

FORMATE ION - OXYGEN FUEL CELLS

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Introduction

Formate ion is one of the more readily oxidizable carbonaceous fuels in basic electrolyte. In the range 80-100° C, formate ion-oxygen fuel cells, using a platinum-palladium catalyst, have a performance approaching that of hydrogen or hydrazine fuel cells. Formate ion-oxygen fuel cells with a platinum-palladium catalyst have been shown to have about twice the output of methanol fuel cells at ambient temperature (1).

Formate salts are easily handled as solids or in solution, are stable, have low toxicity and are potentially low in cost. Formic acid may also be used as the fuel. It also is stable, and potentially low priced. However, its corrosive properties demand that it be handled with some care. Formate solutions in base are stable at 100° C. At this temperature, the fuel is not volatile in contrast to methanol.

The investigations of the formate fuel cells were extended to study the effects of temperature on the cell output. Further studies involved variation of catalyst and electrolyte composition and fuel concentration.

Experimental

A sandwich type fuel cell was used in these studies. Grooved and manifolded stainless steel end plates held the electrodes and allowed uniform flow of electrolyte-fuel and oxygen over the electrode surfaces. An asbestos sheet (0.060 inch thick) served as the separator-spacer between the electrodes (2).

The electrolyte-fuel mixture, heated in an external chamber, was pumped through the cell anode compartment and then back to the external heater chamber. Oxygen was supplied to the cell at or slightly above atmospheric pressure. Appropriate cell temperature was maintained within $\pm 1^\circ$ C with an auxiliary heating pad. The external heating and pumping system was constructed of Teflon, glass and stainless steel materials. The reference saturated calomel electrode (SCE) was connected to the electrolyte system by means of an external Luggin capillary tube.

Porous nickel plaques (0.028 inch thick) were used as catalyst support material. Electrode plating solutions were prepared by mixing appropriate amounts (in accordance with the required catalyst ratio) of the noble metal chloride solutions containing 2 mg. of

metal per ml. and then adjusting the pH level to 1 with hydrochloric acid. A vacuum filtration technique was used to draw the plating solution through the porous nickel plaque at a slow flow rate. The ratio of the Pd/Pt chemideposited on the plaques was the same as that in the mixed plating solutions (3). Plated plaques were then washed with distilled water and stored in a dry atmosphere. A waterproofing coating of Teflon was applied over the catalyzed surface of those platinum-palladium electrodes which were to be used as cathodes to prevent electrode "flooding." All electrodes were plated with a total of 60 mg/in² of noble metal catalysts. The geometric area of the electrodes was 6.25 in²; and the current data presented are expressed in terms of amperes per square foot (ASF).

Fuel cell electrodes were evaluated with a sine wave (4) and a square wave commutator. The square wave current was generated by a mercury switch function generator. Operating power was supplied by a 12 volt storage battery; a second 12 volt battery supplied the power to operate the auxiliaries of the square wave generator. Voltage readings were taken with a Tektronix 564 Storage Oscilloscope and a R.C.A. Senior vacuum tube voltmeter when using the square wave or sine wave commutators, respectively.

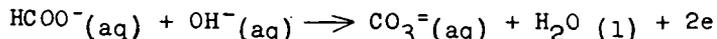
For the half cell studies a current equivalent to 60 ASF was supplied to the cell for a pre-polarization period of five minutes. Experimental data at 60 ASF were then taken, i.e. anodic and cathodic half cell voltages, total cell voltage (ohmic free), and the ohmic voltage (IR drop) of the cell.

The cells were normally kept at the appropriate current density for a three minute polarization period before the potentials were measured. For the lower temperature (30° C) tests, the cell was operated at alternately high and low current densities to maintain a nearly constant temperature in the cell, however, it was not necessary to follow this procedure at 100° C.

Results and Discussion

Anode and Cathode Studies

Formate solutions in basic electrolyte are stable at elevated temperatures, allowing operation of cells near the boiling point of the electrolyte at atmospheric pressure. Studies at ambient and elevated temperatures were conducted to determine the polarization curves for anodes and cathodes using different noble metal catalyst mixtures with formate and oxygen. The standard potential for the anode reaction is 1.02 volts.



Previous studies have shown that formate ion is readily oxidized on an anode catalyzed with a platinum-palladium mixture or with palladium (1, 3). Platinum catalyzed anodes are severely polarized under applied load. Increasing the palladium content of the catalyst improves the activity of the anodes at 30° C (Figure 1). All electrodes had a total noble metal catalyst-loading of 60 mg/in². The palladium anode was the least polarized on initial tests. Upon

extended testing for over a thousand hours at ambient temperature, a ratio of five parts palladium to one part platinum by weight proved to be the superior catalyst (1).

Formate ion fuel cells were shown in these studies to have about twice the performance of methanol fuel cells under the same conditions at ambient temperature. Performance of the methanol anode is not greatly changed (Figure 2) when the cell temperature is raised to 60° C (limited by the vapor pressure of methanol). However, anode performance of the formate cell is markedly improved by the temperature increase.

Anode polarization curves obtained for cells operating at 90° C with 4M potassium formate and 4M potassium hydroxide electrolyte are shown in Figure 3. The porous nickel electrodes were catalyzed with a total of 60 mg/in² of catalyst. The performance of all the anodes improves with temperature (compare with Figure 1). Obviously, the data show that on initial tests, the palladium anode gave the highest potential for currents between 1 and 200 ASF at 90° C. The same trend, noted at the lower temperature, of decreasing anode activity with increasing platinum content was observed, except that the platinum anode was comparable in performance to the palladium and 50 Pd/10 Pt/in² anodes.

The effect at 30° and 90° of increasing platinum content of anodes is depicted schematically in Figure 4. The markedly improved activity of a platinum anode at 90° C was unexpected and is inexplicable at this time.

Previous cathode studies with hydrogen-oxygen cells at ambient temperature have shown that platinum-palladium mixtures are more active than either platinum or palladium (4). In the 4M potassium formate - 4M potassium hydroxide system, the oxygen cathode performance improves with increasing platinum content. The best cathode at 30° has a content of 40 mg Pd/20 mg Pt/in² catalyst. The platinum cathode was highly polarized at 30° C.

The oxygen cathode polarization curves at 90° C for 60 mg/in² of platinum and/or palladium are shown in Figure 5. At the higher temperatures, the activity of the cathode catalyst increases with increasing platinum content. However, again the platinum cathode is least active at the higher currents. The best cathode catalyst had equal amounts of platinum and palladium. The trend of cathodic activity of platinum-palladium mixtures is opposite that of anodic activity of these same mixtures.

The effect of formate ion concentration on the potential of the oxygen electrode at 90° C is shown in Figure 6. A waterproofed porous nickel electrode with equal amounts of platinum and palladium was used as the cathode. Potassium formate concentration in the 4M potassium hydroxide electrolyte ranged between 0.5M to 4M.

It may be seen from Figure 6 that the formate fuel exerts a considerable polarizing effect on the behavior of the cathode; and that the effect is greater with increasing concentration of potassium formate. Furthermore, the polarization of the anode decreases slightly with increasing concentration of fuel. Similar results have been observed for the methanol-oxygen fuel cell (5). Explanations for an increased polarization of the cathode as the concentration of the dissolved fuels are raised have not been considered in

detail. It is for this reason that we should like to present possible hypotheses for this phenomenon. The decrease in anode polarization as the fuel concentration is raised (Figure 6) may be due to either a decrease in diffusion limitation or increase in concentration of fuel in the pre-electrode layer. Since the i-V curves do not exhibit a diffusion limiting current for any of the concentrations studied, it would appear, therefore, that the effect of fuel concentration may be explained approximately by the concentration term in the rate equation.

Although the net reaction at the oxygen electrode is cathodic, this electrode may still function as an anode for formate ion, provided an adequate supply of fuel is present at the electrode surface. If this occurs, the net cathodic current is less, and increased polarization will be observed.

It has been assumed that the anodic and cathodic reactions are totally independent of one another over the voltage range studied. Since formate ion is probably adsorbed on the cathode, it would be reasonable to assume that the surface covered with formate is not available for catalysis of the cathodic reaction. However, the predominating factor controlling the effect of fuel on the cathode polarization in the system discussed in this paper appears to be the formate oxidation current, rather than adsorption of fuel. This explanation is supported by the fact that increased formate concentration results in greater cathode polarization. Furthermore, the performance of the cathode as a function of the catalyst is the opposite of that shown for the anode in Figure 6.

Operating Cells

A cell was constructed using a platinum anode and a 30 mg Pd/30 mg Pt/in² cathode. The selection of these electrodes was based on the catalyst spectrum studies. The performance of the cell using a 4M potassium formate - 4M potassium hydroxide electrolyte is shown in Figure 7. An ohmic free cell voltage of 0.82 volts at 200 amps per square foot was obtained at 90° C.

Based on this data, an operating formate ion-oxygen fuel cell system in strong alkali electrolyte could presently be expected to produce 120-170 ASF at 0.8 volts per cell at 90° C. The system construction would be similar to that of a hydrazine fuel cell (2). This performance approaches that of hydrogen-oxygen and hydrazine-oxygen fuel cells at the same temperatures. Further studies of the effects of temperature, formate ion concentration, and cell design to minimize contact of formate with the cathode should lead to marked improvement in the performance of the formate ion-oxygen fuel cell.

The oxidation of formate ion in this system produces carbonate ion and consumes hydroxyl ion. Continued operation of the system would convert the cell electrolyte to carbonate. If the cell is to be operated at high pH, periodic replacement of the electrolyte would be required. However, if a small reduction in performance is not a detriment, the cell can be operated using a carbonate electrolyte. Figure 8 shows the current-voltage curve of the cell with 4M potassium formate - 4M potassium carbonate electrolyte at 90° C. The

ohmic free cell voltages at 200 and 100 ASF are 0.5 and 0.65 volts, respectively.

The polarization of the formate anode is only slightly greater in the carbonate than in the hydroxide electrolytes. However, the performance of the oxygen cathode is markedly poorer in the carbonate electrolyte. The difference in performance of the two cells shown in Figure 8 is due primarily to the cathode polarization.

In spite of the greater polarization of the cathode in carbonate electrolyte such a system may reasonably be expected to produce 100 to 130 ASF at 0.5 volts at 90° C.

Conclusions

The formate ion-oxygen fuel cell will produce 0.82 volts at 200 ASF (ohmic free) at 90° C with hydroxide electrolyte. Operation of the formate ion cell with a carbonate electrolyte reduced the performance of the cathode, lowering the output to 0.5 volts at 200 ASF (ohmic free) at 90° C.

Palladium and platinum are the best anode catalysts at this temperature. A mixed catalyst containing equal amounts of platinum and palladium is the poorest anode catalyst. At 30° C, however, palladium was the best anode catalyst and activity decreased with increase in platinum content. The mixed catalyst, referred to above, however, is the best for the oxygen electrode at both 30° and 90° C in the presence of formate.

The output of formate ion-oxygen fuel cells approaches that of hydrogen and hydrazine-oxygen fuel cells. This allows the formate ion-oxygen cells to be applied in special applications.

Acknowledgements

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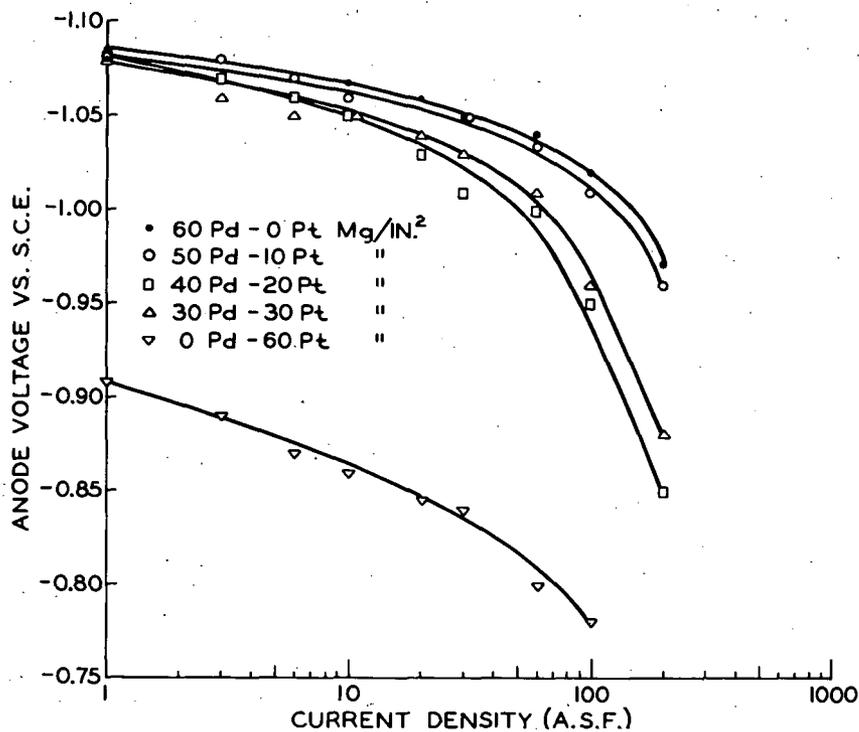


Fig. 1.-EFFECT OF CATALYST ON ANODE POTENTIALS IN 4M POTASSIUM FORMATE AND 4M POTASSIUM HYDROXIDE AT 30°C

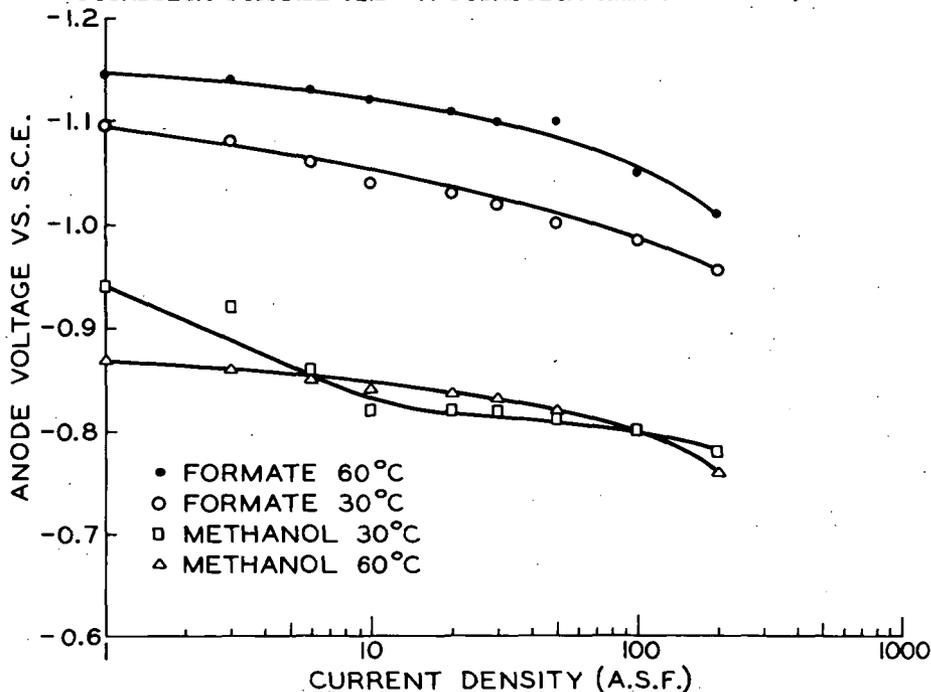


Fig. 2.-ANODE CURRENT-VOLTAGE CURVES FOR THE SYSTEMS 4M METHANOL AND 4M POTASSIUM FORMATE IN 4M POTASSIUM HYDROXIDE AT 30° AND 60°C

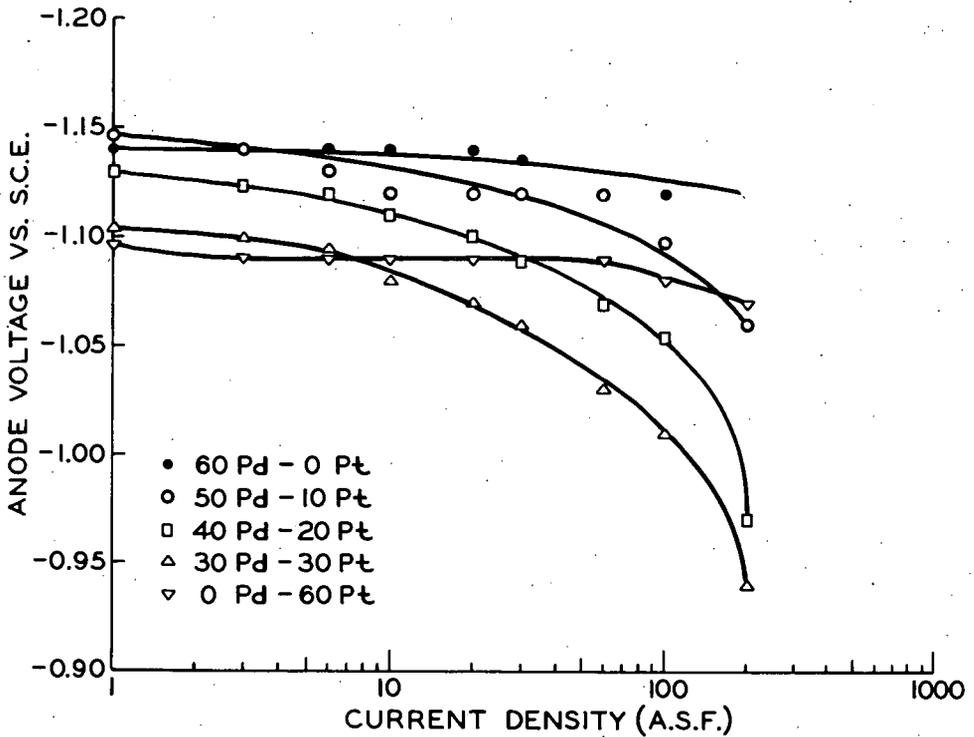


Fig. 3.-EFFECT OF CATALYST ON ANODE POTENTIAL IN 4M POTASSIUM FORMATE AND 4M POTASSIUM HYDROXIDE AT 90°C

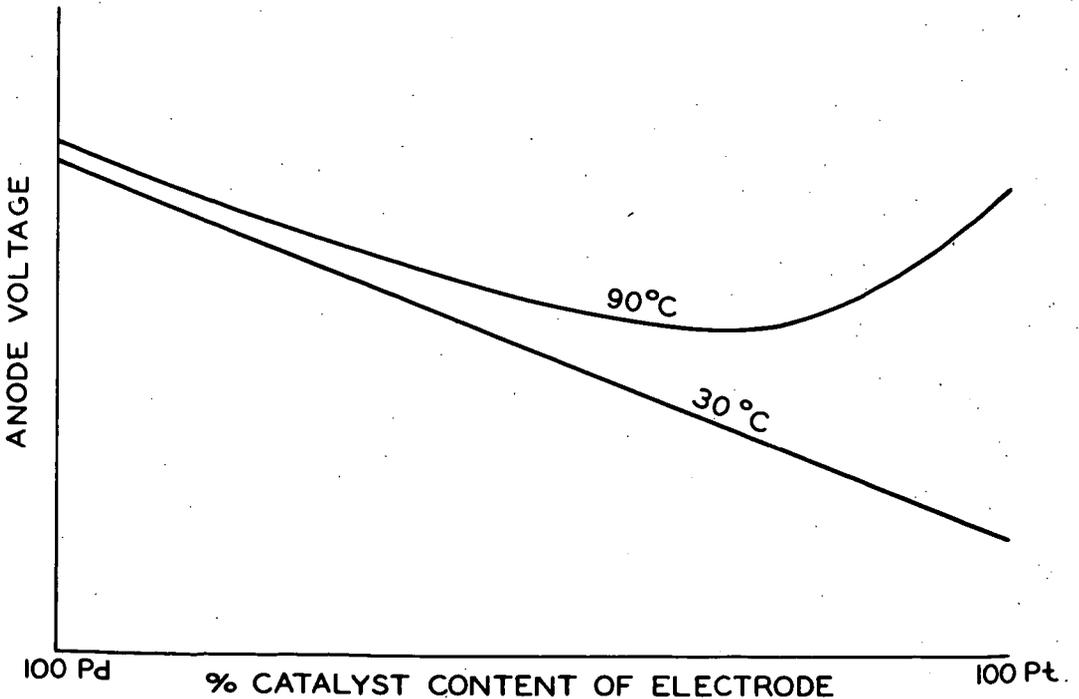


Fig. 4.-SCHEMATIC: ANODE VOLTAGE VS. CATALYST COMPOSITION

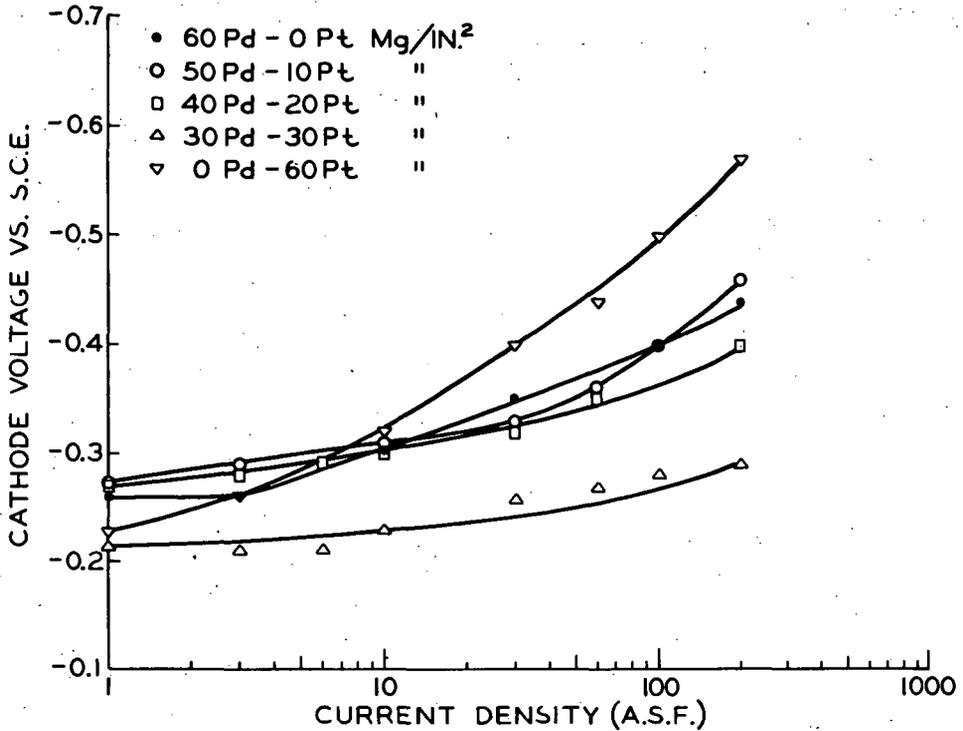


Fig. 5.-EFFECT OF CATALYST ON CATHODE POTENTIALS IN 4M POTASSIUM FORMATE AND 4M POTASSIUM HYDROXIDE AT 90°C

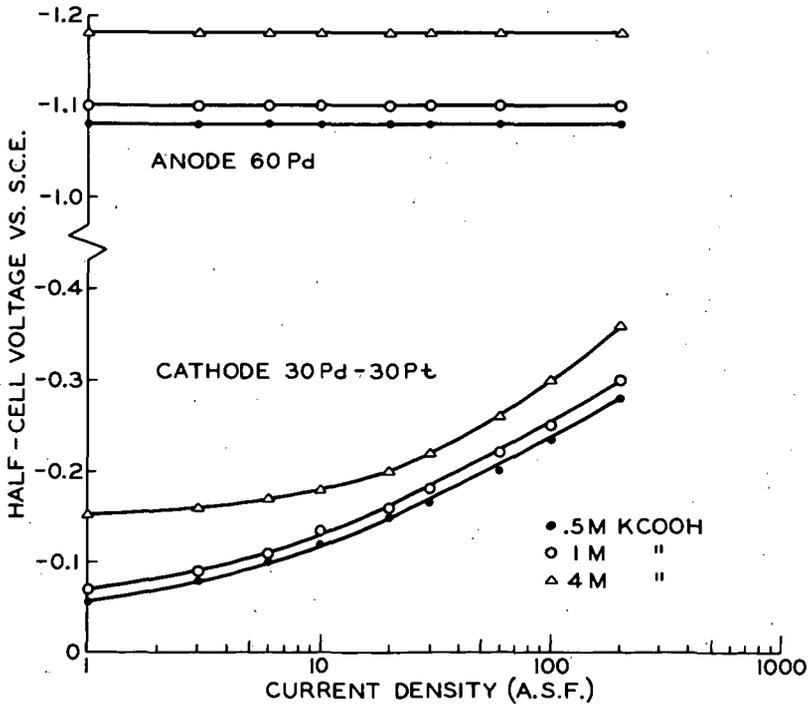


Fig. 6.-EFFECT OF POTASSIUM FORMATE CONCENTRATION ON ANODE AND CATHODE POTENTIALS IN 4M POTASSIUM HYDROXIDE AT 90°C

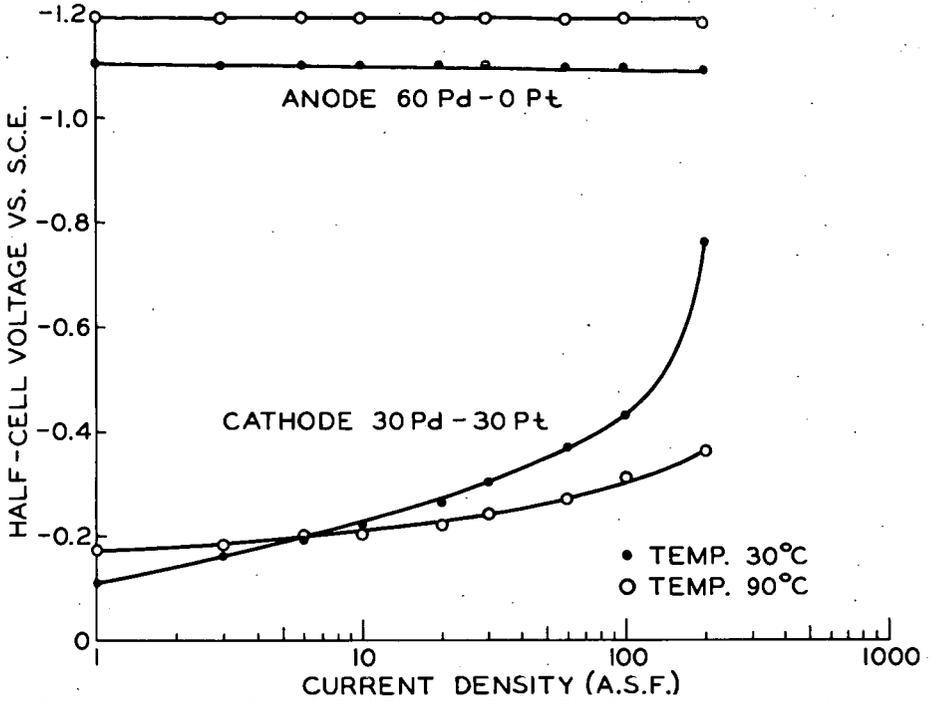


Fig. 7.-HALF-CELL VOLTAGES FOR THE BETTER ANODE AND CATHODE COMBINED IN A SINGLE CELL WITH 4M POTASSIUM FORMATE AND 4M POTASSIUM HYDROXIDE

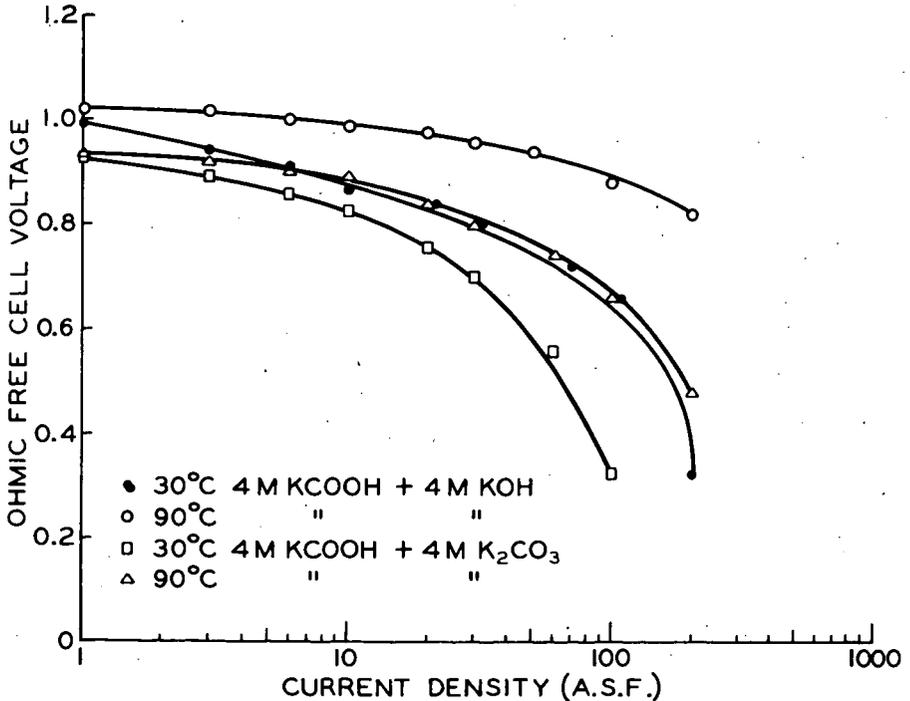


Fig. 8.-CURRENT-VOLTAGE CURVES FOR THE SYSTEMS FORMATE/4M POTASSIUM HYDROXIDE AND POTASSIUM FORMATE/4M POTASSIUM CARBONATE (OHMIC FREE)