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PTFE-bonded Raney Nickel Hydrogen Electrodes in Alkaline Fuel Cells

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Polytetrafluoroethylene (PTFE)-bonded Raney nickel hydrogen electrodes have been prepared and their polarizations have been measured at 62 °C, using 6 M KOH (1 M=1 mol dm^{-3}) as an electrolyte. The electrodes were reproducible in polarization characteristics from electrode to electrode. The polarization resistance was found to be 0.29 Ω cm^2 for the electrode loaded with a 48-mg cm^{-2} catalyst. The limiting current density was 600 mA cm^{-2} for the electrode loaded with a 45.4-mg cm^{-2} catalyst. The influences of the pressure of the press machine and of the PTFE content on the polarizations have been investigated. The polarization resistance decreases with the catalyst loading in the manner to be expected from the reaction mechanism of the gas diffusion through electrolyte film. An experimental evidence for this reaction mechanism has been obtained by measuring the polarization of an electrode of a triple-layered structure containing a silver powder layer.

In most of the Raney nickel electrodes that have thus far been studied, electrolyte penetration into the electrode pores is prevented by the gas pressure applied on the pores from the other side of electrode. To attain a delicate balance between the gas pressure and the capillary force over the whole working area of electrode, a very good uniformity in the pore-size distribution and a careful gas-pressure control are required. Unless the pore sizes are uniform, the hydrogen gas is wasted by bubbling through the large pores, or the working area of catalytic surface is lost by the electrolyte drowning of the small pores. Although the amount of gas wasted by bubbling can be reduced by using a double-layered sintered nickel matrix[1,2] or a finely porous and wettable diaphragm,[3,4] the pore-size uniformity and the control of the gas pressure are still required.

On the other hand, electrodes water-proofed by a repellancy agent do not require such a rigorous pore-size uniformity or such a careful pressure control. However, this type of electrode has rarely been applied to Raney catalysts because the water-proofed metal electrodes have readily suffered from electrolyte drowning at a very low load current and their electrode characteristics have been quite unreproducible.[5]

Polytetrafluoroethylene (PTFE) is the repellancy agent used most frequently because of its good stabilities against heat and electrolytes. The PTFE particles are apt to cross-link with each other when they are milled with the catalyst powder for mixing. The fraction of cross-linked PTFE particles resulting from the mixing process seems to increase with the mixing time and the temperature. The repellancy of electrode and the area of the catalytic surface covered by PTFE, which essentially influence the polarization characteristics, depend not only upon the content of PTFE added, but also upon its cross-linkage. Thus, the polarization characteristics vary with the mixing condition. This is a reason why the PTFE-bonded electrodes are liable to be poorly reproducible. In the present study, the mixing time and the temperature have been kept constant so as to minimize the fluctuations in the polarization data.

The Raney nickel catalysts can be depyrophorized through a slow surface oxidation in air and can be reactivated by a reduction in the hydrogen atmosphere.[6] This permits the Raney catalysts to be handled safely in air for the electrode processing.

Experimental

Preparation of the Catalysts. A melt possessing a mass fraction of 40% Ni (99.95% purity) and 60% Al (99.99% purity) was prepared by means of an induction furnace using an alumina crucible. To avoid the separation of the nickel, the melt was quenched by pouring it into an iron cylinder. The ingot thus obtained was crushed and powdered in a mill to a particle size of less than 37 μm.

The aluminium was leached with a 6 M KOH solution at 40 °C. The Raney nickel thus obtained was washed with water and methyl alcohol alternatively.

Preparation of the Electrodes. A weighed amount of a PTFE dispersion (D-1, Daikin Industrial Company) containing 60% PTFE was added to the Raney catalyst. When the mixture was milled under blowing with a hair-dryer at the room temperature of 20±2 °C for 1 h, it became a paste. This paste was calender-rolled by hand into sheets using spacers 0.1—0.2 mm thick. After having been dried in air overnight, the sheets were boiled in acetone for 2 h to remove the surfactant which had been originally contained in the PTFE dispersion. These sheets were then used as catalyst layers.

Gas-side layers were used to stop the leakage of electrolytes that might occur through the large pores in the catalyst layers. They were prepared by using nickel black powder bound with the PTFE dispersion. Nickel black powder, which had been obtained by heating nickel formate in a hydrogen atmosphere at 250 °C, was milled with the PTFE dispersion in a way similar to that used in the case of Raney nickel. The nickel black sheets obtained by calender-rolling were attached to a stainless steel screen (100 mesh) from both sides and pressed at 200 kg cm^{-2}. The gas-side layer was heated in a nitrogen atmosphere at 380 °C for 15 min to sinter the PTFE particles and to remove the surfactant. The catalyst layers were then attached to the gas-side layer by pressing at pressures ranging from 200 kg cm^{-2} to 1200 kg cm^{-2}. The double-layered electrode thus obtained was heated at 150 °C in a hydrogen atmosphere for 1 h to activate the catalyst.

Measurement of Polarization. The geometrical working area of the electrodes was 7 cm^2. The electrolyte used was a 6 M KOH solution, and it was circulated at a rate of 5 ml min^{-1}. The electrolyte temperature was 62±0.5 °C. The IR voltage drop was eliminated by the current-interruption method.[7]

Results and Discussion

Figure 1 shows plots of the polarization, η, *vs.* the current density, i, for various catalyst loadings. Since they are almost linear up to a polarization of 20 mV, the polarization resistance, ω, which corresponds to the slope can be used as an electrode characteristic. The polarization resistance for the electrode loaded with a 48-mg cm^{-2} catalyst is found to be 0.29 Ω cm^2. It can be compared to the value of 0.31 Ω cm^2 given by Sturm for the supported Raney-Ni-Ti electrodes operated at 60 °C and at a loading of 100 mg cm^{-2}.[8]

The controllable electrode parameters in the present electrode preparation are the PTFE content, the pressure of the press machine, and the catalyst loading. When they are kept constant and a Raney nickel prepared under fixed experimental conditions is used, the performance of electrode should be reproduced. In the present preparative method, however, the thickness of the catalyst layers, which is proportional to the catalyst loading, is scattered from layer to layer beyond the limit required to obtain constant polarization data. To test the reproducibility of performance, therefore, the scattering of data due to the variation in the catalyst loading must be taken into account.

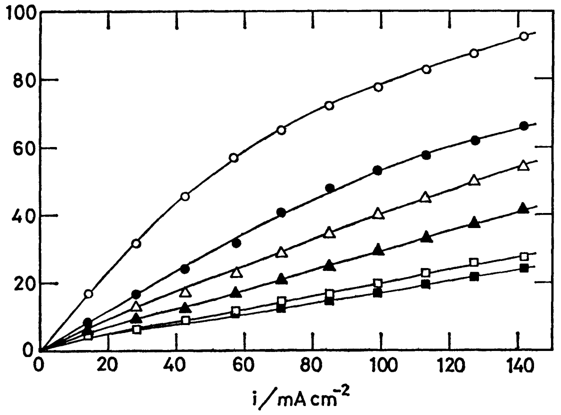

Fig. 1. Polarization curves for PTFE-bonded Raney nickel electrodes.
Catalyst loading ○: 13.5 mg cm^{-2}, ●: 25.9 mg cm^{-2}, △: 37.2 mg cm^{-2}, ▲: 48.0 mg cm^{-2}, □: 64.6 mg cm^{-2}, ■: 125.2 mg cm^{-2}.

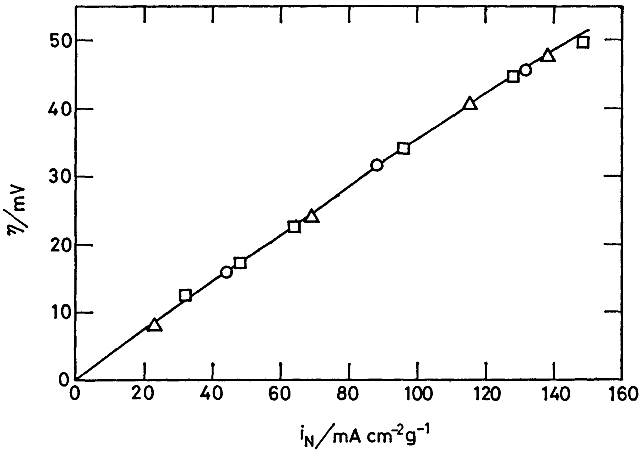

Fig. 2. Reproducibility test in polarization characteristics.
Catalyst loading ○: 13.5 mg cm^{-2}, △: 25.9 mg cm^{-2}, □: 37.2 mg cm^{-2}, current density normalized for catalyst loading.

As will be discussed in a later section, the reciprocal polarization resistance, ω^{-1}, for the thin electrode is proportional to the catalyst loading, since the reaction mechanism can be regarded as that of the gas diffusion through the electrolyte film; the current density at a given polarization is proportional to the catalyst loading. The polarization data, therefore, can be normalized to a loading of 1 g cm^{-2} by dividing i by the loading weight in unit of gram. Figure 2 shows the plots thus normalized for various loadings; i_N in the figure refers to the current density divided by the loading. The plots all fall on essentially the same curve. This proves that the electrodes yield reproducible polarization data.

Figure 3 shows the polarization curves as a function of the PTFE content, indicating that the polarization resistance increases with the PTFE content. This is due to an increase in the area of catalytic surface

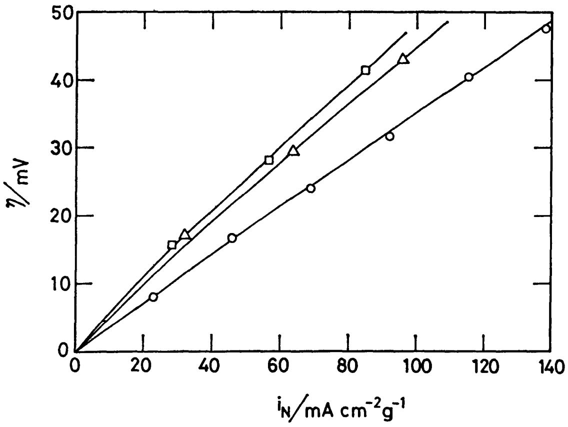

Fig. 3. Influence of PTFE content on the polarization curves.
PTFE content ○: 10.3%, △: 12.8%, □: 18.7%, current density normalized for catalyst loading.

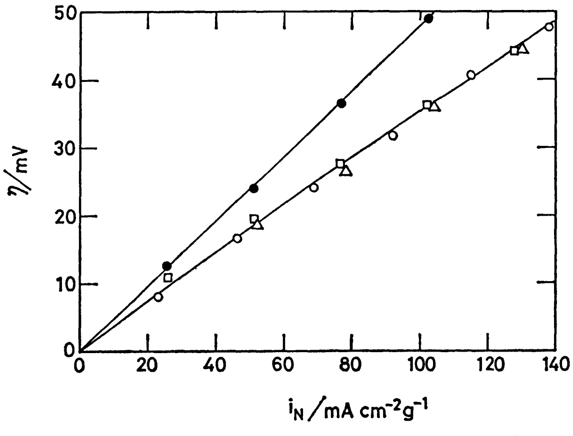

Fig. 4. Influence of the pressure of press machine on the polarization curves.
Pressure △: 210 kg cm^{-2}, ○: 421 kg cm^{-2}, □: 842 kg cm^{-2}, ●: 1260 kg cm^{-2}, current density normalized for catalyst loading.

covered by PTFE.

The pressure of the press machine influences the performance, as is shown in Fig. 4; no significant differences can be observed between the plots in the low-pressure region, and at 1260 kg cm^{-2} the plots deviate markedly. This discrete change is probably due to the calender-rolling, which compacts the catalyst layers as tightly as if they were pressed by the press machine at 842 kg cm^{-2}.

A test piece of electrode was prepared under the preparative conditions of PTFE content=10% and the pressure of press machine=421 kg cm^{-2}. The polarization curve is shown in Fig. 5. A limiting current density of 600 mA cm^{-2} is thus obtained.

Two different mechanisms have been proposed for the porous electrode reactions: a three-phase-boundary zone mechanism and one of the gas diffusion through the electrolyte film.⁹⁾ They are two extreme models with regard to the way of the electrolyte penetration into the pores. The first mechanism is based on the assumption that the electrolyte fills the pores up to the boundaries where the gas, electrolyte, and catalyst encounter each other; they are known as the three-phase-boundaries. Most of the load is sustained by the reaction occurring in the very narrow three-phase-boundary zones. It is less likely that the dried area in the pores contributes to sustaining the load by supplying the activated species toward the boundaries through surface diffusion. Hence, one can expect from this model that the polarization resistance is almost independent of the catalyst loading.

The feature of the second mechanism is that the whole catalytic surface of the pores is covered by thin electrolyte films. These films are thin enough to permit the gas molecules to diffuse. The gas molecules are dissolved into the films, and the electrode reaction takes place at the electrolyte-catalyst interface. The whole catalytic surface participates in the electrode reaction. This contrasts with the three-phase-boundary mechanism. The area of the catalytic surface can be enhanced by increasing the catalyst loading. Thus, one can expect that the polarization decreases with the catalyst loading. On the basis of this model, Mund has expressed the polarization resistance, ω, as a function of the catalyst loading, d, in this form;¹⁰⁾

$$\omega = \sqrt{\rho k}\cdot\coth\sqrt{\rho d^2/k}, \qquad (1)$$

where ρ is the electrolyte resistivity in the catalyst layers, and k, the polarization resistance of the catalysts. When the electrode is so thin that the polarization due to the electrolyte resistivity and the gas diffusibility can be neglected, Eq. 1 can be approximated as $\omega^{-1}\propto d$. This is the case described in the section on the reproducibility test. Figure 6 gives the plots of ω^{-1} *vs.* d for the present electrodes. The plots fall on a curve that is expected from Eq. 1, suggesting that the second mechanism is valid. However, the values for ρ and k are unknown, and a small possibility still remains of the mechanism of the three-phase-boundary zone holding. Further experiments, therefore, are required to judge which mechanism is valid.

For this purpose an electrode of a triple-layered structure containing a sheet of PTFE-bonded silver powder sandwiched by two sheets of a Raney-nickel layer has been prepared. The aim of this electrode is to prevent the activated species in the gas-side layer from diffusing on the surface toward the electrolyte-side layer. The diffusibility of the activated species on the silver surface is probably very small, since the silver powder used is almost inactive as a hydrogen catalyst, as is shown in Fig. 7 (△). Hence, the activated species formed in either of the Raney nickel sheets will not be able to traverse the silver sheet. The three-phase-boundary, if it is the correct mechanism, can be expected to be located in the gas-side Raney nickel layer. In the three-phase-boundary mechanism, the surface diffusion is the only way for the gas-side layer to contribute to sustaining the load. That is prevented by the silver sheet, so that if the

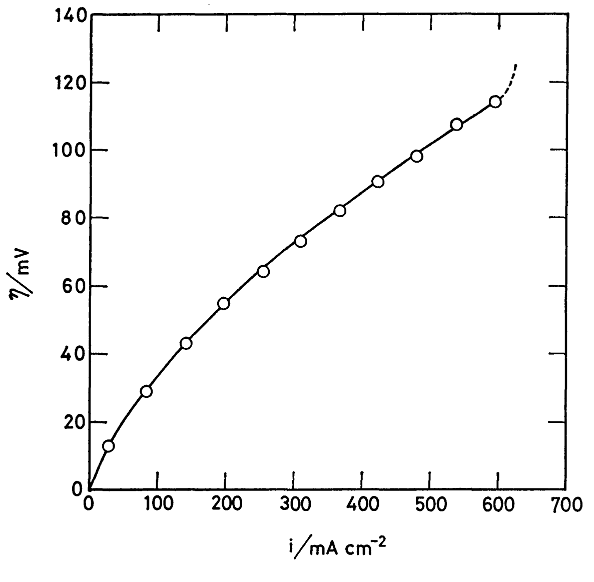

Fig. 5. Polarization curve of PTFE-bonded Raney nickel electrode.
Catalyst loading: 45.4 mg cm^{-2}, PTFE content: 10.4%, the pressure of press machine: 421 kg cm^{-2}.

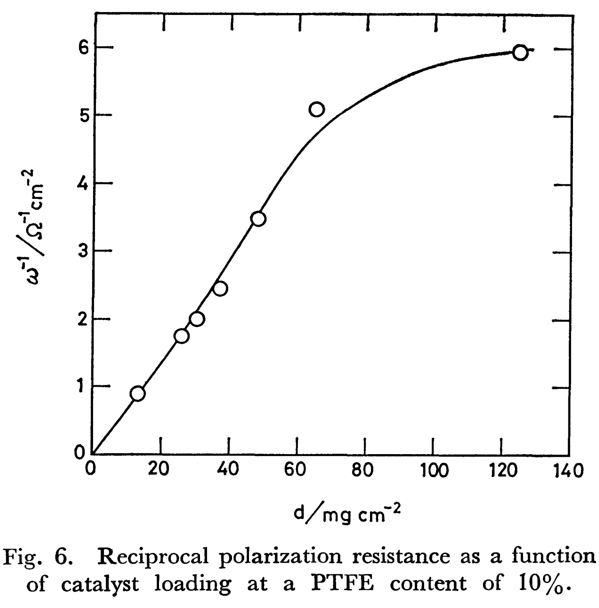

Fig. 6. Reciprocal polarization resistance as a function of catalyst loading at a PTFE content of 10%.

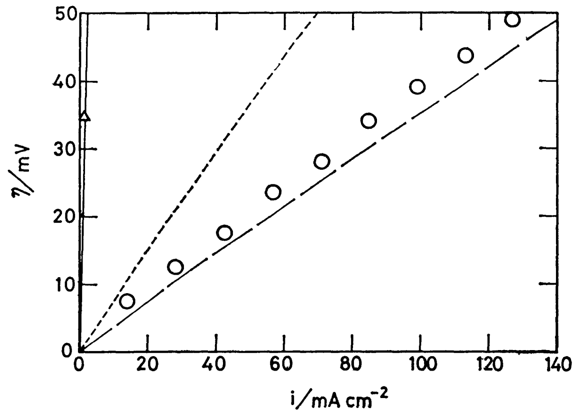

Fig. 7. Polarizations of the triple-layered electrode containing silver catalyst layer.
----: Calculated from the model of three-phase-boundary zone, — — —: calculated from the model of gas diffusion through the electrolyte film, ○: observed, △: electrode loaded with silver catalyst alone.

three-phase-boundary mechanism is valid, this electrode will be as polarized as if it is loaded with the electrolyte-side layer alone.

In the second model, the electrolyte films extend over all three layers so that the two Raney nickel sheets are connected to each other in ionic contact through the films in the silver layer. Therefore, the gas-side catalyst layer shares the load current with the electrolyte-side layer. Thus, the polarization in this case can be expected to be equal to that for a loading of both Raney nickel layers.

The polarization expected for each case can be calculated by using the polarization data in Fig. 2 and the loadings of the electrolyte-side and gas-side layers used. The dotted line and the broken line in Fig. 7 were calculated on the basis of the mechanisms of the three-phase-boundary zone and the electrolyte film respectively. The polarization data observed are closer to the broken line, suggesting that the electrolyte film is more probable.

Another piece of experimental evidence for the electrolyte penetration has been obtained by inserting pieces of filter paper between the layers. The electrode used for this experiment consists of three sheets of Raney nickel layers and a gas-side layer. Three pieces of filter paper were inserted, piece by piece, between adjacent layers. After the measurement of the polarization was over, the filter paper inserted was tested by phenolphthalein to see if it had been wetted by the KOH solution. All the test pieces were found to have been wetted. This experiment indicates that the electrolyte penetrates through all the catalyst layers.

These two experiments lead to the conclusion that the mechanism of the gas diffusion through electrolyte film is valid for the PTFE-bonded Raney nickel electrodes. The role of PTFE is to thin the electrolyte film sufficiently for the diffusion of gas molecules rather than to prevent the electrolyte penetration into the pores.

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