the effect were compared with the mass activity of electrode. Fig. 11 illustrated that the best electrochemical characteristics was shown when the electrode heat treated at 340℃. Heat treatment of the electrode at melting point of PTFE which was confirmed with TGA curve improved the anodic electrode performance and provided the good uniformity of pore size on the electrode.

Raney nickel is pyrophorous in air, the surface of Raney nickel should be oxidized for easy handling by slow controlled oxidation before further processing. Since the air-oxidized Raney nickel powder is no longer catalytically active, it must be reactivated before application as hydrogen electrode in the half cell. With the appearance of saturated value when it was heat-treated more than 1hr at 340℃ in H_2 atmosphere, it could be concluded that at least 1hr of reactivation time was required to maintain the good electrode performance and it was important precondition for reducing oxidized Raney nickel particles.

Long-term performance of the electrode manufactured under the given experimental conditions showed the tendency of increasing the current density during the operation of half cell until it run 3hr from 350mA/cm^2 to 450mA/cm^2. This was seemed to the increase of catalytic activity because the flow of hydrogen gas is attributed to the reduction of remaining unreduced Raney nickel during the reactivation. For more operating time than 3 hrs, the equivalent value of electrode performance was exhibited.

4. Conclusion

PTFE bonded Raney nickel was used as the catalyst for the hydrogen electrode in alkaline fuel cells. Raney niclel catalysts were found to have the highest CO-chemisorption amount when mixed with 5wt % of PTFE. But the current density of the electrode showed the best performance prepared with

the catalyst containing 10wt% of PTFE. The Raney nickel catalyst sintered at 700℃ with the 60% of nickel and 40% of aluminum mixture showed the optimum electrochemical characteristics. The appropriate pressing pressure for manufacturing the electrode was 100kg/cm^2 and recommendable loading amount of catalyst was 0.25g/cm^2. After heat treated at 340℃ and reactivated for 1 hour, the electrochemical characteristics of hydrogen electrode were improved.

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