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# Effect of carbon dioxide on the performance of Ni/PTFE and Ag/PTFE electrodes in an alkaline fuel cell

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The effect of carbon dioxide as impurity in hydrogen and oxygen on the performance of electrodes was studied in a half cell arranged at different concentrations and temperatures. The presence of $CO_2$ in hydrogen was investigated on Ni/PTFE at different concentrations (0–4%) and three temperatures (28, 52, 72° C). Carbon dioxide was found to increase the overpotential due to ionic concentration polarization, but this effect was completely reversible. Impurity levels of $CO_2$ up to 1% in oxygen had no effects on the Ag/PTFE electrode in the short term. Long term performance tests were carried out with $CO_2$ impurity in oxygen at two different concentrations (0.03%, 1%) and at two different temperatures (25° C, 72° C). All experiments showed no degrading effect on the Ag/PTFE electrode with the exception of one at 25° C with 1% $CO_2$. At this run a steady drop of current density was observed due to the formation of $K_2CO_3$ in the micropores which was verified by XRD. In all runs the concentration of KOH electrolyte was kept constant at 25%. The effect of adding $K_2CO_3$ to KOH was also investigated and no loss in electrode currents was observed for 48 h on both Ni/PTFE and Ag/PTFE electrodes.

## 1. Introduction

Fuel cells are an important means of converting chemical energy into electrical energy without the limitation of the Carnot cycle. $H_2/O_2$ alkaline fuel cells are one of the types currently used. One of the possible impurities present in the feed gases is carbon dioxide. Carbon dioxide is found in air if this is used as oxidant and in hydrogen when produced from reforming of natural gas. In alkaline cells, $CO_2$ has an adverse effect on the electrolyte because it reacts with the hydroxyl ions to form carbonate species which may precipitate and block the micropores of the Raney catalyst or may stay as liquid but reduce the ionic conductivity of the electrolyte. Most tests in the literature have been performed with pure gases, so that fewer data are available about the nature and extent of the damaging effect of carbon dioxide. Carbon dioxide reacts with the KOH electrolyte to form carbonate:

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O \qquad (1)$$

Carbonate formation can affect both performance and life by causing solids to deposit in the electrode structure. This deposition, on surfaces or in pores, can reduce performance by choking or can cause mechanical damage such as cracking or flaking. Ko and Juang [1] exposed freshly prepared 37% potassium hydroxide to the atmosphere containing approximately 0.033% $CO_2$ for 10 months. In the end the solution was found to contain little KOH. Katz and Kunz [2] studied the effect of carbonates on the performance of trapped alkaline electrolyte fuel cells using a PTFE-bonded Pt/Pd cathode and a Pd/Pt anode. They found that the major portion of the voltage degradation was recoverable by refilling with fresh electrolyte. They gave reasons for this degradation as follows: that first the consumption of $OH^-$ increased the pH gradient across the cell and, secondly, that the carbonate formation caused a change in the electrolyte vapour pressure and caused loss of water vapour from trapped electrolyte, thus unfavourably redefining the liquid–vapour interface location within the electrode. Kordesch's [3] findings have shown that electrodes operating with carbon dioxide free-air has life expectancy several times greater than that when $CO_2$ is present in the air. The shorter life is attributed to the precipitation of solid carbonates which block the pores of the electrode.

## 2. Experimental details

### 2.1. *Half cell experimental setup*

A schematic diagram of the half cell assembly used in this study is shown in Fig. 1. The *IR* drop was measured by the current interruption technique which was developed and described by the authors in a previous publication [4]. The half cell used was fabricated from Plexiglass and consisted of a gas chamber and a rectangular piece which housed the gas diffusion electrode, a ring shaped sheet of PTFE sealing and the nickel wire current collectors. The rectangular piece was screwed to the gas chamber

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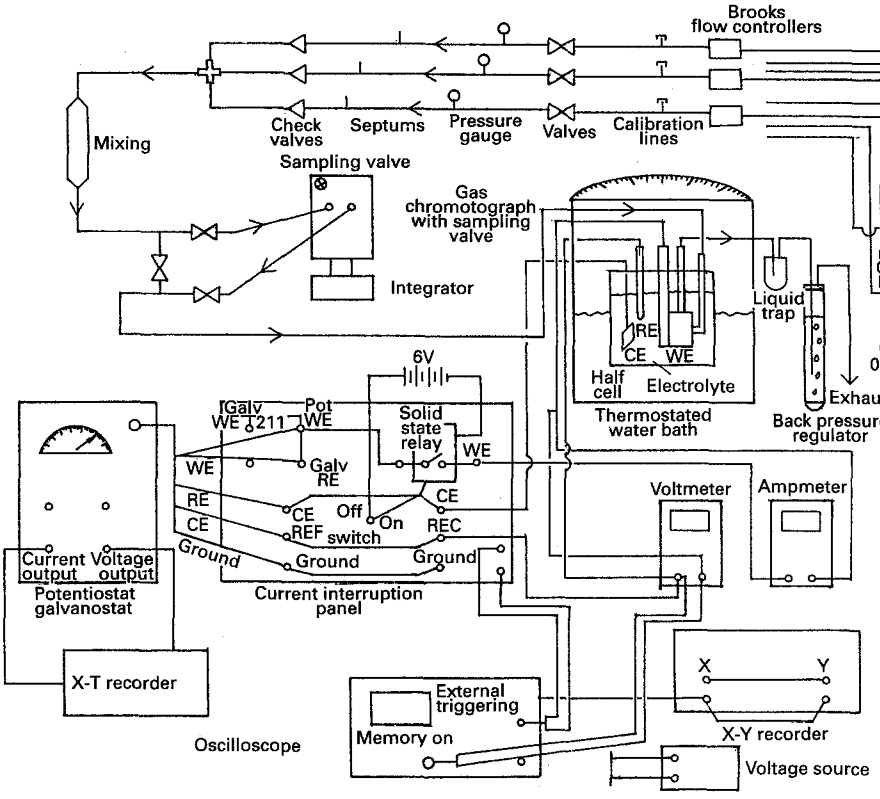

Fig. 1. Experimental setup for impurity studies.

with stainless steel screws. The half cell was mounted into a PTFE container which was filled with the electrolyte such that the electrode was completely submerged. The counter electrode was a 2.5 cm × 2.5 cm nickel plate which was welded onto a nickel rod. The nickel rod was mounted onto the Plexiglass lid of the PTFE container. The reference electrode was a commercially available Hg/HgO electrode filled with 25% KOH solution. The inlet gas was introduced through the side of the gas chamber while the outlet gas left through the top of the chamber to a water head back pressure regulator. Gas flow rates and compositions ($CO_2$ in hydrogen and $CO_2$ in oxygen) were adjusted by using Brooks mass flow meters.

### 2.2. *Electrodes*

The electrodes used were gas diffusion electrodes prepared by mixing Raney metal with PTFE. Raney nickel was used for the hydrogen electrode while Raney silver was used for the oxygen electrode.

A melt containing a mass fraction of 50% nickel and 50% aluminium was prepared in a furnace in an alumina crucible. The alloy obtained was crushed and powdered in a mill to the desired particle size. The aluminium was then leached out by a KOH solution. The Raney metal thus obtained was washed and cleaned with water several times for a few days to remove the KOH solution. Then the Raney metal was kept under vacuum at 100° C and air was added to it step by step. A weighed amount of a PTFE dispersion was added to the Raney catalyst. A reactive mixing technique was applied where the catalyst and PTFE were milled together in order to mix them and to decrease the particle size and optimize particle size distribution. The milling time varied from a few seconds to an hour. During this period PTFE powder was converted into thin PTFE wires. Finally, the paste obtained was rolled on a metal net with a calender. The rotation speed of the calendar varied from 1 to 30 r.p.m.

The nitrogen adsorption technique was used to find the total surface area and the macroporosity (with mesh support). For the Ni/PTFE electrode, the surface area was found to be $20\,m^2\,g^{-1}$, and the porosity was $0.049\,cm^3\,g^{-1}$. While for the Ag/PTFE, the surface area was $37\,m^2\,g^{-1}$, and the porosity was $0.07\,cm^3\,g^{-1}$.

### 2.3. *Activation procedures*

Prior to polarization measurements with the Ni/PTFE electrode, it was necessary to activate the electrode with a cathodic current by hydrogen reduction on the electrode surface. The external circuit was connected galvanostatically and a cathodic current of 25 mA was passed through the half cell for about 48 h at room temperature. If carried out at 50° C, 24 h of activation was found to be adequate. Following an initial short transition period, the electrode potential generally stayed around (−940 mV) with respect to the Hg/HgO reference electrode. Upon stopping the cathodic current (electrolysis mode) at the end of the activation period, the open circuit electrode potential stayed around (−925 mV) at room temperature. The Ag/PTFE electrode, however, did not need activation.

### 2.4. *Polarization measurement*

The potentiostatic experiments were carried out to examine the effect of $CO_2$ impurity in hydrogen on the Ni/PTFE electrode, and $CO_2$ impurity in oxygen on the Ag/PTFE electrode. The $CO_2$ compositions in hydrogen were varied from 0 to 4% in the temperature range 28–72° C. For the oxygen electrode the compositions used were 0.03 and 1% at temperatures of 25 and 72° C. The concentration of the electrolyte was kept constant at 25%. The effect of adding $K_2CO_3$ to KOH was studied at two levels of concentrations, (25% KOH + 5% $K_2CO_3$) and (25% KOH + 10% $K_2CO_3$).

## 3. Results and discussion

### 3.1. *Effect of $CO_2$ in hydrogen on Ni/PTFE electrode*

The presence of $CO_2$ in the hydrogen gas streams caused a considerable loss in electrode activity even at a few percentages. However, this effect was completely reversible under all experimental conditions. A set of potentiostatic steady state polarization data with $CO_2$ present in hydrogen gas was taken at three temperatures (28, 52, and 72° C) and different $CO_2$ concentrations ranging from 0 to 4%.

Figures 2–4 show the steady state polarization curves at 28, 52 and 72° C, respectively, at different $CO_2$ concentrations. The results were plotted as overpotentials against current densities. Since the effect of $CO_2$ was found to be completely reversible upon removing the $CO_2$ from the hydrogen stream, all the overpotentials given in these graphs were calculated with respect to the open-circuit potential (o.c.p.) of the Ni/PTFE electrode operating with pure hydrogen gas.

When the concentration of $CO_2$ in the feed gas increased, the overpotential increased at a temperature of 28° C as shown in Fig. 2. But as the temperature went up to 52°C and 72° C, the differences in overpotential at different levels of $CO_2$ concentrations became smaller as indicated in Figs 3 and 4. Considering the quick and complete reversibility of the cell current, it may be said that loss in performance was due to the reduction of $OH^-$ ions in the micropores of the electrode upon reacting with $CO_2$ gas producing $K_2CO_3$. At a given potential and temperature, the process of $OH^-$ ion movement between the bulk electrolyte and the electrode micropores, the solubility rate of $CO_2$ in the electrolyte in micropores, and the reaction of dissolved $CO_2$ with KOH established an equilibrium. The overall effect was a reduced concentration of $OH^-$ ions which, in turn, pushed the Ni/PTFE electrode potential (including its o.c.p.) in the positive direction with respect to the Hg/HgO reference electrode. This was a result of the Nernst ion polarization due to the change in activity of the hydroxyl ions. At a higher temperature this overall effect was less pronounced since the transport of $OH^-$ ions from the electrolyte to micropores for replacing $CO_3^{2-}$ ions was faster and the solubility of $CO_2$ was less at higher temperatures. Although, higher reaction rates between $CO_2$ and $OH^-$ ions were expected at higher temperatures which might affect the electrode adversely, the governing effect should be the mobility of $OH^-$ ions due to the observation of less pronounced effects.

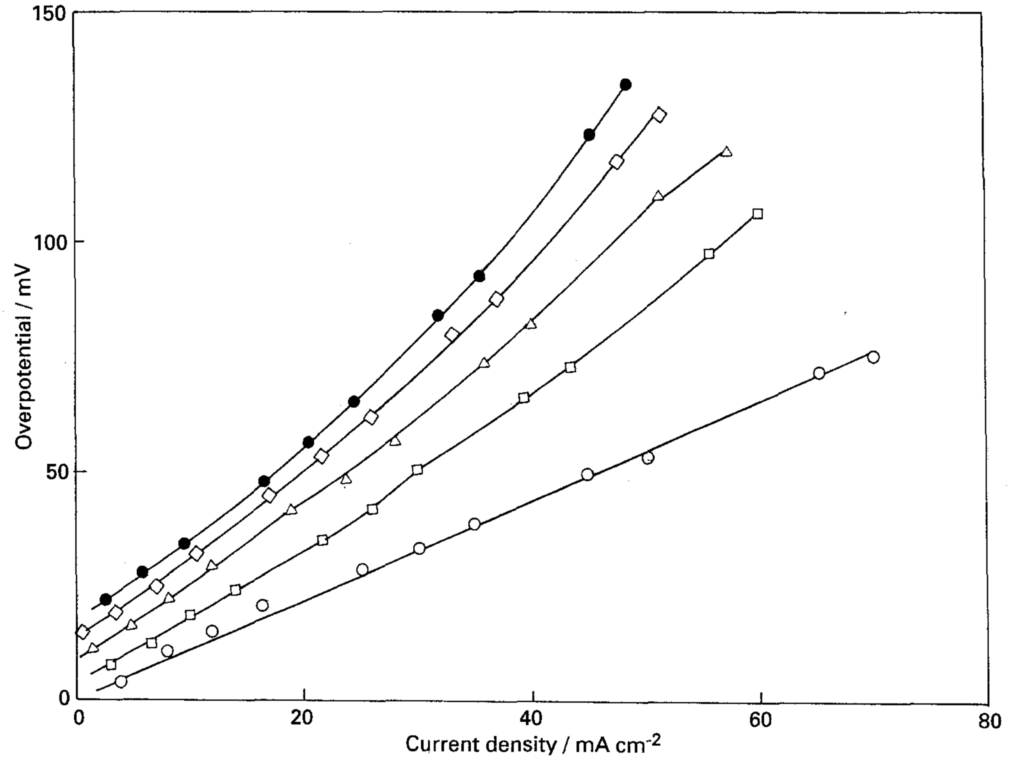

Fig. 2. Steady-state polarization curves with $CO_2$ in hydrogen streams at 28° C in 25% KOH electrolyte. (○) 0% $CO_2$; (□) 1% $CO_2$; (△) 2.7% $CO_2$; (◇) 3.4% $CO_2$; and (●) 4.0% $CO_2$.

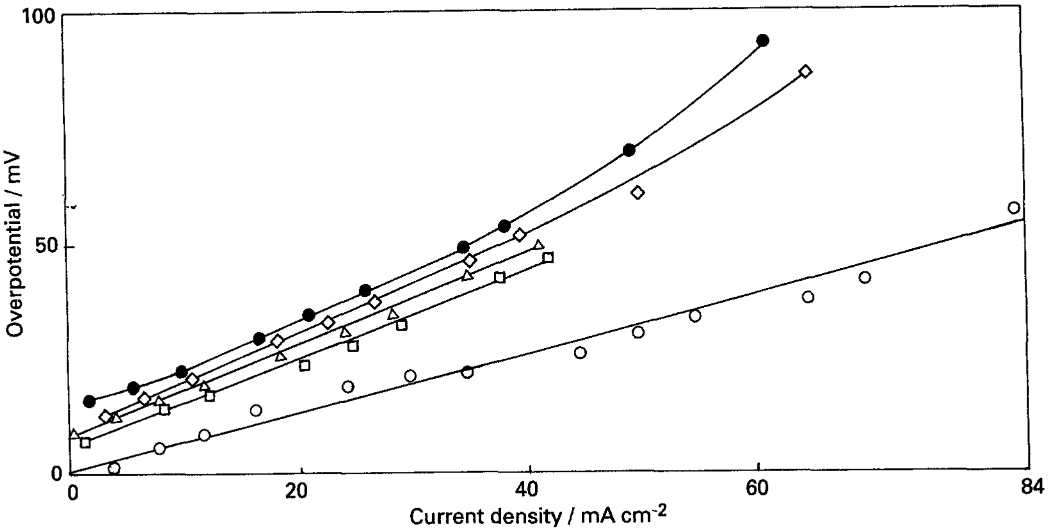

Fig. 3. Steady-state polarization curves with $CO_2$ in hydrogen streams at 52° C in 25% KOH electrolyte. (○) 0% $CO_2$; (□) 2.7% $CO_2$; (△) 2.9% $CO_2$; (◇) 3.4% $CO_2$; and (●) 4.0% $CO_2$.

### 3.2. *Effect of $CO_2$ in oxygen on Ag/PTFE electrode*

Preliminary runs have shown that $CO_2$ impurity up to a concentration of 1% in oxygen had no immediate adverse effects on the Ag/PTFE electrode. Based on this, long term measurement of performance at fixed electrode overpotential was carried out by recording the electrode current with respect to time subjected to certain experimental conditions with $CO_2$ impurity in the gas stream.

Experiments were carried out with 0.03% $CO_2$ and 1% $CO_2$ in oxygen gas stream at 25° C at an overpotential of 220 mV, and also with 0.03% $CO_2$ and 1% $CO_2$ in the oxygen gas stream at 72° C at an overpotential of 160 mV. Results are shown in Fig. 5. The overpotentials were kept at relatively severe conditions. Both runs, which were carried out at 72° C with 0.03% and 1% $CO_2$, showed no degrading effect on the Ag/PTFE electrode over a period of 200 h. This may be explained by the higher solubility of $K_2CO_3$ in the electrolyte preventing possible precipitation and plugging of pores. Similarly, at 25° C, 0.03% $CO_2$ showed no adverse effect on the electrode. However, with 1% $CO_2$ at 25° C, a steady drop in the electrode current densities was observed after 50 h of operation. The drop in current densities amounted to approximately 15% during this period. This drop was attributed to the formation of $K_2CO_3$ in the pores of the electrode blocking the accessibility to active sites for current generation. This was verified by XRD measurements which showed the presence of 7% $K_2CO_3 \cdot 1.5\,H_2O$ on this electrode.

### 3.3. *Comparison of the performance of Ni/PTFE and Ag/PTFE electrode*

It was observed that the presence of $CO_2$ in the feed gases affect the Ni/PTFE performance in terms of higher overpotential, but at the same time has no effect on Ag/PTFE electrode. The difference is due to the following two reasons. First, the macroporosity of Ag/PTFE electrode is 0.070 cm$^3$ g$^{-1}$, which is larger than that for Ni/PTFE electrode (0.049 cm$^3$ g$^{-1}$). This makes it easier for the silver

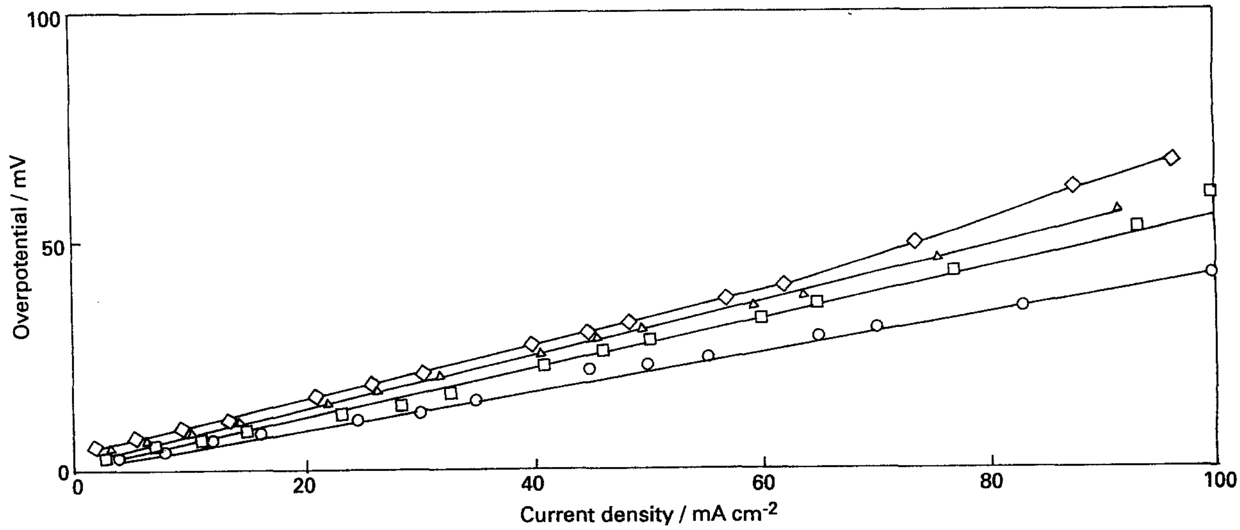

Fig. 4. Steady-state polarization curves with $CO_2$ in hydrogen streams at 72° C in 25% KOH electrolyte. (○) 0% $CO_2$; (□) 2.3% $CO_2$; (△) 2.7% $CO_2$; and (◇) 3.4% $CO_2$.

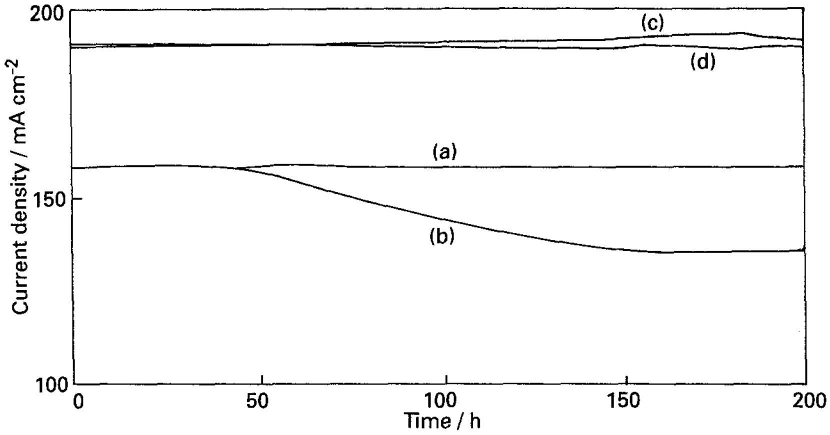

Fig. 5. Effect of $CO_2$ in oxygen stream on Ag/PTFE electrode. (a) 0.03% $CO_2$, $\eta = 220$ mV, $T = 25°$ C; (b) 1.0% $CO_2$, $\eta = 220$ mV, $T = 25°$ C; (c) 0.03% $CO_2$, $\eta = 160$ mV, $T = 72°$ C; (d) 1.0% $CO_2$, $\eta = 160$ mV, $T = 72°$ C.

electrode to compensate the decrease of $OH^-$ in the micropore from the electrolyte in the bulk. Secondly, $OH^-$ is consumed on the anode (Ni/PTFE electrode) by the reaction

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad (2)$$

while $OH^-$ is produced at the cathode (Ag/PTFE electrode) by the following reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (3)$$

This production of $OH^-$ in the micropore of the cathode also compensates the loss of this ion through reaction with dissolved $CO_2$.

### 3.4. *Effect of $K_2CO_3$ in the electrolyte*

The effect of intentionally added $K_2CO_3$ in the KOH electrolyte was investigated at 52° C. The compositions used were (25% KOH + 5% $K_2CO_3$), and (25% KOH + 10% $K_2CO_3$). With each composition, the electrode was kept at an overpotential of 150 mV at 52° C. No loss in electrode currents for both Ni/PTFE and Ag/PTFE were observed for a period of 48 h. This proved that the $K_2CO_3$ added to the electrolyte from outside did not penetrate into and block the pores of Raney catalyst grains. Following this, steady state galvanostatic polarizations were measured with (25% KOH), (25% KOH + 5% $K_2CO_3$) and (25% KOH + 10% $K_2CO_3$). These measurements are shown for the Ni/PTFE electrode in Fig. 6, and for the Ag/PTFE electrode in Fig. 7. It was found that there was no effect of having $K_2CO_3$ in the solution since the concentration of $OH^-$ ions was always kept at 25%

## 4. Conclusion

The main conclusions of this study are as follows:

(i) Presence of carbon dioxide in hydrogen increases the overpotential of the Ni/PTFE electrode. This effect was completely reversible upon reintroducing

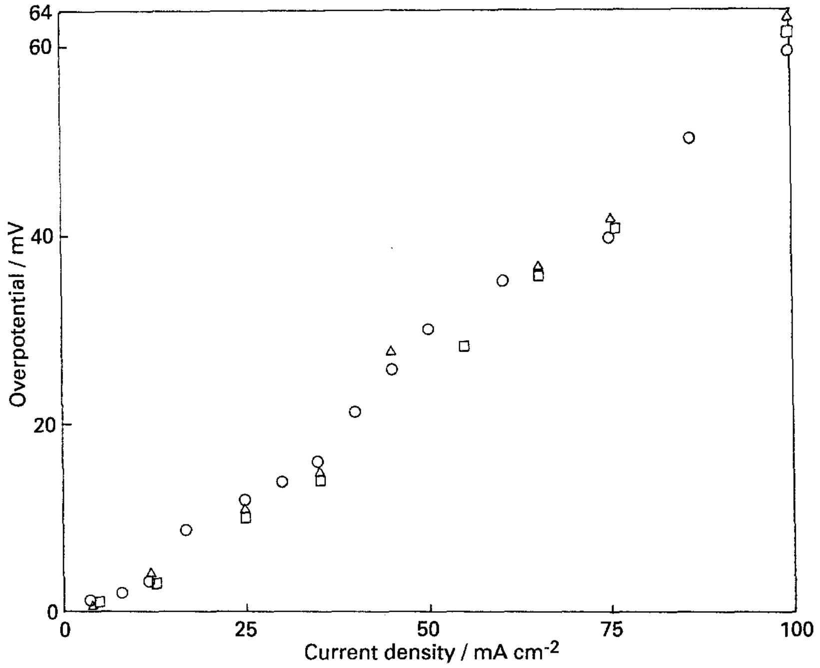

Fig. 6. Effect of $K_2CO_3$ in the electrolyte on the polarization behavior of Ni/PTFE electrode using pure hydrogen at 52° C. (○) 25% KOH; (△) 25% KOH + 5% $K_2CO_3$; and (□) 25% KOH + 10% $K_2CO_3$.

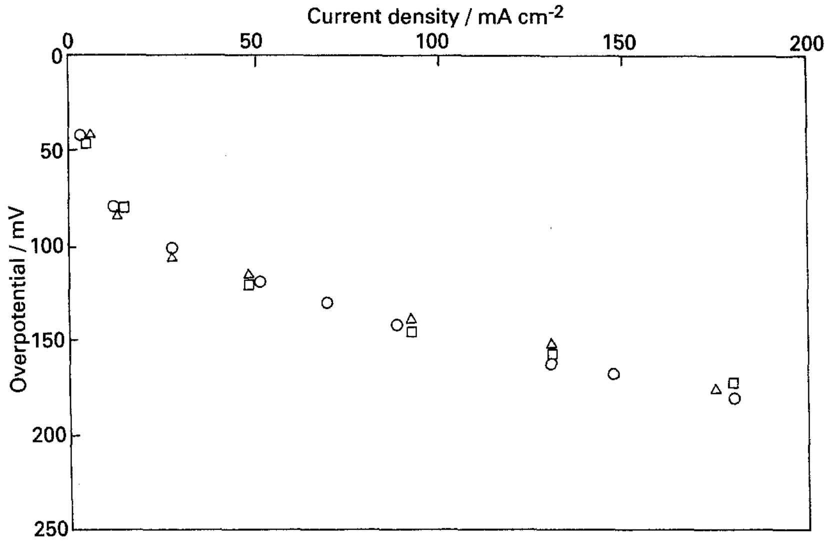

Fig. 7. Effect of $K_2CO_3$ in the electrolyte on the performance of Ag/PTFE electrode using pure oxygen at 52° C. (○) 25% KOH; (△) 25% KOH + 5% $K_2CO_3$; and (□) 25% KOH + 10% $K_2CO_3$.

pure hydrogen and is related to ionic concentration polarization.

(ii) Carbon dioxide in the oxygen stream at a level of 0.03% did not cause deactivation on the Ag/PTFE electrode at all temperatures for a period of 200 h.

(iii) at 25° C, 1% carbon dioxide in oxygen caused a drop in electrode current density with time. Analysis by XRD and SEM revealed the presence of 7% carbonate on this electrode.

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