

# Long-term hydrogen oxidation catalysts in alkaline fuel cells

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## Abstract

Pt/Pd bimetallic combination and Raney Ni catalysts were employed in long-term electrochemical assessment of the hydrogen oxidation reaction (HOR) in 6 M KOH. Steady-state current vs. potential measurements of the gas diffusion electrodes have shown high activity for these types of catalysts. Durability tests of the electrodes have shown increased stability for the Pt/Pd-based catalysts than the Raney Ni at a constant load of 100 mA/cm<sup>2</sup> and at temperatures of 55°C and 60°C, respectively. Surface, structural and chemical analyses by BET surface area, transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were used to characterize the composite electrode/catalyst both before and after the electrochemical testing. © 2000 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Platinum, together with other platinum group metals either as single, binary, ternary or bimetallic combinations, has been the preferred option for use in low or intermediate temperature fuel cells, such as the alkaline fuel cell (AFC), polymer electrolyte fuel cell (PEFC), direct methanol fuel cell (DMFC) and phosphoric acid fuel cell (PAFC), for the hydrogen oxidation reaction (HOR). This is due to the fact that HOR on these catalysts proceeds at a faster rate than the corresponding oxygen reduction reaction. The overpotentials of these electrodes, operating at current densities of < 400 mA/cm<sup>2</sup> is about 20 mV compared to at least 10 to 15 times higher than the oxygen electrode [1]. During the 1970s and early 1980s, high platinum or platinum alloy loadings were used to obtain increased performances, as for example, anodes for PEFC (4 mg/cm<sup>2</sup>), PAFC (5–10 mg/cm<sup>2</sup>) and the AFC (10 mg/cm<sup>2</sup> with 80% Pt and 20% Pd alloys) developed by International Fuel Cells. However, the platinum, platinum alloy or bimetal loading have been recently reduced by 20 to 100 times in all types of the liquid electrolyte fuel cells [2–6]. In these fuel cells, high performances are obtained in the three-dimensional reaction zone of the catalyst–elec-

trolyte–gas phase interface by preparation of highly dispersed catalyst particles supported on a high surface area carbon, thereby enhancing simultaneously their effective utilization. In order to decrease the noble metal loading to such levels and thereby reduce the cost, thin-film layers of the catalyst on the carbon support are utilized in the reaction zone. Moreover, other non-noble transition metals are added to stabilize platinum atoms by reducing the platinum nearest neighbor spacing or by bond formations [7–11]. As the reactions on the surface of the catalyst depends upon the size and shape of the crystallites, high dispersion rates and robust support materials are, therefore, necessary for high activity and stability.

The scope of catalyst precursors for the anode in the AFC in comparison to the other types of fuel cells is wider. Nickel boride, sintered nickel and Raney Ni [12–14] are among those catalysts which have found applications in the electrochemical oxidation step of hydrogen. Raney Ni catalyst, which is also used in hydrogenation, hydrogenolysis and other reactions [15], is among the most active non-noble metals for the anode reaction in gas diffusion electrodes. However, the catalytic activity and stability of Raney Ni alone as a base metal for this reaction is limited. These problems have been circumvented by doping a few percentage of transition metals, such as Ti, Cr, Fe and Mo into the Ni–Al alloy, prior to extraction by KOH [16–18].

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As long-term operation of the electrodes is important in the reduction of the cost of electricity (COE) [19], efforts are made in this study to present long-life tests of the HOR catalysts of Pt/Pd bimetal and Raney Ni. Although much of the literature data have been focused on activity tests and related issues, this study tries to shed light on the coherence of activity and stability in alkaline electrolyte for the HOR. Furthermore, pre- and postmortem characterizations of the cutaway sections of the electrodes with these electrocatalysts were made using surface area BET-measurements, transmission electron microscopy (TEM) observations together with energy dispersive spectroscopy (EDS) analyses were carried out in order to correlate factors influencing the activity and stability tests of the electrodes. Although many parameters, such as PTFE content and type, nitrogen freeze-drying of the PTFE-based diffusion layer, catalyst loading, type of carbon support, types of pore formers, influence of the hydrocarbon solvent, sintering gases and temperatures were investigated, this present report gives assessments on the optimized electrodes.

## 2. Experimental

Gas diffusion electrodes for the HOR were prepared by the rolling method as described in earlier reports [20,21]. The Pt and Pd catalysts (each 10% by weight) on charcoal were obtained from Johnson Matthey Chemicals and the Raney Ni catalyst (BLM-112W) with its admixtures of Cr and Fe was a commercial grade product, obtained from Degussa. Common to both gas diffusion electrodes was the diffusion layer, which consists of 60% PTFE and 40% carbon (Vulcan XC-72). This layer is rolled on a nickel wire screen (100 mesh) to a thickness of 0.7 mm. The active layer (catalyst layer) for the Pt/Pd-based electrode, consisting of PTFE powder (7% w/o) was mixed in dry conditions in a mixer, transferred into a beaker with water or hydrocarbon solvent and homogenized in a high speed magnetic stirrer. PTFE in suspension (10% w/o) was again added to the mixture and milled in a colloid mill and

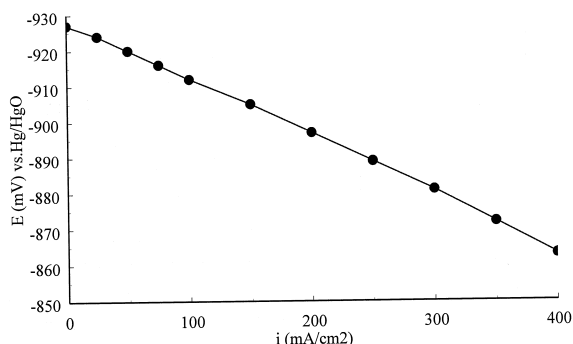


Fig. 1. Polarization curve of a Raney Ni catalyst-based electrode at 60°C.

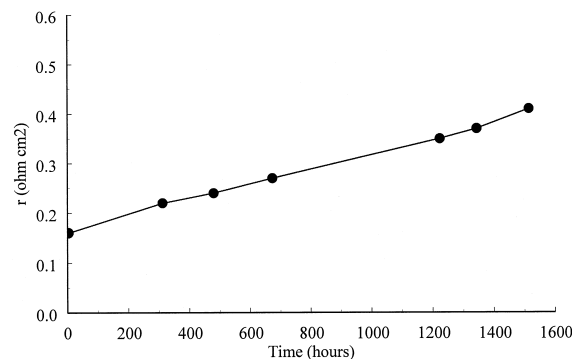


Fig. 2. Time vs. polarization resistance of a Raney Ni-based electrode at a constant current load of 100 mA/cm<sup>2</sup>.

filtered off. The active layer of the Raney Ni-based electrode, which was kept in water to prevent air exposure, was mixed with carbon (Black pearl-2000, 2.7% w/o), PTFE suspension (2.7% w/o) and PTFE powder (10% w/o) in attrition mill with further addition of a high boiling point hydrocarbon solvent. The water was then vaporized at 110°C and the hydrocarbon reduced so that a rollable paste was obtained. The active layer maintained by this procedure prevents the pyrophorosity of the Raney Ni catalyst so that handling is safely managed in air. The respective layers of the catalysts (Pt/Pd and Raney Ni-based catalysts) were rolled to a thickness of 0.5 mm and then double-rolled with the diffusion layer to a composite electrode. The electrodes were compressed at 220 kg/cm<sup>2</sup>, dried at 60°C and sintered at 280°C for 1 h. The sintering was carried out in nitrogen atmosphere for the Pt/Pd-based electrode, while hydrogen gas (25% vol.) was introduced into nitrogen in the case of the Raney Ni-based electrodes.

Electrode specimens with 4 cm<sup>2</sup> geometrical area were spot-welded to a nickel wire, mounted in half-cell configurations, immersed in 6 M KOH and tested at 55°C for the Pt/Pd-based and at 60°C for the Raney Ni-based electrodes, respectively. The counter-electrode was a nickel wire screen and potential readings were made using the Hg/HgO reference electrode (6 M KOH) with a Luggin capillary in contact with the electrode. High purity hydrogen gas was allowed to flow through the rear side of the electrode, viz. to the diffusion layer. Descriptions and measurement principles of the electrochemical cell have been given previously [20]. Current-potential measurements were obtained after the electrodes reached a steady-state operation, usually after less than 1 h. All the polarizations of the electrodes were read without iR compensation. Although the cells were covered to avoid carbon dioxide contact with the electrolyte, it was found necessary to change the electrolyte every 500 h. This step limits the carbon dioxide uptake from the surrounding air and carbonate build-up, which can alter the surface characteristics and kinetics of the electrode reaction ( $1/2\text{H}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{e}^-$ ).

Table 1  
BET-surface area characterizations of the electrode materials and the electrodes

Type	BET-surface area (m <sup>2</sup> /g)	Microporous (< 50 Å) BET-surface area (m <sup>2</sup> /g)
10% Pt on charcoal	757	422
10% Pd on charcoal	727	403
PTFE suspension	5	0
Electrode (non-sintered)	102	0
Electrode (sintered)	166	10
Electrode (tested 2800 h)	262	26

Particle morphology and particle size observations of the electrodes, containing the supported catalysts (platinum and palladium) and PTFE were carried out using TEM (JEOL, JEM-2000 ×). The electrode materials were dispersed on copper grid and were analyzed using a Philips mode with an acceleration voltage rate of 200 kV and magnifications ranging from 100 K to 200 K. The EDS, which is connected to the SEM was used for quantitative analyses of the electrode materials both before and after the electrochemical tests of the electrodes. Surface area, pore volume and pore size distributions of the electrode materials were obtained from N<sub>2</sub> isotherms determined at liquid nitrogen temperature (77 K) on an automatic analyzer from Micrometrics (ASAP 2000). The samples were degassed in vacuo at 473 K prior to the measurements.

### 3. Results and discussions

The steady-state current-potential measurements of the Raney Ni-based electrodes at 60°C and 6 M KOH show a linear relationship (Fig. 1) with a polarization resistance ( $r$ ) as low as 0.16 Ω cm<sup>2</sup>. The surface area of the Raney Ni catalyst containing a small addition of iron and chromium is ca. 70 m<sup>2</sup>/g. The surface area of the electrode after handling of the Raney Ni catalyst, mixing of the high surface area carbon (Black Pearls 2000, 1480 m<sup>2</sup>/g) and PTFE and fabrication steps shows a BET-surface area of 19.5 m<sup>2</sup>/g. The carbon maintains an increase of the total surface area of the electrode as well as improves the inter-particle contact of the electrode materials. Hydrogen diffusion and solubility takes place in the inner surface areas, which are much higher than the geometrical surface

areas of the Raney Ni particles [22]. Therefore, the performance of the catalyst for the HOR initially depends on the electrolyte-filled reaction sites of the micropores, maintaining a well-balanced hydrophobic and hydrophilic structural distribution of the electrode materials.

The dependence of the performance, expressed as the polarization resistance on the long-term stability of the Raney Ni catalyst is shown in Fig. 2. The high performance of the electrode, however, shows continuous deterioration at a constant current load at 100 mA/cm<sup>2</sup>. This corresponds to an initial current load per weight of catalyst of 1.45 A/g with a Raney Ni load of 68.96 mg/cm<sup>2</sup> and with a polarization of 21 mV and after 1500 h of 58 mV. Although the decay rate (24 μV/h) is relatively lower than similar HOR based on Raney Ni catalysts [16], the electrode shows instability at higher current loads. The surface area of the electrode decreased substantially to 1.13 m<sup>2</sup>/g after the electrochemical testing. This phenomenon can be ascribed to the wetting properties of the Raney Ni grains and passivation in the P<sup>H</sup>-potential domain of nickel due to anodic oxidation and transition to nickel oxides [23] and repeated polarisations, which might have contributed to the shift of the chemical stability of the catalyst. The wettability of the electrode increases with time, when most of the micropores are electrolyte-filled. Thus, hydrogen access to the reaction sites becomes limited with no further reaction taking place in the pores of the catalyst, that is, the “drowning” phenomenon of the pores.

Table 1 shows the electrode materials and electrodes prepared by the rolling method. The Pt/Pd on charcoal is characterized by high BET-surface areas, where more than 55% of the areas are composed of microporous areas of less than 50 Å. However, these high surface areas are substantially reduced upon treatment and manufacture of the electrodes. The surface areas show slight increase after heat-treatment or sintering of the electrodes. This means that the original microporous and high surface areas of the Pt/Pd combinations on charcoal are predominantly lost during the preparation steps. During the course of the reaction, however, the BET-surface and microporous areas are increased by almost 100 and 16 m<sup>2</sup>/g, respectively, implying that pores are accessible and filled by the electrolyte for further reaction to take place.

Table 2 shows a qualitative analysis of the catalysts by EDS for both pre- and post electrochemical tests of the

Table 2  
Elemental analysis of Pt/Pd electrodes by EDS

Type of Element	Element (%)		Atomic (%)	
	Unused electrode	Used electrode	Unused Electrode	Used Electrode
Pd	65.90	66.02	77.99	78.06
Pt	34.10	33.98	22.01	21.94
Total	100.00	100.00	100.00	100.00

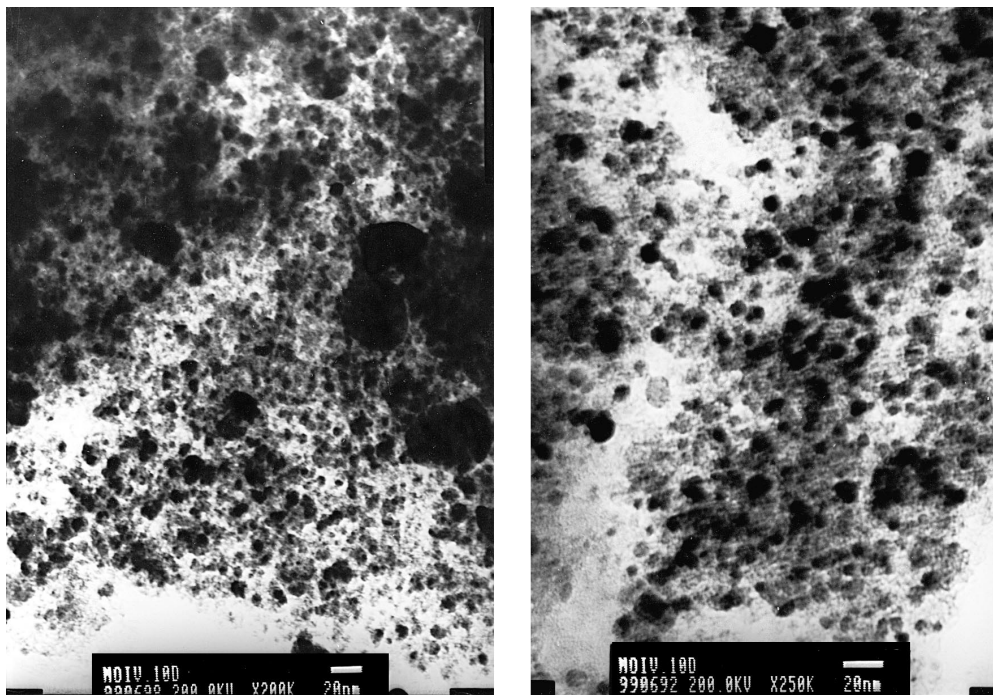


Fig. 3. TEM micrographs of (A) unused electrode (B) after 3600 h of electrochemical testing.

electrodes. The electrode was tested electrochemically for about 3600 h, where a similar electrode was assembled in a long-term performance study with a decay rate of  $3.4 \mu\text{V}/\text{h}$  for more than 11 500 h, which has been reported in a recent work [24]. The elemental or atomic analysis of the electrodes, both unused and used, have shown almost identical composition. Although the potassium content in the test electrode was high due to the penetration and wettability of the electrode structure, a factor was taken into consideration to compensate the Pt/Pd contents. Therefore, the result shows, that the Pt/Pd concentrations were not altered during the HOR giving the necessary stability of these bimetallic catalysts for long-term applications in alkaline electrolyte.

Transmission electron micrographs (TEM) for both the unused and used electrodes are shown in Fig. 3A and B. The corresponding average particle size of the unused

electrode is  $30 \text{ \AA}$ , while for the electrochemically tested electrode is  $110 \text{ \AA}$ . This agrees with the earlier findings [2,9] that catalyst particles in an alkaline electrolyte tend to coalesce, producing larger agglomerates. This coalescence of very small catalyst crystallites may be attributed to migration in contact with the electrolyte as a result of surface energy and diffusion.

Fig. 4 shows the current-potential characteristics of a Pt/Pd based electrode. The total catalyst loading was  $1.1 \text{ mg}/\text{cm}^2$  with a catalyst composition of each metal corresponding to  $0.55 \text{ mg}/\text{cm}^2$ . The performance shows that by decreasing the amount of Pt to low levels and by adding Pd in a similar loading, high activity of HOR could be attained. Fig. 5 shows the polarization resistance of the electrode at various measuring hours. The oscillations of the curve, especially after ca. 1000 h are due to mainly

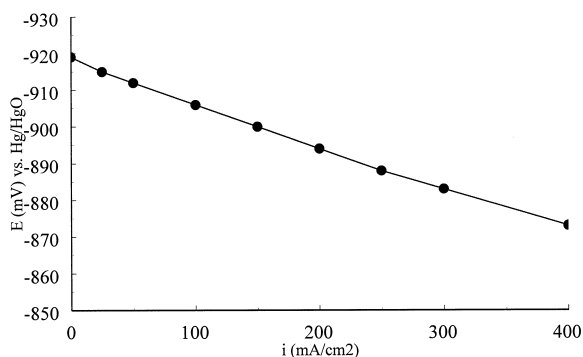


Fig. 4. Polarization curve of a Pt/Pd-based electrode at  $55^\circ\text{C}$ .

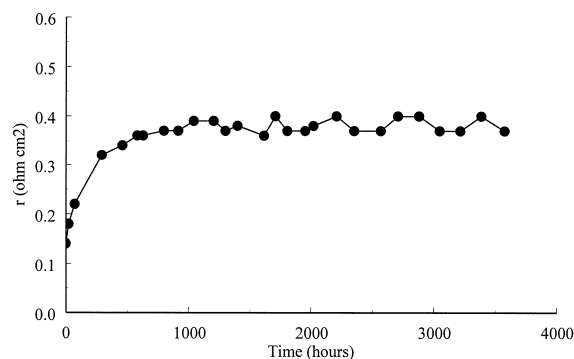


Fig. 5. Time vs. polarization resistance at a constant current of  $100 \text{ mA}/\text{cm}^2$  for Pt/Pd-based electrode.

carbonation of the electrolyte and intermittent exchange of a fresh electrolyte. At the initial current-potential measurement of the electrode, the polarization resistance was as low as  $0.14 \Omega \text{ cm}^2$  with a steep rise in the polarization resistance to  $0.22 \Omega \text{ cm}^2$  after only 75 h. This substantial increase of polarization resistance is in accordance with other similar electrodes. Statistical data over 15 electrodes show, that the polarization resistance at the start of the electrochemical test was  $0.14 \Omega \text{ cm}^2$ . But after 160 h, the polarization resistance increased to  $0.25 \Omega \text{ cm}^2$ . This increase in the polarization corresponds to a decay rate of  $69 \mu\text{V}/\text{h}$ , which is a significant loss of the total performance of the electrode. On further tests of the electrodes from 160 to 640 h, the polarization resistance slightly increases to  $0.33 \Omega \text{ cm}^2$ . However, the polarization decay discontinues and is almost constant for the consecutive hours of operation. These observations are in line with the above findings, elaborated by the TEM images. The morphologies and particle sizes of the Pt/Pd bimetallic combinations after the electrochemical testing are altered, leading to a loss of catalyst surface area. The Pt/Pd surface area loss thus in the initial hours strongly influences the performance behavior of the electrode.

#### 4. Conclusions

Raney Ni catalyst with Fe and Cr mixtures has shown high activity for the HOR. However, the long-term operation of the electrode has shown increased decay of the performance due to mainly the wettability of the inner pores and changes of the chemical structure of the precursor material during repeated polarisations. These phenomena may be circumvented by further modifications of the hydrophilic and hydrophobic nature of the electrode and by keeping the potential of the electrode not beyond the limited value, which can lead to the oxidation of the catalyst.

The Pt/Pd-based electrodes with low loadings of both catalysts have shown substantial performances and stability. The initial performance, however, deteriorates after merely short period of electrochemical testing. This increased decay rate of the electrode may be attributed to the morphological changes of the catalyst. Although the concentrations of the catalysts before and after the electrochemical studies are the same, the morphological changes of the catalysts have been confirmed by TEM analysis.

The particle sizes of the Pt/Pd catalysts have increased more than thrice of the initial particle sizes. After the consecutive steps of electrode deterioration, the electrode potential, however, remains constant without any considerable decay rates.

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