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Dual solution-type HCHO fuel cell systems using an anion exchange resin membrane with electroless-plated Cu or Pd anode

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Loading characteristics of a prototype HCHO fuel cell systems with an anion exchange membrane which separates the anolyte from the catholyte were investigated. Electrodes of Cu or Pd, deposited by an electroless-plating technique onto the membrane, showed high electrocatalytic activity to the anodic oxidation of HCHO in 1 M NaOH solution. The system with Cu anode and 1 M NaOH for both anolyte and catholyte showed high loading characteristics but poor durability, whereas that with 1 M K_2CO_3 showed low characteristics because of lowered pH of the anolyte. It was shown that a dual solution-type cell with 1 M K_2CO_3 anolyte and 1 M NaOH catholyte yielded improved characteristics as compared with the simple K_2CO_3 system. The output level was, however, at an unsatisfactory level owing to poor membrane conductance. The temperature dependence of the output performance was studied in the range 7–55° C.

1. Introduction

Formaldehyde in alkaline solution is readily electro-oxidized on group IB metals [1–6]. Among these, Cu, being more active than Pt, is a particularly promising candidate for the anode material. The following problems must, however, be solved in order to realize an alkaline-type HCHO fuel cell system: (1) loss of HCHO fuel due to the Cannizzaro reaction, $2HCHO + OH^- \rightarrow CH_3OH + HCOO^-$, which proceeds at a significant rate in strong alkaline solutions; (2) consumption of alkali along with the progress of the oxidation reaction; (3) oxidation of HCHO only to $HCOO^-$ on the Cu anode. The last problem has been investigated previously [5–8]. Although the other difficulties may be removed by the use of carbonate solutions [5], the oxidation of HCHO becomes considerably slower due to lowered pH.

In this work, anolyte and catholyte were separated by the use of an anion exchange membrane and the Cu or Pd anode was prepared by an electroless-plating technique on the membrane surface. The aim of the work was to avoid the decrease of the electrocatalytic activity of the anodes in weak alkaline solutions by supplying OH^- from a strong alkaline catholyte through the membrane, which should be in-phase with the fuel cell operation.

2. Experimental details

Cu or Pd was deposited on one side of an anion exchange membrane (Tosoh, EA-45) by an electroless-plating technique, namely, by exposing one face to a $CuSO_4$ or $PdCl_2$ solution, and the other to a $NaBH_4$ solution. The electrode was prepared in a circular form of 18 mm in diameter (apparent surface area, 2.5 cm^2); the amount of metal deposited was approximately 5.8 and 3.6 $mg\,cm^{-2}$ for Cu and Pd, respectively.

Figure 1 shows the cell used for the electrochemical measurements. As the anode had low electrical conductivity (10–15 Ω for Cu and 5–10 Ω for Pd between opposite edges of the deposited layer), a Ni net was used as a current collector; Ni is known to be inactive to HCHO oxidation in alkaline solutions [7]. These were placed between anolyte (A) and catholyte (C) using silicon rubber gaskets. A Pt net was used as the O_2 cathode. The electrode potentials were measured against Ag/AgCl reference electrodes, R_a or R_c, in contact with the anolyte or catholyte, respectively, but are quoted after conversion to the RHE scale.

The electrochemical measurements were carried out

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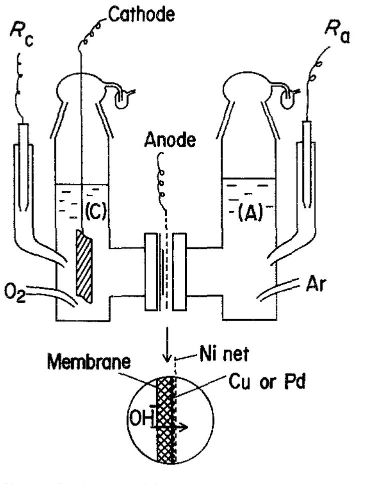

Fig. 1. The cell used. Ag/AgCl reference electrodes, R_c and R_a are in contact with catholyte and anolyte, respectively. 1 M NaOH; 0.6 M HCHO; sweep rate, 50 mV s^{-1}.

at ambient temperature under a stream of Ar in the anode compartment and of O_2 in the cathode compartment. The anolyte contained 0.6 M HCHO in all the experiments. The HCHO contained 7% CH_3OH as a stabilizer, but it has no noticeable influence on the HCHO oxidation rate [5] nor is it oxidized under the experimental conditions involved in this work.

3. Results and discussion

3.1. *Electrocatalytic activity of Cu and Pd anodes*

Figure 2 shows typical cyclic voltammograms observed on the Cu and Pd anodes. The current density at 0.30 V RHE was 48–51 mA cm^{-2} based on the apparent area of the Cu anode and 4–5 mA cm^{-2} on Pd. The activity of the Cu anode was comparable with those of Cu-based amorphous alloys reported earlier [6].

3.2. *Cell resistance*

In Fig. 3a, the solid curves show dependences on the load current (i) of the electrode potentials (ϕ) of the Cu anode and O_2 cathode measured against R_a, and in Fig. 3b the output cell voltage (E) and power density (P) against the load current. The loading characteristics of the anode were of satisfactory level, as anticipated from the cyclic voltammogram in Fig. 2, while those of the cathode were rather poor. The broken curve in Fig. 3a was measured against R_c, the other reference electrode in contact with the catholyte. The difference ($\Delta\phi$) in the cathode potentials measured against R_a and R_c was nearly proportional to the load current and practically independent of the alkaline solutions used (Fig. 4). It was thus evident that the poor characteristics are an artifact mainly caused by low electric conductivity between the anode and the cathode. Further, a major part of the electric

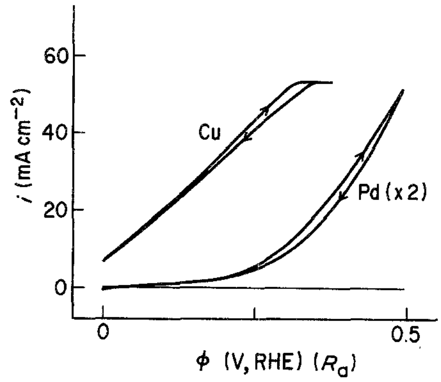

Fig. 2. Cyclic voltammograms observed in 1 M NaOH + 0.6 M HCHO on Cu and Pd anodes. Potential sweep rate: 50 mV s^{-1}.

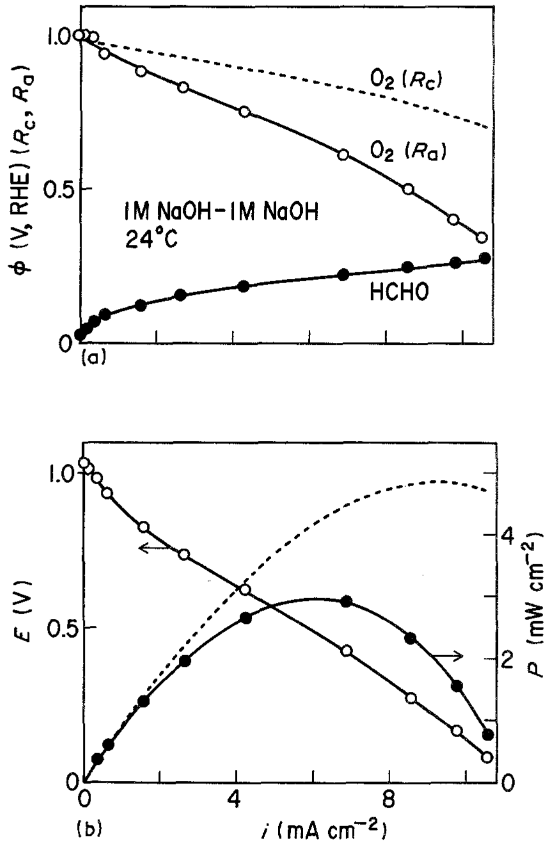

Fig. 3. Load current dependences of (a) electrode potentials and (b) cell voltage in a dual solution-type HCHO fuel cell with Cu anode. The solid curve for O_2 cathode was obtained by the use of R_a and broken curve by R_c.

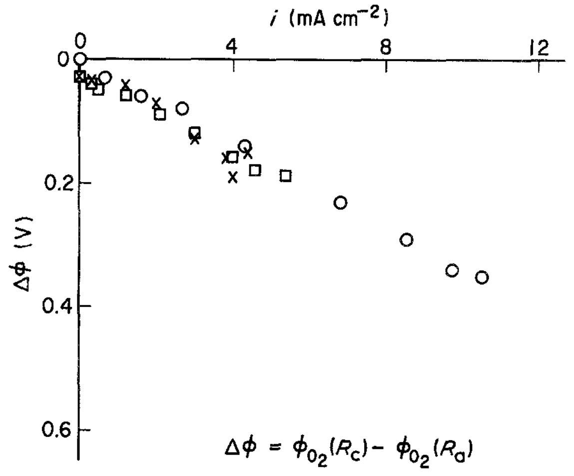

Fig. 4. Difference between O_2 cathode potentials measured from R_c and R_a as plotted against the load current in a dual solution-type HCHO fuel cell with different combinations of solutions. (0.6 M HCHO) Cu/M-Pt(O_2); (○) 1 M NaOH–1 M NaOH; (x) 1 M K_2CO_3–1 M K_2CO_3; (□) 1 M K_2CO_3–1 M NaOH.

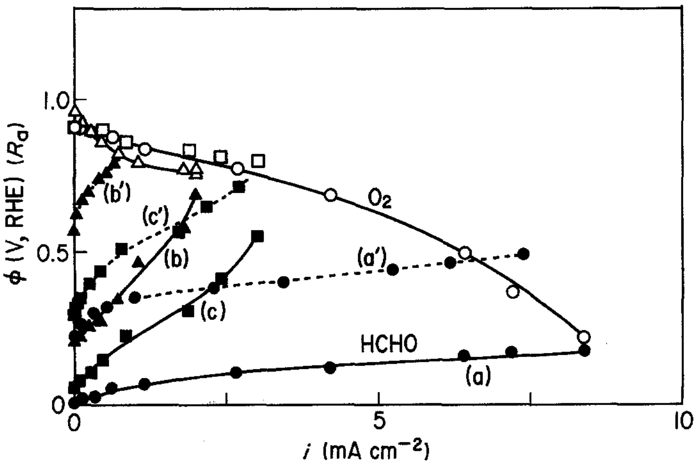

Fig. 5. Electrode potentials vs load current characteristics of a dual solution-type HCHO fuel cell in three different combinations of solutions. Oxygen cathode (open symbols) and fuel anodes (closed symbols) of Cu (solid curves) and Pd (broken curves). (○, ●) 1 M NaOH(A)–1 M NaOH(C); (△, ▲) 1 M K_2CO_3(A)–1 M K_2CO_3(C); (□, ■) 1 M K_2CO_3(A)– 1 M NaOH(C).

resistance estimated from the slope, about 30 Ω cm^{-2}, originates from the membrane. The output power density, if corrected for this loss, is much higher (broken line in Fig. 3b).

3.3. *Dual solution systems*

Figure 5 shows typical relations between the electrode potentials (ϕ) referred to R_a and the load current (i) in three combinations of solutions. The O_2 cathode potential was almost the same among them, but the anode characteristics were different. It is seen from the solid curves that Cu is very active to the HCHO oxidation in case a, namely, the 1 M NaOH(A)–1 M NaOH(C) system, but far less so in case b, the 1 M K_2CO_3(A)–1 M K_2CO_3(C) system. On the other hand, case c, the 1 M K_2CO_3(A)–1 M NaOH(C) system provided more favourable anode ϕ–i characteristics than in case b. The maximum output power, 0.91 mW cm^{-2}, in case c is larger than 0.42 in case b, though it is smaller than 2.5 in case a, as summarized in Table 1.

Analogous tests with a Pd anode were also carried out (Fig. 5, broken curves). As Pd is less active than Cu towards the HCHO oxidation because of its low activity to the rate-determining first charge-transfer step of the reaction [5], the output characteristics are generally poorer than those with Cu. The maximum output power density, e.g. 0.50 mW cm^{-2} in case c′, the 1 M K_2CO_3(A)–1 M NaOH(C) system, was about a half of that with a Cu anode in a similar system.

Naturally, flow of the load current means transport of, in principle, an equivalent amount of OH$^-$ through the anion exchange resin membrane. Consequently, the reason for improved ϕ–i characteristics in 1 M K_2CO_3(A)–1 M NaOH(C) (case c or c′) as compared with those in 1 M K_2CO_3(A)–1 M K_2CO_3(C) (case b or b′) may be ascribed to supply of OH$^-$ ions from the catholyte to the anolyte side of the membrane, which accelerates the HCHO oxidation reaction on the anode located on the anolyte-side membrane surface. The consumption of OH$^-$ is in turn compensated by the production of an equivalent amount of OH$^-$ at the O_2 cathode.

Also from Fig. 5, the difference in anode currents between the 1 M K_2CO_3(A)–1 M NaOH(C) and the 1 M K_2CO_3(A)–1 M K_2CO_3(C) systems at a given electrode potential, namely the increase in the current caused by the use of 1 M NaOH for the catholyte instead of 1 M K_2CO_3, was 1–2 mA cm^{-2} both for Cu and Pd. This probably indicates the limiting rate of transport of OH$^-$ through the membrane used. As this value is rather small, development of anion exchange membranes with improved mobility of OH$^-$ is required in order to realize high performance of dual solution-type fuel cells.

3.4. *Output voltage during sustained operation*

Figure 6 shows the cell voltage (E) measured with a constant load resistance which yields nearly a maximum output power for the case of (A) Cu anode and (B) Pd anode during sustained operations in three different solution systems. In the case of the Cu anode (Fig. 6A), the initial value was the highest in case a, namely the 1 M NaOH(A)–1 M NaOH(C) system,

Table 1. Output characteristics of dual solution-type HCHO fuel cells in different solution systems

Anode	*Case*	*Electrolyte*		*E* (V)	*Data at max. output*		
		Anolyte	*Catholyte*		*E* (V)	*i* (mA cm^{-2})	*P* (mW cm^{-2})
	a	1 M NaOH	1 M NaOH	0.98	0.61	4.2	2.5
Cu	b	1 M K_2CO_3	1 M K_2CO_3	0.86	0.53	0.79	0.42
	c	1 M K_2CO_3	1 M NaOH	0.83	0.48	1.9	0.91
	a	1 M NaOH	1 M NaOH	0.82	0.40	2.8	1.1
Pd	b	1 M K_2CO_3	1 M K_2CO_3	0.35	0.12	0.20	0.08
	c	1 M K_2CO_3	1 M NaOH	0.75	0.35	0.40	0.50

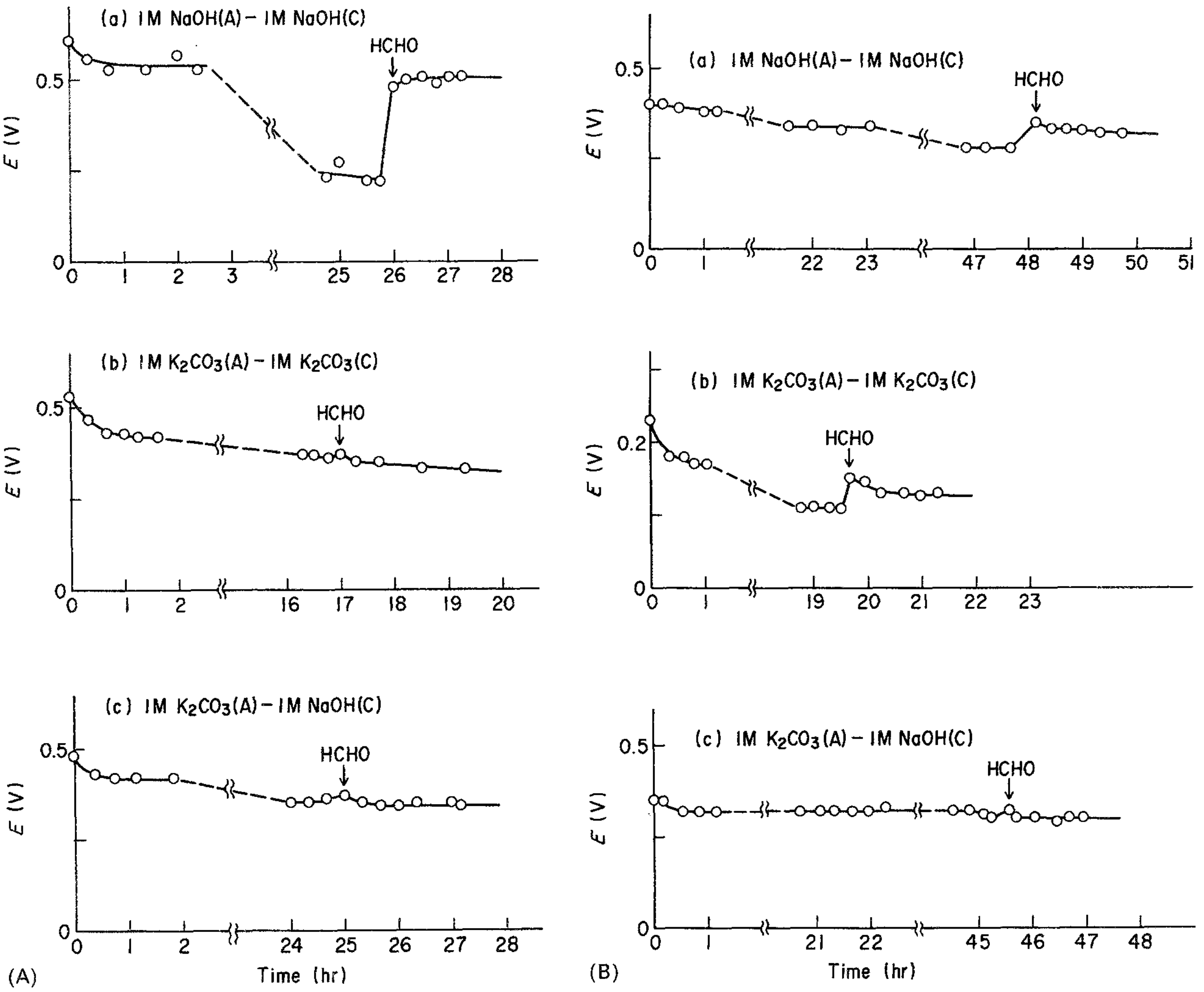

Fig. 6. Dependence of cell output voltage upon time of operation in dual solution-type HCHO fuel cells in three different combinations of solutions. (A) Cu and (B) Pd. (a) and (b) 1 M NaOH and 1 M K_2CO_3, respectively, in common for anolyte and catholyte; (c) 1 M K_2CO_3(anolyte) and 1 M NaOH(catholyte).

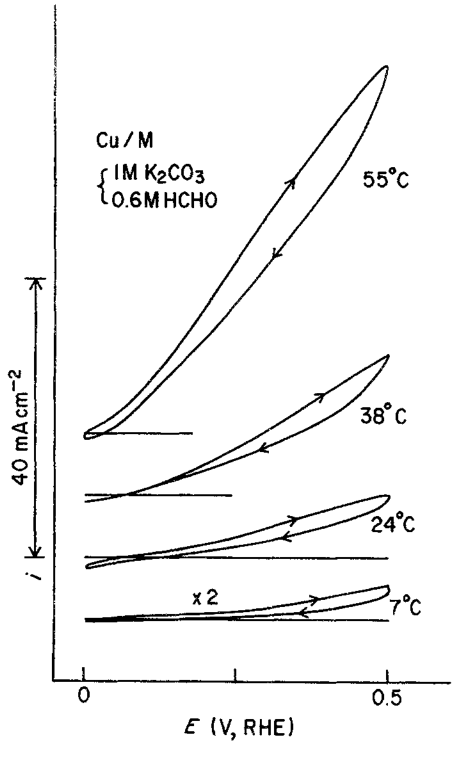

Fig. 7. Cyclic voltammograms observed on Cu anode in 1 M K_2CO_3 at various temperatures. Potential sweep rate: $50\,\mathrm{mV\,s^{-1}}$.

among the three solution systems, but it was not maintained in prolonged operation and lowered to less than a half of the initial value in 1 day. This was recovered almost to the initial level when an amount of HCHO corresponding to 0.6 M concentration was added (indicated by an arrow). This indicates that the decrease is not due to lowered activity of the anode but to lowered concentration of HCHO due to the Cannizzaro reaction [6].

Although the output characteristics in case b, the K_2CO_3(A)-1 M K_2CO_3(C) system, were less favourable than in case a, the decay was much slower. Further, case c, the 1 M K_2CO_3(A)-1 M NaOH(C) system, exhibited a similar time dependence to that in case b, while having improved output characteristics.

Similar time dependences were observed with the Pd anode (Fig. 6B). The cell voltage in case a did not decay as rapidly as in the case of the Cu anode in prolonged operation. This is probably because Pd is active in the oxidation, not only of HCHO, but also of the reaction intermediates H_2 and $HCOO^-$ [7, 8]. In case b, however, the electrode potential was lowered more than in case a after prolonged operation and there was little recovery even on addition of HCHO. This indicates that Pd is deactivated in the carbonate solution [5]. It was interesting that the cell voltage was not lowered in case c, even after prolonged operation over 2 days. This might be related to the supply of OH^- through the membrane, but the reason for the sustained activity is not yet well understood.

3.5. *Temperature dependence*

Figure 7 shows the temperature dependence of the cyclic voltammograms observed on the Cu anode; the activation energy obtained from currents at 0.40 V RHE was 13 kcal mol^{-1}.

4. Summary

(1) Cu and Pd anodes prepared by an electroless-plating technique onto an anion exchange membrane showed a satisfactory level of electrocatalytic activity to HCHO oxidation.

(2) A system of 1 M K_2CO_3(anolyte)–1 M NaOH (catholyte), the two solutions being separated by the membrane, gave rise to higher output power and longer time of operation than a single 1 M K_2CO_3 solution system.

(3) The electrical conductivity of the membrane used was insufficiently high to allow high output power.

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