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Competitive oxidation of formaldehyde and formate on amorphous copper-palladium-zirconium alloy electrodes in alkaline media

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Raney-type Cu-Pd alloy electrodes were prepared from amorphous Cu-Pd-Zr ternary alloys by treatment with aq. HF, and competitive anodic oxidation reactions of HCHO and $HCOO^-$ were studied on these electrodes in alkaline media. The initial HCHO oxidation product was $HCOO^-$ even on Pd or Pd-rich alloy electrodes which should be more active to the $HCOO^-$ oxidation than to HCHO. The product $HCOO^-$ was oxidized only after a large decrease of the HCHO concentration in the electrolyte. The oxidation rate of $HCOO^-$ was considerably lowered by the existence of even a small amount of HCHO, as well as by the introduction of CO. These results suggest that the HCHO electro-oxidation is accompanied by production of a surface contaminant such as adsorbed CO. The optimum nominal Pd atomic fraction in the Cu-Pd alloy electrodes suitable for the steady simultaneous oxidation of HCHO and $HCOO^-$ in mixed solution was shown to be 0.25 and 0.4 in 1.0 M NaOH ($M = \text{mol dm}^{-3}$) and 0.5 M K_2CO_3, respectively.

1. Introduction

Formaldehyde is a potential fuel for fuel cells as it is rapidly oxidized on electrodes of group IB metals, particularly Cu and Au, in alkaline media [1–8]. The following reaction mechanism appears to be established through studies in the field of fuel cells [1–8], electro-organic chemistry [9] and electroless plating [10, 11]:

$$\mathrm{HCHO} + \mathrm{OH}^- \rightleftharpoons [\mathrm{HOCH_2O}]^- \qquad (1)$$

$$[\mathrm{HOCH_2O}]^- \xrightarrow{A} [\mathrm{HOCH_2O}] + e^- \qquad (2)$$

$$[\mathrm{HOCH_2O}] + \mathrm{OH}^- \longrightarrow \mathrm{HCOO}^- + \mathrm{H(a)} + \mathrm{H_2O} \qquad (3)$$

$$2\mathrm{H(a)} \longrightarrow \mathrm{H_2}\uparrow \qquad (4)$$

where H(a) is the intermediate hydrogen adatom and $\xrightarrow{A}$ denotes the rate-determining step. As seen, these electrodes can only partly oxidize HCHO, forming $HCOO^-$ and H_2 simultaneously. On the other hand, it has been demonstrated in our recent publication [12] that the Raney-type Cu-Pd electrodes prepared from amorphous Cu-Pd-Zr ternary alloys with the bulk composition of Cu : Pd $\simeq$ 1 : 3 possess equally high levels of electrocatalytic activity for the individual oxidation of HCHO and $HCOO^-$ in 1.0 M NaOH. Further, no hydrogen gas was evolved, or it was oxidized, during the anodic HCHO oxidation. Thus, the alloy electrodes also catalyse the following two reactions,

$$\mathrm{HCOO}^- + 3\mathrm{OH}^- \longrightarrow \mathrm{CO_3^{2-}} + 2\mathrm{H_2O} + 2e^- \qquad (5)$$

$$\mathrm{H(a)} + \mathrm{OH}^- \longrightarrow \mathrm{H_2O} + e^- \qquad (6)$$

and, accordingly, they may be effective in oxidizing HCHO completely.

It became apparent later, however, that the anodic oxidation reactions of HCHO and $HCOO^-$ interfere with each other: in particular, the $HCOO^-$ oxidation is influenced by the existence of HCHO. It is aimed in this work to study, in more detail, the interference between the anodic oxidations of HCHO and $HCOO^-$ in mixtures.

2. Experimental details

2.1. *Electrode preparations*

A series of amorphous alloys with the nominal composition of $Cu_{1-x}Pd_xZr_2$ ($x = 0, 0.25, 0.50$, and 0.75) and $Pd_{0.255}Zr_{0.745}$ prepared by a melt-quench technique in the form of ribbons 0.8–1.2 mm wide and about 20 μm thick were supplied from Riken Co., Ltd. To make the electrodes, short pieces of the ribbons (about 3 mm long) were spot-welded to Ta wires which were sealed into Pyrex glass tubings. The surface was then etched with 1.0 M aq. HF for several tens of seconds at room temperature in order to dissolve Zr and its oxides. This procedure leads to the formation of a porous or Raney-type layer on the electrode surface.

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It has been shown in our earlier XPS work [12] that surface compositions of such HF-treated Cu-Pd-Zr alloy electrodes are slightly (some 10%) enriched in Pd at the surface. The nominal bulk composition will mainly be referred to in this paper, except for mentioning the surface composition in the part of discussion on the alloy composition dependence.

2.2. *Electrochemical measurements*

The surface roughness factors (RF) of the electrodes were evaluated from the double-layer capacitance measured by a galvanostatic pulse technique. Polarization measurements were carried out potentiostatically in a conventional three-compartment glass cell according to the method described elsewhere [12]. The cyclic voltammograms and steady-state polarization behaviour were observed in 1.0 M NaOH and 0.5 or 1.0 M K_2CO_3 solutions containing HCHO, HCOONa, and/or CH_3OH, under purified Ar gas. An Ag/AgCl and a pt-Pt hydrogen electrode were used as reference electrodes, but all potential values are given on the RHE scale.

2.3. *Chemicals and composition analysis of solution phase*

The chemicals used were of reagent grade; HCHO was obtained from a 35 wt% formaldehyde solution which contained 7 wt% CH_3OH for stabilization. Changes of the solution composition during a prolonged anodic oxidation were followed in a small-sized glass compartment (volume of the solution 1.70 ml, apparent electrode area 5 cm^2) separated from the counter electrode compartment with an anion exchange membrane (Lot. No. TASN-17, Toyo Soda Manufacturing Co., Ltd.). The solution was analysed by a gas chromatograph using columns of TSR-1 and PEG-6000 (Gasukuro Kogyo, Inc.).

3. Results and discussion

3.1. *Change of the solution composition*

A typical example of composition change of the solution observed during the anodic oxidation of 0.3 M HCHO in 1.0 M K_2CO_3 on an HF-treated a(amorphous)-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrode is shown in Fig. 1 as a function of the amount of electricity applied. The experiment was carried out under an Ar atmosphere under a potentiostatic condition at 0.50 V(RHE) and lasted for several days. The current was about 1 mA cm^{-2}(app.) in the earlier stage of electrolysis, but decreased appreciably with time. The corresponding amounts of electricity which would have been needed for the composition changes to take place (but not taking CH_3OH into account, see below) are in good agreement with those actually applied, as shown on the right-hand side ordinate of Fig. 1 (dotted line).

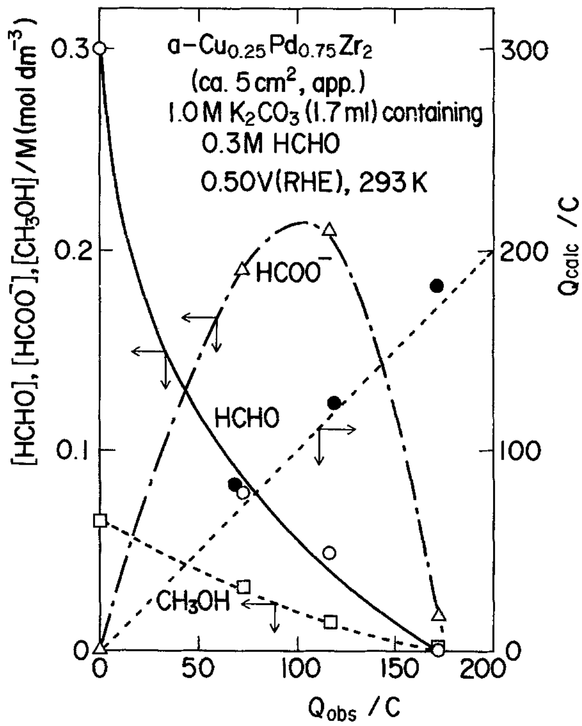

Fig. 1. Change in the solution composition (HCHO (○), $HCOO^-$ (△), and CH_3OH (□)) with the amount of electricity (Q_{obs}) applied during the anodic HCHO oxidation on an HF-treated a-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrode. Apparent area of the electrode; 5 cm^2, solution; 1.70 ml of 1.0 M K_2CO_3 containing 0.3 M HCHO, reaction at 0.50 V(RHE), 293 K. The amount of electricity (Q_{calc}) calculated from the composition data is shown on the right-hand side ordinate.

The decrease of CH_3OH concentration in Fig. 1 was puzzling at first: one may neglect the electro-oxidation of CH_3OH as the rate is known to be slower by two orders of magnitude than that of HCHO oxidation. Also, if one accounts for this decrease as due to its electro-oxidation, then the amount of electricity calculated exceeds the value actually applied. A close agreement between the amount of $HCOO^-$ produced and that of HCHO disappearing from the solution should indicate the $HCOOCH_3$ formation as insignificant. Further, permeation of solution components through the membrane was estimated to be insignificant (e.g. ~6% for the HCHO component, or less with CH_3OH during the whole duration of the experiment). It was then confirmed that this decrease of CH_3OH concentration was caused by evaporation during the experiment (evaporation of HCHO was not significant: for example, loss of HCHO from 1.0 M K_2CO_3 solution which contained 0.30 M HCHO and 0.056 M CH_3OH was not noticeable even after a major part of CH_3OH was lost by evaporation).

As seen in Fig. 1, the oxidation of $HCOO^-$ takes place only after a large portion of HCHO was consumed. This observation reveals that HCHO is oxidized first to $HCOO^-$ even on Pd-rich alloy electrodes, such as used in the present case, which are known to be active towards $HCOO^-$ oxidation. Accordingly, the oxidation of HCHO solution soon yields a $HCOO^-$-rich mixed solution. Experiments on the mixed systems are, therefore, required in order to understand the more detailed behaviour of the HCHO oxidation.

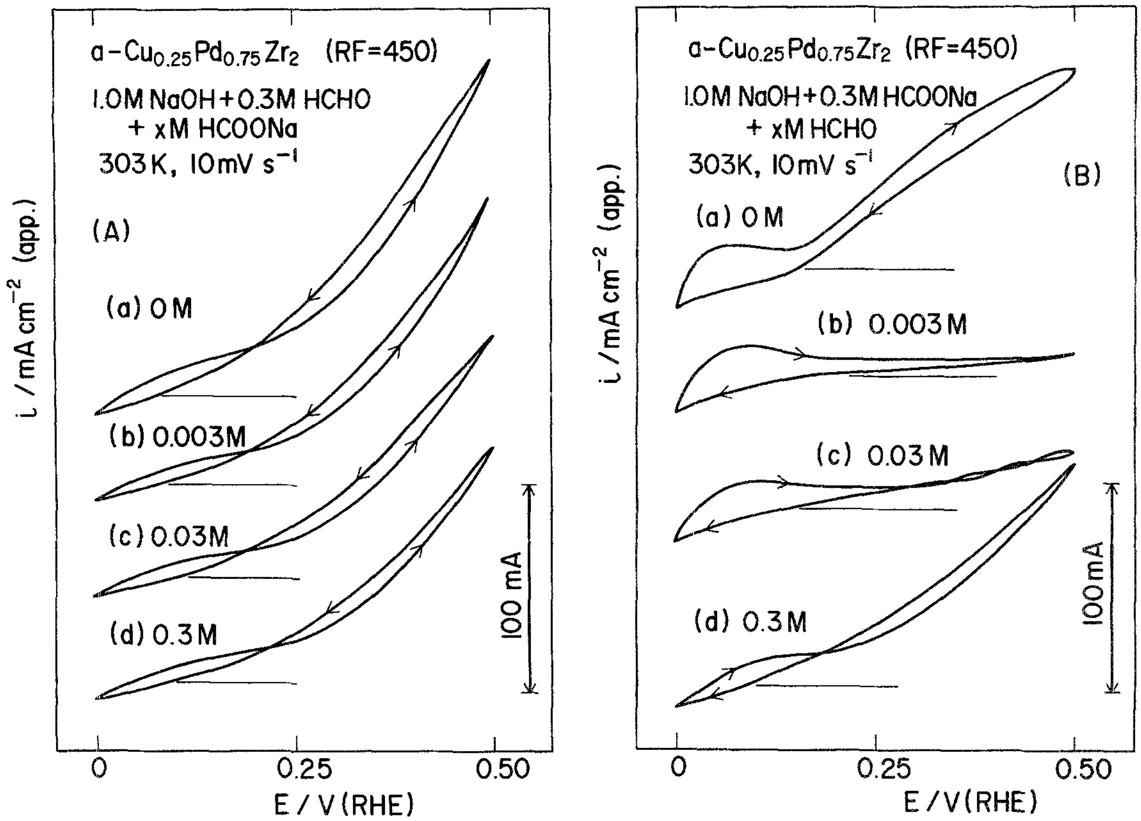

Fig. 2. Typical cyclic voltammograms observed on the HF-treated a-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrode (RF = ca. 450). 1.0 M NaOH containing (A) 0.3 M HCHO + x M HCOONa and (B) 0.3 M HCOONa + x M HCHO. 303 K. Potential sweep rate; 10 mV sec^{-1}.

3.2. *Oxidation characteristics of the HCHO – $HCOO^-$ mixed fuel*

Typical cyclic voltammograms observed on the HF-treated a-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrodes in a HCHO–$HCOO^-$ mixed solution with 1.0 M NaOH are shown in Fig. 2. In the case of HCHO (Fig. 2A), the oxidation current curve changed only to a minor extent by the addition of $HCOO^-$ up to the same level of concentration as HCHO. As a common feature, the anodic oxidation current started to flow above about 0.1 V and the curve shapes were similar to each other.

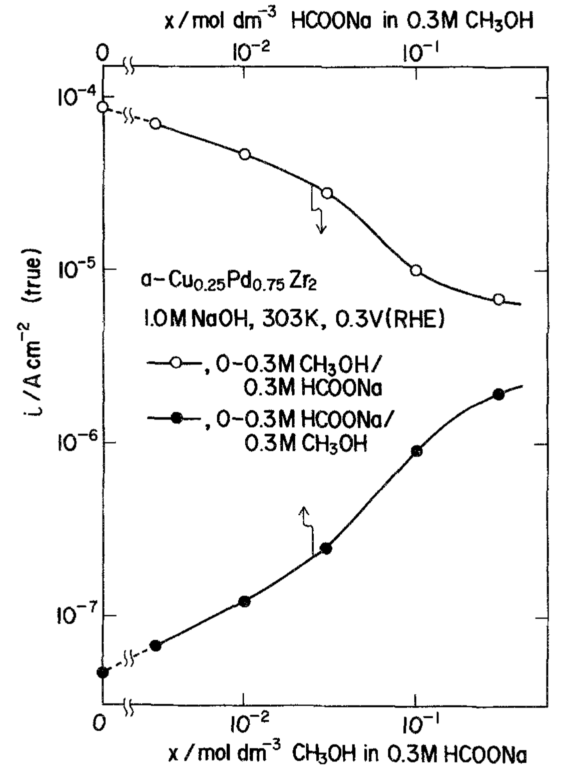

Fig. 3. Effect of addition of CH_3OH on the oxidation rate of 0.3 M HCOONa (○) or, conversely, of HCOONa on 0.3 M CH_3OH (●) at 0.30 V(RHE). HF-treated a-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrode (RF = ca. 450), 1.0 M NaOH, 303 K.

On the other hand, in the case of $HCOO^-$ system, the addition of a small amount of HCHO caused a drastic decrease of the oxidation current (Fig. 2B, curve (b) as compared with curve (a)). However, addition of a larger amount of HCHO, e.g. more than 0.03 M, caused a degree of restoration, curves (c) and (d). The shape and position of the oxidation current curves in the HCHO-rich mixed solution suggest that the observed anodic current may be attributed to the oxidation of HCHO rather than of $HCOO^-$ (compare curve (a) in Fig. 2A with curve (d) in Fig. 2B).

The effect of addition of CH_3OH on the rate of the $HCOO^-$ oxidation was tested (Fig. 3, open circles) in order to see if the interference mentioned was caused by CH_3OH which was contained in the HCHO reagent as a stabilizer. The $HCOO^-$ oxidation current is lowered with increase of the CH_3OH concentration, but the degree of the retardation was far weaker than that caused by the addition of HCHO: the fraction of the current decrease caused by the addition of 0.003 M CH_3OH was less than 20% while that by HCHO was about 95%. It is, therefore, concluded that the retardation of $HCOO^-$ oxidation by the addition of the HCHO solution (containing 7 wt% CH_3OH) was mainly caused by HCHO itself. On the other hand, the oxidation current in CH_3OH solution increased with the addition of $HCOO^-$ (Fig. 3, closed circles). This is understood as due to contribution of $HCOO^-$ oxidation.

It has been shown by *in situ* infrared spectroscopic observations [13] that this interference due to HCHO is caused by CO intermediates, probably directly derived from molecular HCHO. The CO intermediates presumably occupy the electrocatalytically active sites for $HCOO^-$ oxidation by adsorption and play a role of poisoning (see below).

3.3. *The CO poisoning and alloy composition*

Retardation of the anodic $HCOO^-$ oxidation was also observed with the introduction of gaseous CO. Fig. 4 shows typical cyclic voltammograms observed on a-$Cu_{0.75}Pd_{0.25}Zr_2$ and a-$Cu_{0.25}Pd_{0.75}Zr_2$ alloy electrodes before and after the CO introduction. For both electrodes the reaction current was drastically lowered, but the extent of retardation was greater on the electrodes with higher Pd content in the alloys.

Anodic currents of $HCOO^-$ oxidation on electrodes of various alloy composition in 1.0 MNaOH and 0.5 M K_2CO_3 under CO atmosphere (Fig. 5, solid and broken curve, respectively) are compared with that observed in 1.0 M NaOH but under Ar atmosphere (dotted curve). As seen, the retardation of the anodic $HCOO^-$ oxidation by CO is very significant but its degree is diminished at high Cu contents in the alloy electrodes. Presumably, the adsorption of CO is weaker on electrode surfaces with higher Cu contents, as anticipated from the fact that CO adsorbs extensively on Pd but not on Cu [14]. These observations indicate that there exists an optimum composition in Cu-Pd alloy electrodes which is suitable for a long time or steady oxidation of the HCHO–$HCOO^-$ mixed fuel.

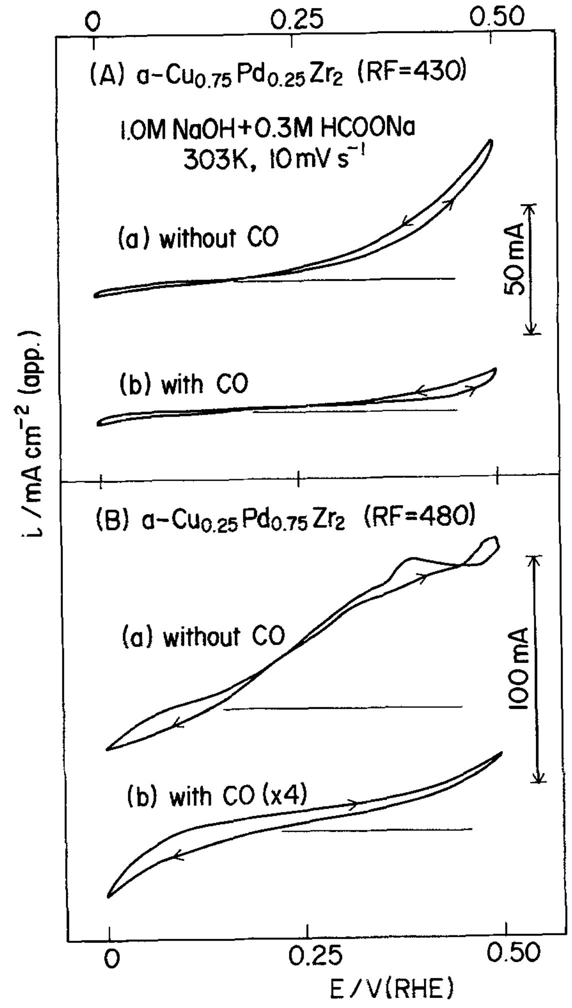

Fig. 4. Typical cyclic voltammograms observed on HF-treated (A) a-$Cu_{0.75}Pd_{0.25}Zr_2$ (RF = 430) and (B) a-$Cu_{0.25}Pd_{0.75}Zr_2$ (RF = 480) alloy electrodes before (curves a) and after (curves b) the introduction of CO. Solution; 1.0 M NaOH containing 0.3 M HCOONa, 303 K. Potential sweep rate; 10 mV sec^{-1}.

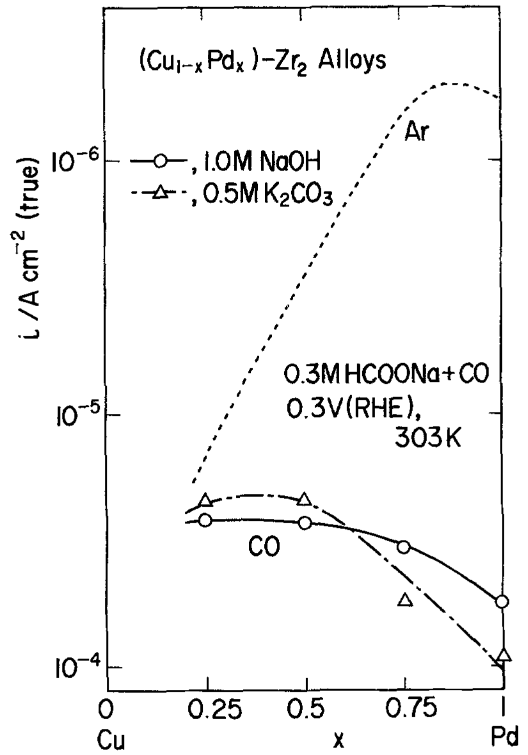

Fig. 5. Rate of $HCOO^-$ oxidation at 0.30 V (RHE) on CO-contaminated HF-treated a-$Cu_{1-x}Pd_xZr_2$ alloy electrodes plotted against bulk composition in atomic fraction of Pd. Solutions; 1.0 M NaOH (solid curve) or 0.5 M K_2CO_3 (broken curve) containing 0.3 M HCOONa, 303 K. The dotted curve represents the oxidation current in 1.0 M NaOH + 0.3 M HCOONa solution under Ar atmosphere [2].

The alloy composition dependence of the competitive oxidation of $HCOO^-$ and HCHO was studied in 1.0 M NaOH or 0.5 M K_2CO_3 in the presence of 0.3 M HCOONa and 0.003 M HCHO (Fig. 6). It is seen that the oxidation current is highest on the alloys with the bulk Pd contents around 0.25 and 0.4 in 1.0 M NaOH and 0.5 M K_2CO_3, respectively. These values should correspond to somewhat larger Pd contents at surface [12], as indicated on the upper abscissa in Fig. 6. These Pd contents are lower than the value which is required for efficient hydrogen oxidation during the anodic HCHO oxidation (dotted curve). As reported earlier [12], a higher bulk Pd atomic fraction than 0.5 is needed for the complete oxidation of the hydrogen intermediate. The optimum Pd atomic fraction (X) for HCHO fuel cells may be taken at 0.5–0.7 at the cost of somewhat lowered electrocatalytic activity for the HCHO oxidation.

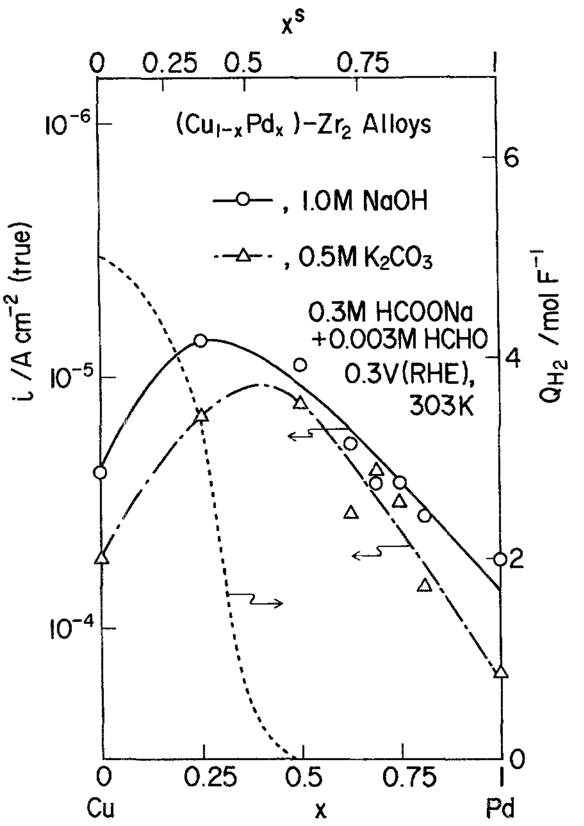

Fig. 6. Oxidation current density at 0.30 V (RHE) vs. bulk Pd atomic fraction (X) of HF-treated a-$Cu_{1-x}Pd_xZr_2$ alloy electrodes in a mixed solution of HCHO and $HCOO^-$. Surface Pd composition (X^s) [2] is also given on the upper abscissa. Solutions: 1.0 M NaOH (solid curve) or 0.5 M K_2CO_3 (broken curve) containing 0.3 M HCOONa and 0.003 M HCHO, 303 K. The dotted curve represents the amount of hydrogen evolved during the anodic HCHO oxidation in 1.0 M NaOH containing 0.3 M HCHO [2].

4. Conclusions

The oxidation of HCHO on Raney-type Cu-Pd alloy electrodes in alkaline solution produces $HCOO^-$ in the initial stage, and hence the system soon yields a HCHO-$HCOO^-$ mixed solution. The rate of oxidation of $HCOO^-$ is strongly retarded by a minor amount of HCHO which probably produces adsorbed CO. The retardation is also caused by the introduction of CO. The oxidation current in a mixed HCHO-$HCOO^-$ solution is maximized at bulk Pd contents of 0.25–0.4, but alloy electrodes with Pd content around 0.5 are preferable from a practical view-point in order to assure simultaneous oxidation of hydrogen, which otherwise evolves during the HCHO electro-oxidation.

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