Novel methods of stabilization of Raney-Nickel catalyst for fuel-cell electrodes

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Abstract

Two new methods of stabilizing Raney-Nickel (Raney-Ni) catalyst for making fuel-cell anodes were studied. In the first method, the catalyst was oxidized with aqueous H_2O_2 solution, while in the second, oxygen/air (O_2/air) was used in a slurry reactor. Effects of different concentrations of H_2O_2 (5–25 wt.%) and different pressures (10–20 psig) of gas were investigated. The stabilized catalyst was characterized using BET surface area, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The catalyst was used in fuel-cell anodes and the electrochemical performance was determined in an alkaline half-cell. The results were compared with electrodes prepared using conventionally stabilized catalysts. The hydrogen peroxide-treated catalyst has higher BET surface area and produces electrodes with lower polarization. In addition to this, H_2O_2 treatment is convenient, fast and needs simple equipment which involves no instrumentation. Use of oxygen in a slurry reactor to stabilize the catalyst is also convenient but electrode performance is relatively poor. © 1998 Elsevier Science S.A.

1. Introduction

For terrestrial applications of fuel-cells, substitution of noble metal with Raney-Nickel (Raney-Ni) has been a subject of research for years due to its lower cost, lower operation temperature, high surface area, and high activity. Nickel is thermodynamically stable as bulk metal to $+100$ mV SHE at pH 14 and 25°C, but as the pH approaches zero, its domain of stability is -500 mV SHE [1]. This permits its use in alkaline media. The catalyst is prepared by leaching aluminum from Ni–Al alloy with hot concentrated alkali solution. Some of the generated hydrogen during the leaching reaction adsorbs in the micropores of the catalyst and makes it highly pyrophoric.

The pyrophoric character of the catalyst can be eliminated by complete removal of hydrogen from Ni sites and by forming a thin oxide layer of certain thickness on the surface. This process is known as depyrophorization or stabilization of the catalyst. The nickel oxide layer that forms on the metal surface enhances the adsorption of hydrogen and makes it more electrochemically active than the bare nickel due to increased surface roughness [2].

Conventional stabilization utilizes controlled surface oxidation invented by von Sturm and Thieleking [3]. In this method, the catalyst is dried in nitrogen atmosphere and then small doses of oxygen/air (O_2/air) are introduced to oxidize it slowly under controlled temperature within the range of 60–90°C. The temperature should be higher than 40°C to give a sufficient rate of oxidation, but should not exceed 90°C. At a higher temperature, the higher oxidation rate and the exothermic nature of the reaction increases the possibility of a sharp temperature rise and this may lead to catalyst sintering. Hence, this method requires a good control system and involves the risk of sintering. Long duration of reaction and high consumption of pure nitrogen are the other disadvantages [4]. To overcome these problems, two methods are proposed and studied in this investigation. In the first method, H_2O_2 is used as an oxidizing agent. The catalyst particles are mixed with a dilute H_2O_2 solution. In the second method, an oxidizing gas (O_2/air) is passed into a slurry of catalyst and water. The stabilized catalysts produced from the new and conventional methods are characterized and used to prepare PTFE-bonded, gas-diffusion anodes. The electrochemical performance of these electrodes is measured in an alkaline half-cell for comparison.

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2. Experimental

2.1. Leaching

Aluminum from a fine powder of 50–50 wt.% Al–Ni alloy was leached using 25 wt.% NaOH solution to produce porous and pyrophoric catalyst. The reaction was carried out at 343 K for 80 min in a CSTR at 1000 rpm speed. These parameters were chosen on the basis of an experimental study by Chaudhary et al. [5]. The aluminum compounds produced during the leaching process were removed by washing the catalyst with distilled water until neutral pH is reached.

2.2. Stabilization of Raney-Ni

Thoroughly washed Raney-Ni was passivated by the three methods described below. To avoid interference of the leaching parameters, samples were drawn from one lot of leached catalyst.

2.2.1. Conventional method

The washed catalyst was stabilized using the recommendation of Justi et al. [6]. A known mass of washed catalyst, which was still wet, was placed in a vacuum oven. Approximately 300 mbar pressure was maintained in the oven. Nitrogen gas was introduced into the oven until the pressure was atmospheric. The pressure was reduced to 300 mbar again by applying vacuum. The process was repeated 6–7 times to ensure an inert atmosphere. The temperature in the oven was maintained at 40°C. The catalyst was left in that condition for several hours. The change in the catalyst was observed intermittently through the viewing window of the oven. Once the catalyst powder was dried, a small dose of oxygen was introduced into the oven until the pressure was 400 mbar. At the same time, the temperature of the catalyst was controlled carefully. If the temperature rose sharply, nitrogen gas was introduced into the oven. When the catalyst was cooled to the previous temperature, the process was repeated. Introduction of the oxygen doses was continued until atmospheric pressure was reached. A small sample of dry catalyst was kept in a watch-glass and monitored carefully. If the catalyst was successfully passivated, no visual burning occurs.

2.2.2. H_2O_2 treatment method

The apparatus used for the H_2O_2 treatment is shown schematically in Fig. 1. The reactor has three necks to accommodate a thermometer, a stirrer, and a funnel. The whole assembly is kept in water bath. H_2O_2 solution (250 ml) of known concentration was poured into the reactor. Then, 50 g of the catalyst was added and stirring was started. A vigorous reaction occurred with bubbling and effervescence. The reaction was allowed to continue until the bubbling and effervescence stopped. The catalyst was filtered and dried in vacuum under nitrogen atmosphere.
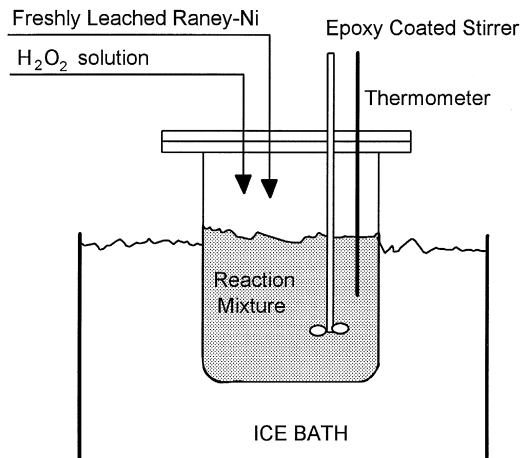

Fig. 1. Apparatus for passivation by H_2O_2 treatment.

The dried catalyst was characterized and then used to make test electrodes. Different concentrations of H_2O_2 (5–25 wt.%) were used to study the effect of concentration.

2.2.3. Direct gas oxidation method

Catalyst stabilization was carried out in a slurry reactor of 55 mm diameter and 300 mm length with a fritted-glass filter bottom. The oxidizing gas (O_2/air) was bubbled into a slurry of freshly leached catalyst and water. Approximately 15 g of washed catalyst was mixed in 100 g of water. Gas at a controlled pressure and flow rate was passed for several hours. One sample at the end of each hour was pipetted out and filtered into a Gouch filter. The filter with the catalyst was dried in vacuum. After complete drying, the sample was exposed to air. The pyrophoric character of the sample was observed visually. When the sample no longer exhibited visual burning, the catalyst was taken out and dried. In this study, three variations in the oxidizing gas were considered, namely, oxygen at 10 and 20 psig and air at 20 psig.

Table 1
Parameters of electrode preparation

Parameter	Value
Loading of catalyst (mg cm^{-2})	120
PTFE content (wt.%)	8
Milling time (s)	60
Cooling while milling (on/off)	On
Surfactant	Brij-96
Amount of surfactant	2 ml in 500 ml slurry
Vacuum for filtration	500 mbar/300 mbar
Clearance between rolls (μm)	400
Removal of surfactant	Once
Activation time (h)	25
Activation temperature (°C)	25
Electrolyte	25 wt.% KOH
Temperature of polarization (°C)	25
Hydrogen gas pressure (kPa)	148

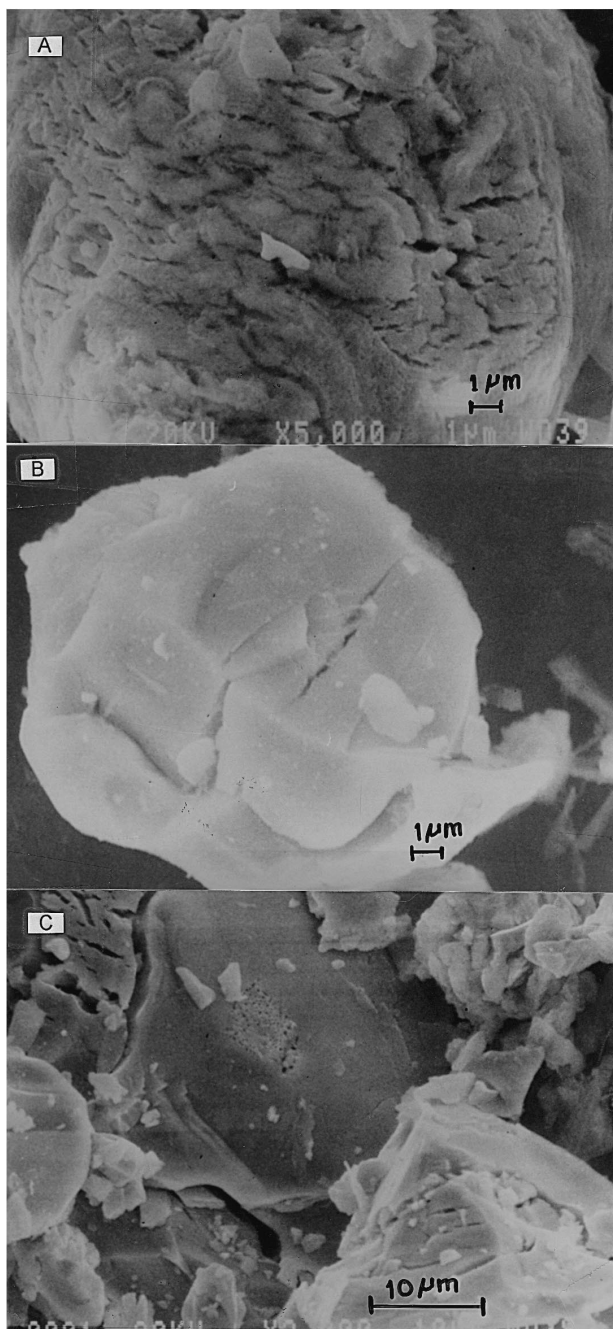Fig. 2. Scanning electron micrographs of (a) H_2O_2 treated, (b) conventionally passivated and (c) direct gas oxidized catalyst samples.

2.3. Performance evaluation

The effectiveness of the proposed methods was compared with the conventional one by preparing hydrogen oxidation gas-diffusion anodes and measuring their polarization in an alkaline half-cell. The filtration method was used to make PTFE-bonded, gas-diffusion electrodes. Polarization data were obtained using an alkaline half-cell and a potentiostat (model 273A EG&G PARC). The filtration method and performance evaluation technique are

detailed elsewhere [7,8]. The parameters used for electrode preparation were kept constant at values listed in Table 1 so that the data represent only the effect of the stabilization method. The stabilized catalysts from all three methods were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and BET surface area.
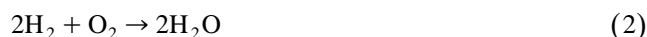
3. Results and discussion

3.1. H_2O_2 treatment

When H_2O_2 comes in contact with Ni particles, it decomposes and the following exothermic reaction takes place.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (1)$$

The generated oxygen reacts with adsorbed hydrogen.

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (2)$$

The second possibility is the reaction of H_2O_2 directly with hydrogen.

$$OH_2O_2 + H_2 \rightarrow 2H_2O \qquad (3)$$

In addition, oxygen reacts slowly with nickel on the surface to form a passivated NiO layer. All of these reactions are exothermic and generate considerable heat. As the
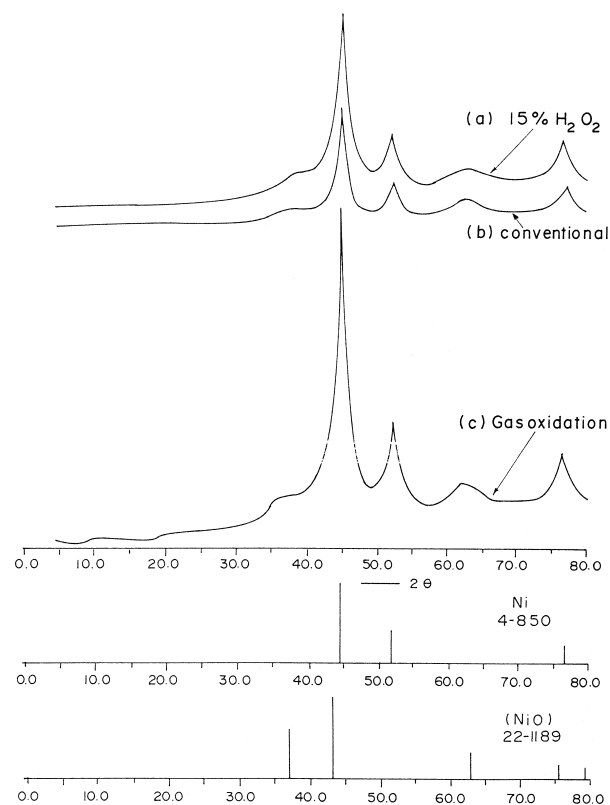

Fig. 3. X-ray diffraction patterns of (a) H_2O_2 treated, (b) conventionally passivated and (c) direct gas oxidized catalyst samples.

Table 2
BET surface area of catalyst samples

Method	Parametric value	BET surface area ($m^2\ g^{-1}$)
Conventional controlled surface oxidation	−	51
H_2O_2 treatment (wt.%)	5	35
	10	48
	15	65
	25	63
Direct gas in slurry reactor (psig oxygen)	10	18
	20	19
Direct gas in slurry reactor (psig air)	20	18

reaction is taking place in aqueous medium, the heat generated will be removed by water. This avoids excessive heating of the catalyst and reduces the possibility of catalyst sintering. In addition, the available oxygen at the catalyst surface can be controlled by varying H_2O_2 concentration.

Fig. 2a and b are electron micrographs of H_2O_2-treated and conventionally stabilized catalysts. The morphological features of the two catalysts are similar. The particles are quite regular and have different sizes from submicrons to 500 μm. The particles have sharp edges and are not fused with one another. This suggests that no appreciable sintering has taken place. The XRD patterns of conventionally stabilized and H_2O_2-treated catalysts (15 wt.%) are shown in Fig. 3a,b. The X-ray patterns also contain the standard peaks of NiO and Ni. The NiO peaks are present in all three patterns but their heights are much smaller than those of the nickel peaks. This indicates that NiO is present in all the samples, but at a lower level than nickel. It can be hypothesized that the NiO is concentrated on the surface while the bulk of the catalyst is nickel. The BET surface area was measured for all samples and the values are listed

in Table 2. The BET surface area for H_2O_2-treated samples increases with increasing concentration, although there is no appreciable change after the concentration has reached 15 wt.%.

The galvanostatic polarization data of electrodes prepared with catalysts stabilized by different methods provide the most important criteria for comparing the effectiveness of the individual methods. The polarization curves of anodes prepared with a catalyst stabilized by H_2O_2 treatment and by the conventional method are shown in Fig. 4. The electrode prepared with H_2O_2-treated catalyst has better activity. This can be attributed to its higher BET surface area. In Fig. 5, the overpotential is plotted against the H_2O_2 concentration at various current densities. The overpotential decreases with increasing concentration. The drop in overpotential is not significant beyond 15 wt.% H_2O_2. At lower concentrations of H_2O_2, sufficient oxygen for complete stabilization is not available and results in partial surface oxidation. Catalyst burning occurs when this sample is dried and brought in contact with air. This is evident by lower surface area at lower H_2O_2 concentration. Once the H_2O_2 concentration is sufficient to provide

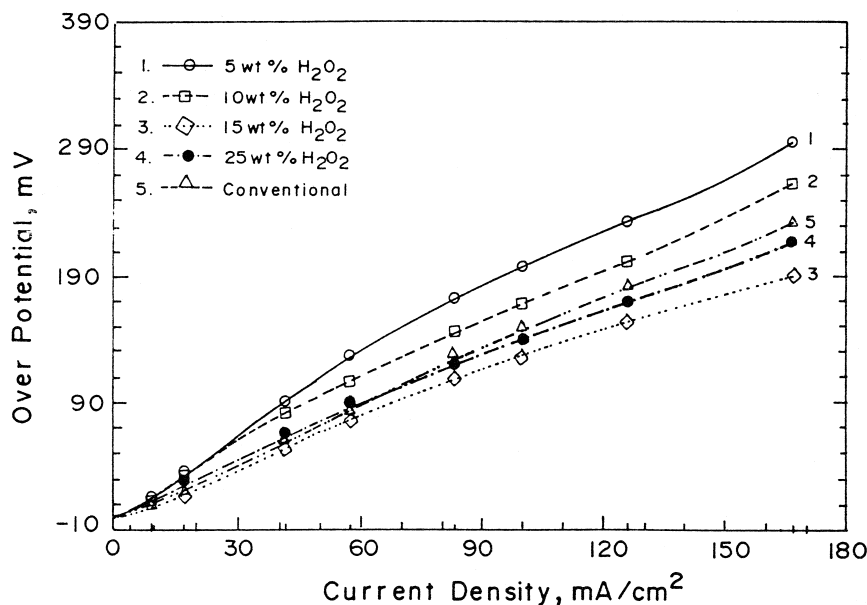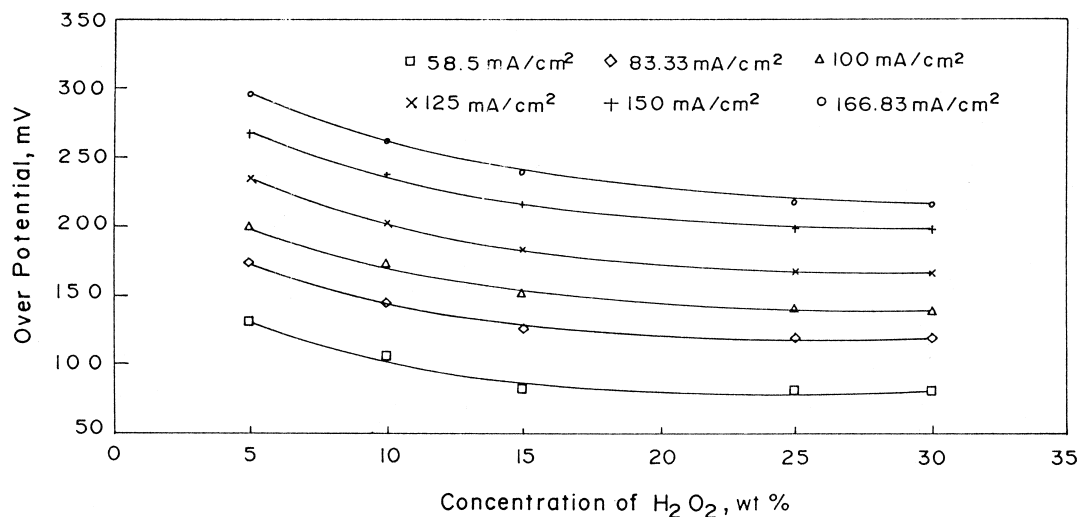Fig. 4. Comparison of polarization of anodes prepared by H_2O_2 treated and conventionally stabilized catalysts at 25°C.

Fig. 5. Effect of H_2O_2 concentration on overpotential at 25°C.

adequate oxidizing capacity, the catalyst stabilizes completely and has maximum surface area. Hence, 15 wt.% H_2O_2 provides the better stabilization.

3.2. Direct gas oxidation

The direct oxidation of the pyrophoric catalyst is caused by the dissolved gaseous oxygen in water. The morphology of the stabilized catalyst is similar to that of a conventioned type, cf., Fig. 2b,c. The XRD patterns, see Fig. 3b,c, feature both NiO and Ni peaks and also a relatively small quantity of Ni. The BET surface area in this case is smaller, as shown in Table 2. Polarization curves of anodes prepared with the direct oxidized catalyst are shown

in Fig. 6. The overpotentials of the anodes with gas-stabilized catalyst are higher than those with conventionally stabilized catalyst. The poor performance is in accordance with the low BET surface area. Justi et al. [6] found that the optimum temperature for obtaining stable NiO layer is $\sim 60°C$. When stabilizing with O_2/air, the temperature reaches only 40°C. Therefore, the formation of stable NiO is unlikely. In gas oxidation, the gas has to be dissolved first in water and then diffuse to the nickel surface. As the solubility of O_2 in water is low, the rate and the amount of oxygen reaching the surface will both be low. This will result in slow and partial oxidation and give lower temperatures and partial stabilization. When dried, the pyrophoric nature may not be apparently visible but the microporous
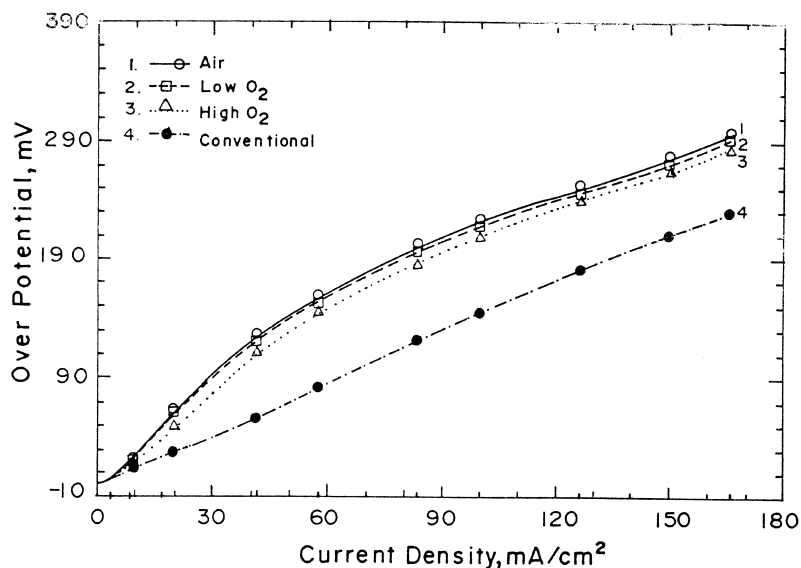

Fig. 6. Comparison of polarization of anodes prepared by direct gas oxidized and conventionally stabilized catalysts at 25°C.

structure will be adversely affected due to heat generation and partial sintering.

4. Conclusions

Both proposed methods, namely H_2O_2 treatment and direct gas oxidation, are promising. The H_2O_2 treatment is more attractive due to superior performance and several advantages, notably, faster operation, simpler apparatus, and less possibility of accidental sintering. Treatment with 15 wt.% H_2O_2 gives higher surface area (65 m^2 g^{-1}) and lower overpotential. Although direct oxidation method is advantageous, the performance of the catalyst is relatively poor.

Acknowledgements

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