

밀폐형 알칼리 2차전지를 위한 수소산화 촉매전극의 제조 및 특성 연구

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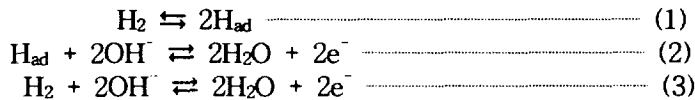
Fabrication and Characteristics of Hydrogen Oxidation Catalyst Electrodes
in a Sealed Rechargeable Alkaline Battery

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Introduction

When a rechargeable alkaline battery is overcharged, oxygen and hydrogen gases are generated from the water electrolysis. In particular, evolution of hydrogen can cause pressure build-up leading to a dangerous case of explosion in a sealed battery. It is therefore necessary to develop an auxiliary catalyst electrode which can safely reconvert generated hydrogen back to water electrochemically.

At the three phase zone among the solid electrode material, liquid electrolyte, and gaseous hydrogen, the oxidation reaction mechanism in an alkaline solution is described by the Tafel-Volmer mechanism¹⁾



Hydrogen oxidation reaction involves diffusion within the electrode and thin electrolyte film formed on catalyst electrode surface. Through adsorption and ionization reaction, the dissolved reactant transfers to the reaction site and reacts with OH⁻ in the electrolyte²⁾. The critical step in obtaining high hydrogen oxidation performance is the stable three phase zone³⁾. To achieve this zone, it is essential to prepare an electrode optimally consisting of hydrophobic region for gas contact and hydrophilic region for the electrode reaction.

In this work, hydrophobic to hydrophilic part ratio is controlled by the amount of teflon and carbon black conducting support incorporated into the electrode. The present study surveyed the kinetic characteristics and the effect of electrode performance from the different preparation conditions.

Experimental

i) preparation of catalyst powder

Ketjen black(IC-600JD) is dispersed in water, and Pt black(or Pd black) powder(Aldrich) is added to this solution. After mixing and filtering, the catalyst powder is obtained.

ii) preparation of catalyst electrode

The catalyst powder was mixed with Teflon suspension and TAB1(Teflonized Acetylene black; containing of mixture of carbon black/PTFE (2/1) with no catalyst) which plays an important role in formation of macropore to facilitate hydrogen diffusion. The mixture was filtered and dried in an oven at 60°C for 2 hours. The sample then was rolled on current collector(nickel screen) with an average thickness of 200 μ m.

In 30% KOH, at a normal temp., polarization curve was obtained using a sealed electrochemical cell by a potentiodynamic and a galvanostatic methods(potentiostat/galvanostat, SI 1286 solartron).

Results and Discussion

Fig. 1 shows the cyclic voltammogram of Pd/C, Pt/C electrodes at a sweeping rate of 5mV/s under hydrogen gas atmosphere (0.5 atm).

For Pt/C electrode, there was a steep current increase on increasing to -0.5V (vs. Hg/HgO). The electrode displayed a maximum oxidation peak at -0.2V. [I region; hydrogen oxidation region].

A surface oxidation and oxygen evolution behavior appeared at the region of 0.1 ~ 0.5 V [II region]. Toward the negative direction, through reduction region 0.4 ~ -0.2V [III region], oxidation peak appeared at -0.5V, again. This peak is assumed to be due to exposure of new surface with reduction reaction (PtOx \rightarrow Pt). In the case of Pd/C electrode, the electrode shows a similar trend compared to Pt/C electrode. However, the reduction region did not appear. Accordingly, with further cycling, because of performance decrease due to oxide effect in the case of Pd/C electrode, Pt/C electrode showed better feasibility as an auxiliary catalyst electrode.

Fig. 2. shows the relation between the Teflon content and electrode performance. Electrode containing 40 wt% Teflon content provided an optimum anode performance. At Teflon contents greater than 40 wt%, the performance decrease was likely due to an increase in wettability of the electrode and reduction of effective reaction surface area.

For the electrode containing 20 wt% Teflon, the performance was very low, because the gas was hindered from being diffused into the porous layer through wetted interface⁴⁵⁾. The electrode containing 40 wt% Teflon showed Tafel slope values of 176 mV/decade and exchange current values of 6.334 mA.

Fig. 3 shows the effects of a catalyst content in the electrode performance on electrochemical hydrogen oxidation. The performance increased proportionally with the increasing platinum content up to 25 wt%. In the figure, electrode having a platinum content of 25 wt% was examined

as a critical point. If the platinum content was higher than 25 wt%, anodic performance was lowered, due to decrease in utilization with smaller effective surface area. Tafel slope of 158.54 mV/decade and exchange current of 29mA was obtained at 25 wt%.

In the low overpotential region, $I-\eta$ relation of Pt/C electrode with pressure variation in experimental cell is shown in Fig. 4. From the relation between η and i , charge transfer resistance and exchange current was calculated. When hydrogen pressure increased from 1 to 3atm, the charge transfer resistance was found to decrease from 2.604 Ω to 2 Ω , and the exchange current was found to increase from 4.847 mA to 6.311 mA.

Fig. 5 is $I-\eta$ relation with pressure variation at Tafel region and Fig. 6 is $\log(i)$ vs $\log[H_2]$ relation from a result of Fig. 5. With increasing overpotential, electrochemical reaction order and reaction rate constant were calculated at 0.29 ~ 0.313 and 2.215×10^{-6} ~ 4.32×10^{-6} , respectively.

Reference

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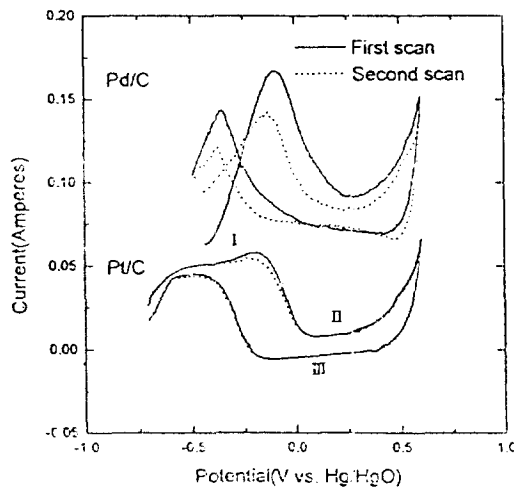


Fig. 1. Comparison of potentiodynamic cyclic voltammograms of Pd/C and Pt/C electrodes in 30% KOH solution (at 0.5 atm).

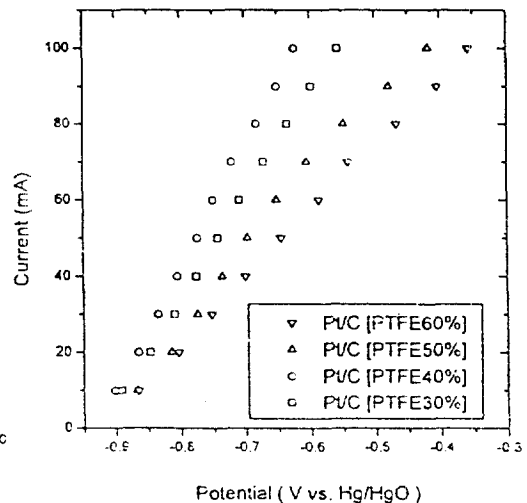


Fig. 2. Current-Potential characteristics of Pt/C electrode with four different PTFE contents (30, 40, 50, and 60 wt%).

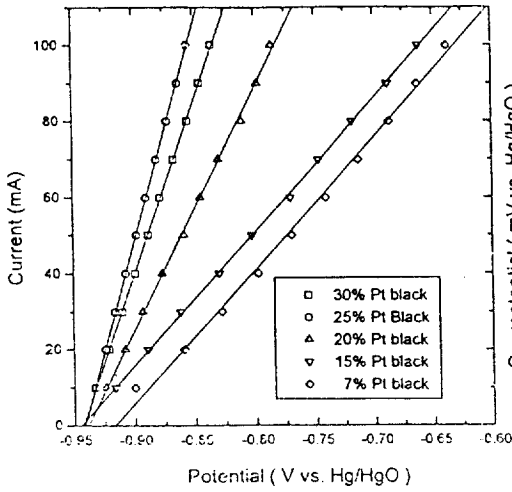


Fig. 3. Current-Potential characteristics with catalyst contents into Pt/C electrode.

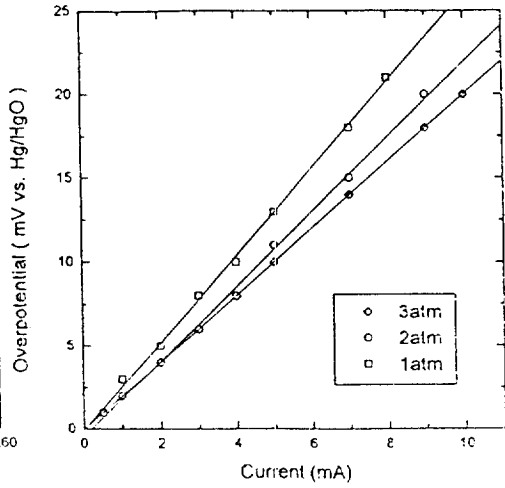


Fig. 4. Overpotential-Current characteristics of Pt/C electrodes with pressure at low overpotential region ($\eta < 20$ mV).

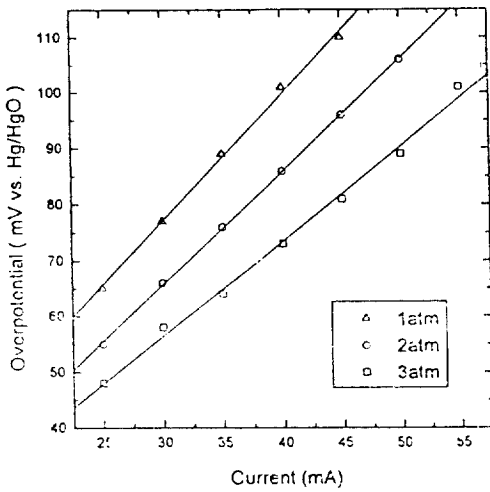


Fig. 5. Overpotential-Current characteristics of Pt/C electrodes with pressure at Tafel region ($\eta > 50$ mV)

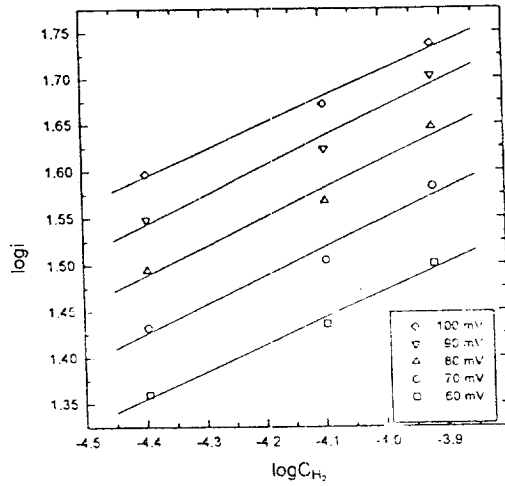


Fig. 6. Relation between current and hydrogen concentration at constant overpotential (60, 70, 80, 90 mV)