



## Short communication

# Hydrogen oxidation characteristics of Raney nickel electrodes with carbon black in an alkaline fuel cell

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## Abstract

The characteristics of hydrogen oxidation of Raney nickel electrodes containing carbon black in an alkaline fuel cell are investigated in 6 M KOH at 80°C. The addition of conductive material to these electrodes is shown to increase both the limiting current density for hydrogen oxidation and the diffusivity of hydroxide ions. The catalytic activity of Raney nickel electrodes containing carbon black is about twice that of an undoped electrode. A Raney nickel electrode with 8 wt.% Vulcan XC-72 exhibits the highest performance due to the high conductivity and high diffusivity of hydroxide ions at the electrode. The pore volume of the micropores increases with increase in the content of carbon black, but the pore volume of the macropores gradually decreases. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Alkaline fuel cell; Raney nickel; Carbon black; Hydrogen oxidation; Conductive material

## 1. Introduction

Environmental pollution emanating from the combustion of fossil fuels is encouraging the development of fuel cells as new clean energy systems. The alkaline fuel cell (AFC) has several advantages over other fuel cells. First, it has a higher conversion efficiency of fuel. Second, it sustains higher current density. Third, it uses inexpensive non-noble metals as catalysts. Finally, it operates in low temperature. Many workers have demonstrated that the AFC system is suitable for mobile electricity generators such as space shuttles, submarines, electrical vehicles, portable electrical sources [1,2].

The Raney nickel catalyst used for the hydrogen electrode in an AFC should be depyrophorized by a slow surface oxidation because its pyrophorization in air. Since the passive film, which is non-conductive, increases the resistance of the electrode, it reduces the conductivity and the catalytic activity of Raney nickel. Though Raney nickel has excellent hydrogen adsorption ability and relatively large surface area, it has the disadvantage of a high electrolyte diffusion resistance due to low pore volume and small pore size. Therefore, it is expected that a Raney

nickel electrode prepared with the addition of carbon blacks will decrease the KOH diffusion resistance and thus will have a lower polarization resistance than an electrode with an untreated catalyst.

Kenjo [3] and Kenjo and Nakajima [4] investigated the effect of catalyst loading, polytetrafluoroethylene (PTFE) content, electrode thickness and electrolyte concentration on the polarization in Raney nickel hydrogen electrodes. It was found that the polarization resistance increased with rising KOH concentration, and this was attributed to the decrease of hydrogen diffusivity and solubility in the micropores.

Jenseit et al. [5] and Al-Saleh et al. [6] found an improvement in performance with a copper-impregnated Raney nickel electrode. The former workers showed that a loading of ~ 15 wt.% copper gave the best performance. Al-Saleh et al. indicated that the effect of copper impregnation was to give a high exchange current density and a low activation energy. Tomido et al. [7] reported that spongy Raney nickel electrodes prepared by spraying molten aluminum on nickel spongy plate yielded good thermal and electrical conductivity, as well as good mechanical strength. They observed that the polarization resistance was low and that the electrode characteristics improved with increase in the temperature of the heat-treatment used in alloying. Kenjo [8] found that a

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chromium-doped Raney nickel electrode enhanced the activity of hydrogen oxidation. The same author revealed [9] that the current-limiting factors of PTFE-bonded Raney nickel electrodes are the KOH diffusivity and the catalytic activity of catalyst layers. The former determines the effective thickness for increasing the limiting current density. Gas diffusivity is not an important factor with the electrode.

The purpose of this study is to improve the performance of Raney nickel electrodes by adding conductive materials. On adding carbon black, investigations are made of the catalytic activity, mass activity, KOH diffusivity and pore-size distribution.

## 2. Experimental

### 2.1. Preparation of Raney nickel electrode

The electrodes consisted of a double layer: catalyst layers sustain the catalyst powder and gas-diffusion layers arrest electrolyte leakage. Polytetrafluoroethylene (PTFE) was used as a binder and hydrophobic agent for the catalyst and gas-diffusion layers. A weighed amount of carbon black was added to a mixture of the Raney nickel catalyst ( $< 50 \mu\text{m}$ , Sigma Aldrich), PTFE dispersion (Teflon 30J,  $0.2\text{--}0.4 \mu\text{m}$ , Du Pont) and isopropyl alcohol. Carbon black was Vulcan XC-72 (specific surface area  $254 \text{ m}^2 \text{ g}^{-1}$ ). The mixture was milled at room temperature to form a paste, which was then rolled by hand into sheets. The surfactant which had been originally contained in the PTFE dispersion was removed by acetone. The PTFE content was 10 wt.% with respect to Raney nickel and 40 wt.% with respect to carbon black. Gas-diffusion layers were prepared similarly by mixing nickel powder (INCO nickel powder type 255, specific surface area  $0.68 \text{ m}^2 \text{ g}^{-1}$ ) with the PTFE dispersion and isopropyl alcohol. The sheets obtained were attached to a nickel screen, pressed, and then heated at  $350^\circ\text{C}$  to bestow hydrophobic characteristics. Raney nickel electrodes were prepared by pressing together a gas-diffusion layer attached to a nickel screen and a catalyst layer.

The zirconia layers used for multi-layered electrodes to investigate KOH diffusivity were prepared by binding  $\text{ZrO}_2$  powder with PTFE binder and then rolling into sheets [8].

### 2.2. Measurement of KOH diffusivity of catalyst layers

The multi-layer electrode developed by Kenjo [8] was applied to estimated KOH diffusivity. The test layer is a catalyst layer in which KOH diffusivity is to be measured. The working layer is a catalyst layer which reacts with KOH solution diffusing through the test layer. The  $\text{ZrO}_2$  layer, which is a non-electric conductor and a highly porous layer to diffuse electrolyte, is located between the

test and working layers. The KOH diffusivity of the test layer is determined from the polarization difference of the working layer with or without the test layer.

### 2.3. Measurement of polarization

A reversible hydrogen electrode (RHE) was used as the reference electrode. Platinum screen was employed as the counter electrode. The geometrical working area of the electrode was  $1 \text{ cm}^2$ . The electrolyte was 6 M KOH and the electrolyte temperature was maintained at  $80^\circ\text{C}$ . The ohmic drop was eliminated by a current-interruption method.

## 3. Results and discussion

### 3.1. Influence of carbon black content on polarization in Raney nickel electrodes

The Raney nickel catalyst has not a very high electrical conductivity because the catalyst surface has a thin passive film by the depyrophorization process. Jenseit et al. [5] and Al-Saleh et al. [6] investigated the electrode performance of copper-impregnated electrodes. The Raney nickel electrodes were produced by a rolling method with a mixture of Raney nickel catalyst, PTFE powder, and  $\text{Cu}_2\text{O}$ . Copper as a conducting material is a non-porous powder. At the hydrogen equilibrium potential, the  $\text{Cu}_2\text{O}$  in the electrode is reduced to copper metal. In this study, carbon black (Vulcan XC-72), which has a large surface area and a high conductivity, was used in the Raney nickel electrode to increase the conductivity of the electrode and to improve the gas and electrolyte diffusion. Vulcan XC-72 is widely used as a component in fuel cell electrodes.

The polarization curve for Raney nickel electrodes with carbon black are shown in Fig. 1. The polarization characteristics of the hydrogen oxidation are influenced by the

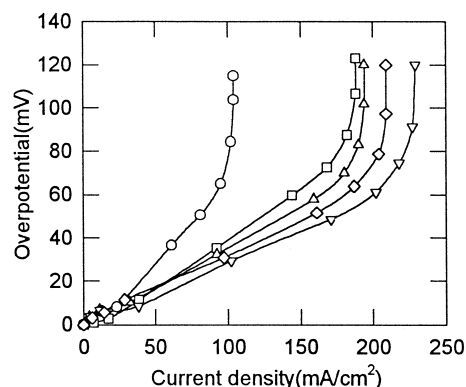


Fig. 1. Influence of carbon black content on polarization curve of Raney nickel electrodes at  $80^\circ\text{C}$  in 6 M KOH. Raney nickel loading:  $60 \text{ mg cm}^{-2}$ . Carbon black content:  $\circ$ , 0 wt.%,  $\square$ , 2 wt.%,  $\triangle$ , 5 wt.%,  $\nabla$ , 8 wt.%,  $\diamond$ , 10 wt.%.

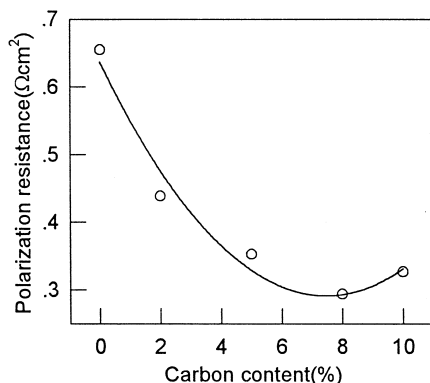


Fig. 2. Polarization resistance of Raney nickel electrodes with carbon black. Raney nickel loading:  $60 \text{ mg cm}^{-2}$ .

carbon black content of the electrode; increase in the loading improves the hydrogen oxidation and the limiting current density. From these data, an addition of 8 wt.% carbon black gives an optimum performance of the Raney nickel electrode.

The difference in behaviour between Raney nickel electrodes with 2 wt.% and without carbon black addition is due to the large increase in the ionic and the electric conductivities in the Raney nickel electrode with carbon black. The limiting current density rises continuously from 2 to 8 wt.% carbon black, and it can be concluded that this brings about an increase in both gas and electrolyte diffusion due to a change in the pore structure of the Raney nickel electrode. When 10 wt.% carbon black is added to Raney nickel electrodes, the limiting current density ( $i_L$ ) decrease slightly as a result of a decrease in the contact area between the electrolyte and the catalyst.

The polarization curves are essentially linear for a load of less than  $100 \text{ mA cm}^{-2}$ . The polarization resistance can be calculated from the slope in this load range and can provide a measure of the catalytic activity. Plots of polarization resistance vs. carbon black content are given in Fig. 2. The polarization resistance decreases continuously on

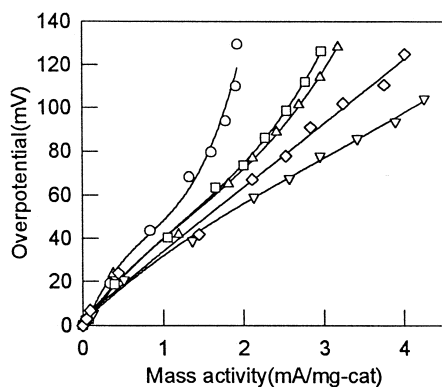


Fig. 3. Influence of catalyst loading on polarization curve of Raney nickel electrodes with carbon black. Thickness of catalyst layer:  $0.55 \text{ mm}$ . Carbon black content:  $\circ$  0 wt.% ( $105 \text{ mg cm}^{-2}$ ),  $\square$  2 wt.% ( $94 \text{ mg cm}^{-2}$ ),  $\triangle$  5 wt.% ( $90 \text{ mg cm}^{-2}$ ),  $\nabla$  8 wt.% ( $84 \text{ mg cm}^{-2}$ ),  $\diamond$  10 wt.% ( $74 \text{ mg cm}^{-2}$ ).

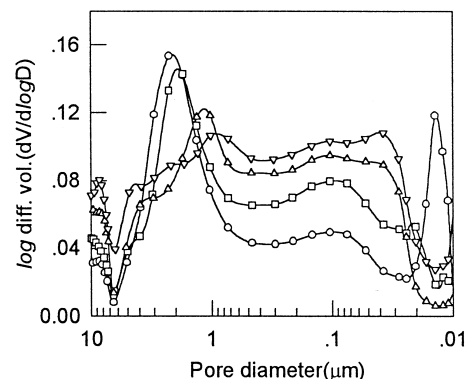


Fig. 4. Pore volume distribution of Raney nickel electrodes with carbon black. Carbon black content:  $\circ$  0 wt.%,  $\square$  5 wt.%,  $\triangle$  8 wt.%,  $\nabla$  10 wt.%.

increasing the amount of carbon black. The data indicate that the polarization resistance is minimal at a content of 8 wt.% and that the addition of 10 wt.% carbon black results in a slight increase. It is supposed that this is probably due to an increase in the conductivity and to an increase in the contact area of the Raney nickel with the electrolyte. It also suggests that there is an increase in both the gas and the electrolyte diffusion by modification of the pore structure.

The influence of carbon black loading on the normalized polarization curve of Raney nickel electrodes is shown in Fig. 3. Mass activity corresponds to current density divided by the Raney nickel loading. Clearly, the addition of carbon black improves the catalytic utilization of the Raney nickel electrode. On the other hand, the mass activity of Raney nickel electrode with 10 wt.% carbon black is decreased. This implies that carbon black addition increases the catalytic active sites but simultaneously decreases the inner resistance in the electrode. Raney nickel electrodes without carbon black are mass-transfer limited but Raney nickel electrodes with carbon black are not.

Plots of the pore-volume distribution as a function of the pore diameter for Raney nickel electrodes with carbon black are given in Fig. 4. The pore-size distribution was measured by a mercury intrusion porosimeter (Micromeritics poresizer 9320). The pore volume of the micropores ( $< 0.1 \mu\text{m}$ ), i.e., a space formed between the carbon black particles, increases in proportion with the increase in carbon black content. By contrast, the pore volume of the macropores ( $> 0.1 \mu\text{m}$ ), i.e., the space formed between agglomerates of carbon black particles or agglomerates of Raney nickel particles, gradually decreases [10]. The large pores ( $1\text{--}2 \mu\text{m}$ ) appear to be formed by agglomerates of Raney nickel particles. Carbon black is inserted between agglomerates of Raney nickel particles.

### 3.2. Variation of KOH diffusivity in catalyst layers with addition of carbon black

Fig. 5 shows the polarization curves of multi-layered Raney nickel electrodes which are composed of a test layer

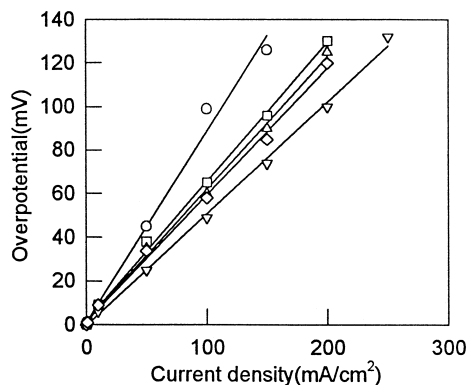


Fig. 5. Polarization curve of multi-layer electrodes for measurement of KOH diffusivity in electrode. Working layer: Raney nickel electrode with 8 wt.% carbon black. Carbon black content of test layer:  $\circ$  0 wt.%,  $\square$  2 wt.%,  $\triangle$  5 wt.%,  $\nabla$  8 wt.%,  $\diamond$  10 wt.%.

(Raney nickel electrode with carbon black, thickness 200  $\mu\text{m}$ ), a zirconia layer (ion conducting and non-electron conducting layer) and a working layer (Raney nickel electrode with 8 wt.% carbon black).

The influence of carbon black content of the KOH diffusivity in Raney nickel electrode is shown in Fig. 6. The KOH diffusivity is calculated using the equation reported by Kenjo [8] and the current density of the

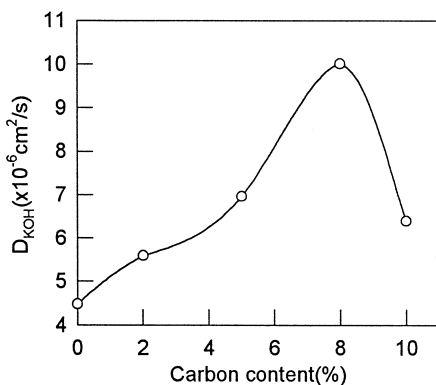


Fig. 6. KOH diffusion coefficient of Raney nickel electrodes with carbon black.

working layer is based on the polarization curves of multi-layered Raney nickel electrodes. The KOH diffusivity increases continuously with increasing carbon black content up to 8 wt.%. This improvement in performance results from an increase in the number of micropores.

#### 4. Conclusions

As the amount of carbon black is increased, the limiting current density of Raney nickel electrodes increases and the polarization resistance decreases. Because of the physical properties of carbon black, Raney nickel electrodes with carbon black become highly microporous. There is an increase in the conductivity and in the diffusion of both gas and electrolyte due to the change in the pore structure of the electrode. The limiting current density increases for carbon additions of 2 to 8 wt.%, but decreases at a content of 10 wt.%. This is due to the physical properties of the carbon black and a hindrance to gas diffusion by the excessive electrolyte amount. The pore volume of the micropores is increased in proportion with the increase in carbon black content but the pore volume of the macropores gradually decreases.

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