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Anodic formaldehyde oxidation on Pt, Pd, Au and Pd–Au alloy electrodes in NaOH and Na_2CO_3 solutions

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Electro-oxidation of HCHO on Pt, Pd, Au and Pd–Au alloy electrodes was carried out. In 0.2 M HCHO with 1 M NaOH, Au was electrocatalytically the most active, much more so than Pt or Pd, and was not seriously poisoned by brief contact with CO. The activity of the Pd–Au alloys lay between Au and Pd. In 0.2 M HCHO with 0.4 M Na_2CO_3, Pt and Au exhibited moderate activities. The possible use of HCHO as a fuel for fuel cell uses was favourably indicated.

1. Introduction

In this paper we report on the possible use of formaldehyde as a fuel cell fuel. As summarized in Table 1, the thermodynamic data of some simple carbonaceous compounds indicate that HCHO in basic medium gives the most negative oxidation potential during its full four-electron oxidation or partial (assumed) two-electron oxidation. This suggests the possibility that oxygen reduction and fuel oxidation overpotentials, which inevitably lower the energy conversion efficiency, can be made relatively less serious in this system.

Nevertheless, the practicability of using this reaction strongly depends on the rate and kinetics of the fuel oxidation and, in this respect, very few investigations have been published on the use of formaldehyde as a fuel [1–6]. Further, most work was concerned only with Pt in acidic solutions. As seen below, however, the behaviour in alkaline media, and the possible use of active electrocatalysts other than Pt is of special interest. The advantages suggested are a more negative (both reversible and working) oxidation potential as compared with that of methanol and hence a larger output cell voltage when combined with, e.g. an oxygen–air electrode, a much greater reactivity and hence output current and less serious decay of the oxidation current with time (diminished catalyst poisoning).

2. Experimental details

Experiments were carried out in an ordinary three-compartment pyrex glass cell, the two side compartments being separated from the main one with solution-wetted closed stopcocks. Smooth Pt, Au and Pd–Au alloy foils (Tanaka Noble Metals, Tokyo), 50 μm thick, and Pd foil (Ventron, Alfa Division), 10 μm thick, each in a rectangular form of approximately 1 cm^2, were used as the test electrodes. These foils were spot-welded to 0.5 mm diameter Ta wire supports which were in turn sealed into pyrex glass tubing. The experimental cell and the electrodes were cleaned with warm chromic acid and rinsed with pure water from a Millipore pure water system.

The roughness factor values of the electrodes evaluated from double layer capacitance measurements were fairly close to each other: Pt, 3.8; Pd, 4.2; $Pd_{90}Au_{10}$, 3.9; $Pd_{70}Au_{30}$, 3.1; $Pd_{40}Au_{60}$, 3.3; and Au, 3.2. All the current density values reported below are, nevertheless, given on the apparent geometric surface area basis. The HCHO used (35% solution, GR grade, Nakarai, Tokyo) nominally contained 7% CH_3OH. The data reported below are, therefore, concerned with the oxidation of HCHO in the presence of CH_3OH. Further additions of CH_3OH up to 0.5 M concentration caused no significant difference in the current–potential relationships.

Table 1. Basic data on the full and partial electro-oxidation of CH_3OH, HCHO and HCOOH (HCOONa)

		Full oxidation		*Partial oxidation*		
Compound	G^0	Q	E^0	*Product*	Q	E^0
CH_3OH (aq)	−41.70	6	0.03 (acid soln.) 0.07 (alk. soln.)	HCHO	2	0.23
HCHO (aq)	−31.0	4	−0.07 (acid soln.) −0.22 (alk. soln.)	HCOOH	2	−0.06 (acid soln.) −0.25 (alk. soln.)
HCOOH (aq)	−85.1	2	−0.20	–	–	–
$HCOO^-$ (aq)	−80.0		−0.19	–	–	–

G^0: Standard Gibbs free energy in kcal mol^{-1}.
Q: Amount of electricity of oxidation in F mol^{-1}.
E^0: Standard electrode potential in V (RHE).

All the experiments were carried out at 30° C under a purified He gas atmosphere. The cyclic voltammetry technique was mainly used but steady-state polarization measurements were also carried out in order to observe the durability of the electrocatalytic activity. The electrode potential data cited below are referred to the RHE in the same acid or alkaline solution, but not containing HCHO.

3. Results and discussion

3.1. *Electro-oxidation of methanol and formaldehyde on Pt*

Typical voltammograms obtained on a smooth Pt electrode during the oxidation of 0.4 M CH_3OH in acid (0.05 M H_2SO_4) and in alkaline (1 M NaOH) media are shown in Fig. 1(A) and (B), respectively. The oxidation in the alkaline solution gives the current peak slightly higher and at less positive potentials as compared with that in the acidic solution. Otherwise, the general behaviour is very similar in these solutions.

It is known that the electro-oxidation of HCHO on Pt in acidic solutions takes place more rapidly than that of CH_3OH [1–3]. The oxidation current appearing at 0.95 V RHE on the positive potential sweep curve (range of the scan, 0–1.5 V) in 0.2 M HCHO with 0.05 M H_2SO_4 observed in this work on a smooth Pt electrode (Fig. 1C), was typically about 10 mA cm^{-2} (apparent), which was almost three times larger than the oxidation of 0.4M CH_3OH in the same acid (Fig. 1A). Apart from this larger oxidation current, however, the voltammogram has general characteristics common to the case of the CH_3OH electro-oxidation. Thus, the oxidation current drops rapidly at electrode potential more positive than 1 V (0.7 ~ 0.9 V in the case of CH_3OH), and a hysteresis of significant magnitude is seen between the positive and nega-

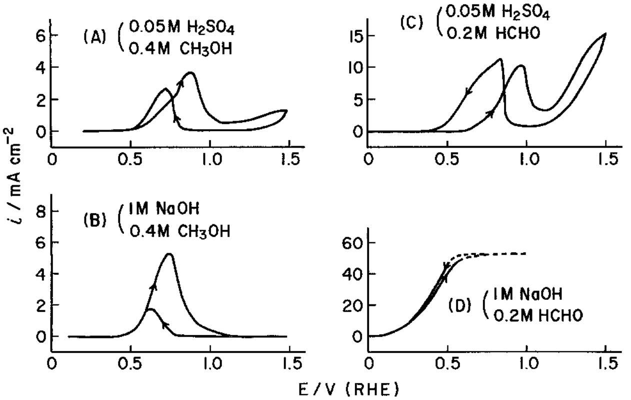

Fig. 1. Typical potential sweep curves for the anodic oxidation of CH_3OH and HCHO on Pt in acidic and alkaline solutions.

tive sweep voltammogram curves. Such behaviour is often considered to be due to accumulation on the electrode surface of poorly reacting reaction intermediates or products, which give rise to serious decay of the electrocatalytic activity. The use of HCHO in acidic media, therefore, does not offer significant advantage as compared with CH_3OH. (Incidentally, Pd, Au, or Pd–Au alloy electrodes employed later were electrocatalytically far less active than Pt in *acidic* media).

The electro-oxidation of HCHO on Pt in *alkaline* solution was found to be notably different and the oxidation current was very high, typically $30\,mA\,cm^{-2}$ at a potential as low as 0.4 V (Fig. 1D). The oxidation started at potentials as low as 0.1 V RHE as compared with 0.5 V which was required in the case of CH_3OH (Fig. 1B), and the maximum oxidation current was an order of magnitude larger than the peak current observed in the acidic solution (Fig. 1C). The oxidation rate is comparable with that of hydrogen oxidation, because of less serious diffusion limitations due to the much higher solubility of HCHO in water.

3.2. *Electro-oxidation of HCHO on Pd, Au and Pd–Au alloys*

It is noteworthy that the oxidation rate was higher on Au than on Pt or Pd–Au alloys (Fig. 2). The polarization curves in Fig. 2 were recorded similarly with the use of the potential sweep technique in the range of the potential scan between 0 and 0.3 V. This was much narrower than in ordinary potential sweep experiments, and did not permit the electrodes to receive any anodic activation during the potential cycling. Accordingly, the electrocatalytic activity data observed in Fig. 2 were not of a transient short-time nature. On the smooth Au foil, the oxidation current at 0.10 V was already $0.5\,mA\,cm^{-2}$, as shown in Fig. 2(A), or $40\,mA\,cm^{-2}$ at 0.40 V (not shown). In addition, the positive and negative sweep voltammogram curves practically coincided with no indication of hysteresis (not quite so for Pt). These features are entirely different from the case of the oxidation of CH_3OH, and suggest the absence of accumulation of self-poisoning reaction intermediates.

The results presented in Figs 2(B) and 3 were obtained on electrodes exposed to CO which was introduced into the cell for a few minutes and then purged with He. The electrocatalytic activity of Au was little influenced by this brief contact with CO, whereas that of Pt, as well as of the Pd–Au alloys, was strongly diminished. Thus, Au is shown to be a far better electrocatalyst in this reaction than Pt.

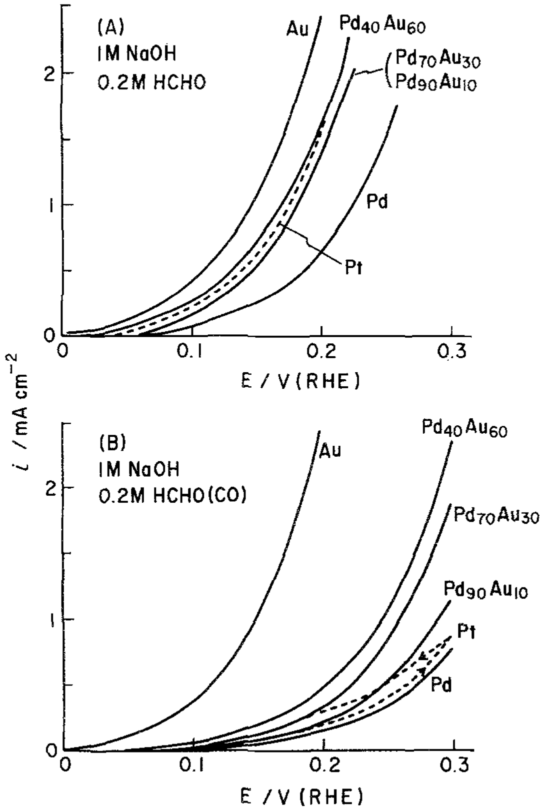

Fig. 2. Anodic oxidation of 0.2 M HCHO on Pt, Pd, Au and Au–Pd alloy electrodes in 1 M NaOH. (Portions of potential sweep curves taken in the range 0–0.3 V with sweep rate $10\,mV\,s^{-1}$. (A), before, and (B), after the exposure of the electrodes to CO (see text).

The relation between the electrocatalytic activity and the alloy bulk composition was reproduced from Fig. 2 by reading the current at 0.2 V RHE and this is shown in Fig. 4. It has been demonstrated earlier [7–10] that the surface composition of the Pd–Au alloys is close to the bulk composition. As seen, the Pd–Au alloys had characteristics between the pure component metals, Au and Pd, and no particular enhancement was seen in terms of their composition. No

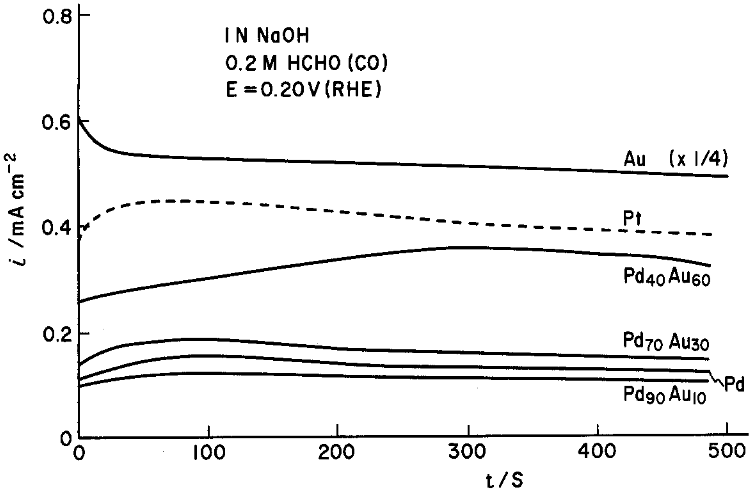

Fig. 3. Time-dependence of the anodic oxidation current of 0.2 M HCHO in 1 M NaOH at E = 0.20 V RHE. (Electrodes exposed to CO, see text.)

(positive) synergetic effect between Au and Pd was indicated in this reaction.

The durability of the electrocatalytic activity is shown in Fig. 3. In general, the degree of decay of the activity was much smaller than that usually observed in CH_3OH oxidation. The oxidation current about 10 min after the application of a constant electrode potential was highest on Au; the value at $E = 0.20$ V RHE was about 2 mA cm^{-2} (4-fold scale reduction in the figure) which was 5 times as large the current as on Pt.

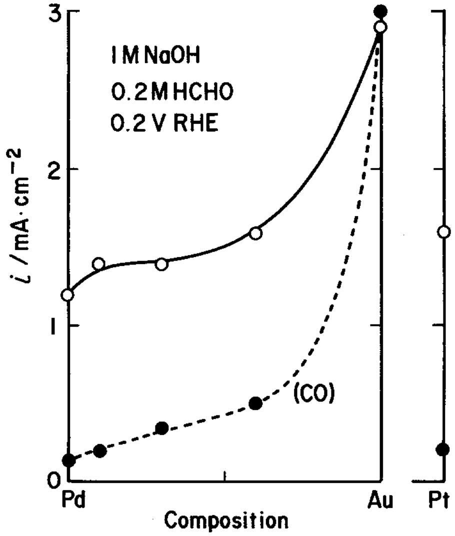

Fig. 4. Electrocatalytic activity, as represented by the oxidation current at 0.2 V RHE in Fig. 2, vs alloy composition. Solid curve, before, and broken curve, after brief contact of the electrode with CO. Results on the Pt electrode are shown for comparison.

3.3. *Electro-oxidation of HCHO in Na_2CO_3 solution*

The high rate of oxidation of HCHO in the alkaline solution as reported above might still not be indicative of possible use in practical fuel cells, because the oxidation reaction could consume the alkali in the solution, presumably forming formate or carbonates. The formate might be further electro-oxidized if a suitable electrode material is used, but regeneration of NaOH from Na_2CO_3, the final product, may in turn require an energy-demanding process. Thus, the system may be practical only when the alkali is also used as a part of the fuel. Also, evaluation of H_2 as a byproduct, in spite of the potential more positive than RHE, is suggested and this will be more serious in strong alkaline media [11, 12]. Accordingly, in order for HCHO, or any other carbonaceous compounds, to be utilized as a fuel, the oxidation should preferably be possible at a reasonable rate in near neutral or acidic solutions.

Results obtained in 0.2 M HCHO with 0.4 M Na_2CO_3 are shown in Fig. 5. This system produces bicarbonate, $NaHCO_3$, but this may readily be decomposed at temperatures above 65° C. It is seen that the electrocatalytic activity of Au is considerably lowered but it remains at a reasonable level comparable with Pt, in contrast with entire loss of activity in acidic solutions. Although the activity decay with time is more extensive than in the case of 1 M NaOH, the oxidation current of the order of 1 mA cm^{-2}

at 0.60 V after 10 min (or of 0.1 mA cm^{-2} at 0.40 V, not shown) on the smooth Au electrode is highly promising from the standpoint of a practical fuel cell system. Further investigations, particularly on the reaction mechanism and the possible use of other electrode materials, are currently in progress.

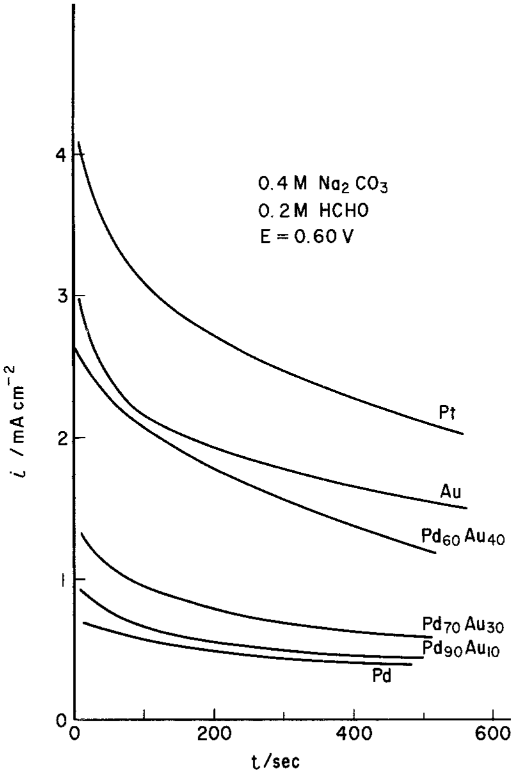

Fig. 5. Time-dependence of the anodic oxidation current of 0.2 M HCHO in 0.4 M Na_2CO_3 at E = 0.60 V RHE.

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