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Cu AND Cu-BASED AMORPHOUS ALLOY ELECTRODES FOR ANODIC FORMALDEHYDE ELECTRO-OXIDATION

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The electrodes of Cu and Cu-based amorphous alloys, a-$Cu_{35}Ti_{65}$ and a-$Cu_{33}Zr_{67}$, were very active for the HCHO electro-oxidation in alkaline solutions. The oxidation started at electrode potentials as low as 0.1 V (RHE) and the HF-treated amorphous alloys exhibited high current densities around 40 mA cm^{-2} (app.) at 0.2 V.

Fuel cells which employ organic fuels such as methanol or its derivatives are very desirable especially when we are to construct small scale transportable electric power sources. These fuels are more advantageous in storage and handling than hydrogen. A breakthrough in this case must, however, be accomplished in developing a good electrode system on which these fuels can be electrochemically readily oxidized. In this context, we have found recently that Au and Ag show a high electrocatalytic activity for the electro-oxidation of formaldehyde in alkaline solutions.[1] In this letter, we report the electrodic characteristics of Cu and some Cu-based amorphous alloys towards this reaction.

The Cu electrodes were prepared from an ordinary Cu plate (thickness, 0.3 mm; purity, 99.5%) in a rectangular form of 10 × 5 mm and their surface was etched with dilute nitric acid. The Cu-based amorphous alloy electrodes were made from alloy ribbons (0.9 mm in width and ca. 20 μm in thickness)[2] and treated with aq HF prior to the electrochemical measurements, as described elsewhere.[3] The electrodes were spot-welded or clipped on Ta lead wires which were sealed in Pyrex glass tubings.

The electrochemical measurements were carried out in 1 M (M = mol dm^{-3}) NaOH containing various amounts of formaldehyde (0.003 - 1.0 M) under a stream of purified Ar gas. The formaldehyde (GR grade, Nakarai Chemicals, Tokyo) contained 7 wt% CH_3OH. A standard SCE or a Pt-Pt RHE was used as a reference electrode : All the potential values mentioned in this work are given on the RHE scale. Details of the cell and other experimental procedures were described previously.[1]

The rest potential was usually observed to be around -50 mV. Although this value is significantly more positive than the theoretical oxidation potential of HCHO (-0.22 V vs. RHE), it is the most negative potential observed among systems employing various carbonaceous fuels.

The electrocatalytic activity of Cu was very high for the eletro-oxidation of HCHO. In Fig. 1, we show typical cyclic voltammograms obtained on the Cu electrode in 1 M NaOH containing various amounts of HCHO. Even with HCHO of very

low concentration (10^{-2} M), the oxidation current was already quite significant. Thus, the oxidation became noticeable at potentials around 0.1 V and the hysteresis on the cyclic voltammograms, which is commonly observed in the electro-oxidation of carbonaceous compounds such as methanol, was small or almost absent in the range of 0 - 0.5 V. In addition, the electrocatalytic activity was very stable for a long period (several days) as compared with that observed in the oxidation of methanol on Pt electrodes. The Tafel plots of the oxidation current had a linear portion with the slope of about 120 mV decade^{-1}, which indicated that HCHO was oxidized by a rate-determining one-electron transfer reaction mechanism.

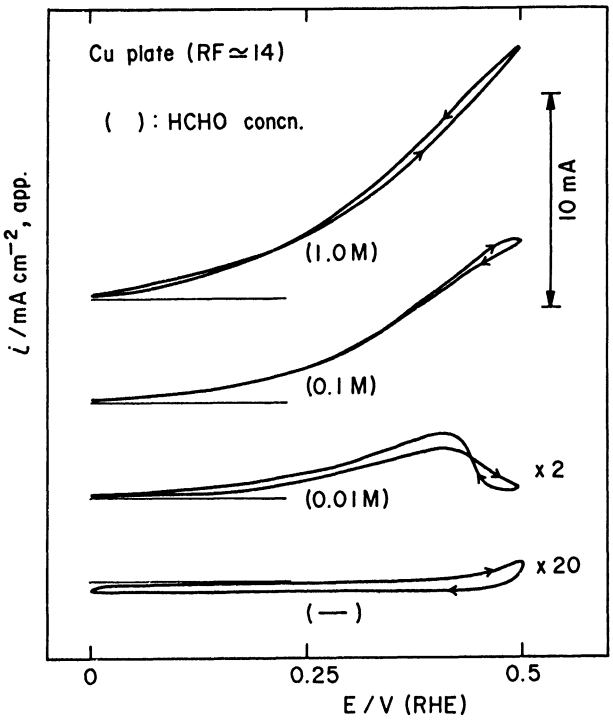


Fig. 1. Typical cyclic voltamograms observed on a Cu electrode in 1 M NaOH containing 0.01 - 1.0 M HCHO at 303 K. Potential sweep rate: 10 mV s^{-1}.

Much a larger electro-oxidation current was observed on the HF-treated amorphous Cu-Ti and Cu-Zr alloy electrodes which had large roughness factor (RF) values. The relationship between the current density and RF for the Cu and Cu-based amorphous alloy electrodes are shown in Fig. 2. The current increased initially in a proportional way with the RF values and the highest value reached on the a-$Cu_{33}Zr_{67}$ at 0.2 V was as high as 40 mA cm^{-2}. In the region of very high RF values, however, the current had a tendency to reach a saturation value: This might indicate that all the surface area of the porous alloy electrodes was no longer used effectively in the oxidation of HCHO. Nevertheless, the curve suggests that the electrode with the RF value of 100 - 200 is quite satisfactory for the HCHO electro-oxidation. The linear portions of their Tafel plots gave a slope of 120 mV decade^{-1}, similar to those in the case of the smooth Cu electrodes.

A kind of "induction period" was seen in Fig. 2 at low RF values. This might suggest that the amorphous alloys became electrocatalytically active only after they lost a significant amount of Ti or Zr so that their surface became sufficiently rich in Cu.

The dependence of the oxidation current density on the formaldehyde concentration on the Cu electrodes are shown in Fig. 3 (open circles). The log-log plot has no simple linearity but yields a smooth bending curve. At low concentrations, however, it is seen that the experimental data has a general tendency to approach a line with the slope of unity.

It appears reasonable to take the methyleneglycol ion,[4] $H_2CO\ OH^-$, as the reacting species, since the oxidation rate increases with increase in both HCHO and OH^-. The equilibrium constant of formation of methyleneglycol ion from HCHO and

OH^- was obtained from the difference in the pH value of NaOH solutions and those containing equimolar amounts of HCHO as K = 4.7 M^{-1}.

Also presented in Fig. 3 (filled circles) is the relation between the oxidation current and the concentration of methyleneglycol ion (M) evaluated from the reactant concentrations and the K value thus obtained. It may be concluded that the reaction is essentially of the first order with respect to M at low concentrations . The decrease of the reaction order in the higher concentration region may require more information before any definite interpretions be made; It is nevertheless likely that the methyleneglycol ion is adsorbed on the electrode surface prior to its discharge and the adsorption gradually approaches a full coverage in this high concentration region.

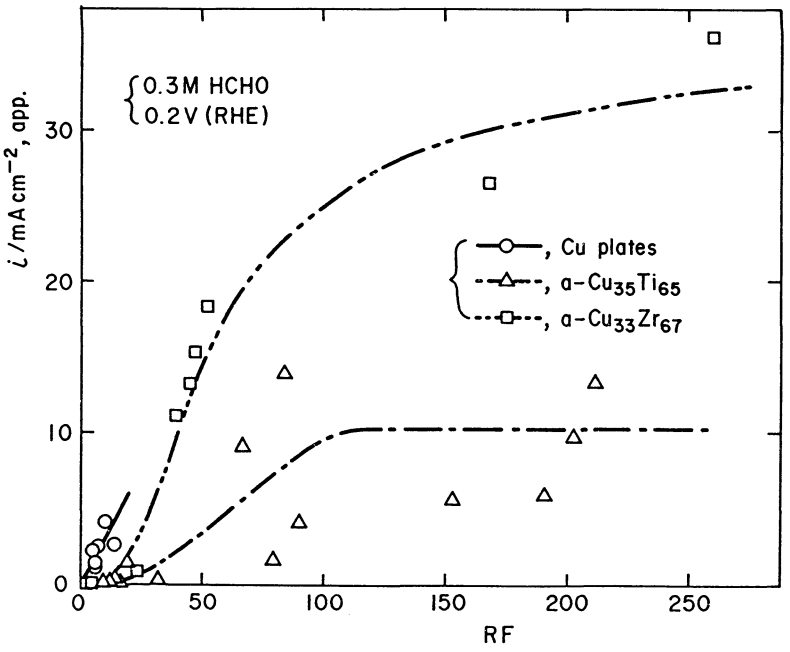


Fig. 2. Current density vs. roughness factor on Cu and Cu-based amorphous alloy electrodes in 0.3 M HCHO in 1M NaOH at 303 K. The i values are read at 0.2 V (RHE) on the cyclic voltammograms obtained with the potential scan range of 0 - 0.5 V and the scan rate of 10 mV s^{-1}.

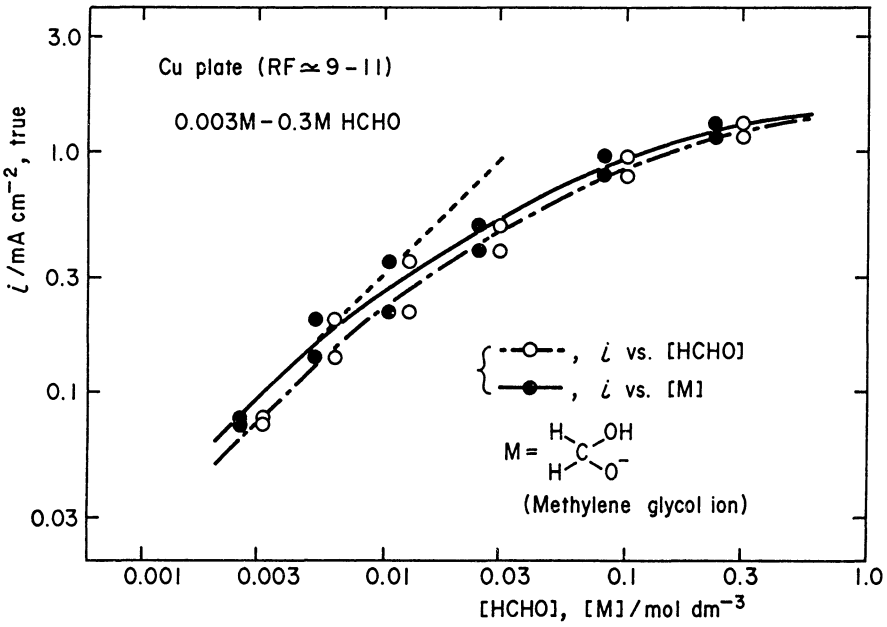
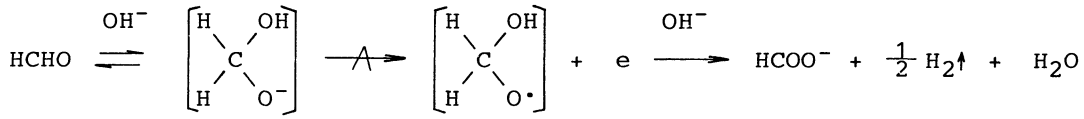


Fig. 3. Current density vs. formaldehyde (open circles) and methylene glycol ion (filled circles) concentration observed on Cu plates in 1 M NaOH at 303 K.

The number of electrons involved in the electro-oxidation was evaluated from the quantity of electricity required when a given amount of HCHO was completely electro-oxidized at a constant electrode potential. The number obtained was 0.97 equivalents mol^{-1} at 0.23 V in 1 M NaOH solution. As the partial oxidation of HCHO to $HCOO^-$ should

involve two electrons per HCHO molecule, value of unity indicates a different type of electro-oxidation. Meanwhile, evolution of hydrogen during the reaction, in spite of more positive electrode potentials than that of the RHE, was reported by Saito[5] on metal electrodes including Cu, and this was also confirmed in the present work.

Those experimental observations altogether support the reaction route which involves the methyleneglycol ion, as proposed previously.[5] Taking the one-electron transfer characteristics of the rate-determining step as obtained in this work, we may write



where $\not\rightarrow$ denotes the rate-determining step. This mechanism should be able to account for the experimental observation of the first order in HCHO and OH^-, the linear Tafel line with the slope of about 120 mV $decade^{-1}$, one electron involved in the overall reaction, and the hydrogen evolution along with the electro-oxidation reaction.

In summary, the electro-oxidation of HCHO on Cu-based electrodes, particularly the HF-treated amorphous alloys containing Ti or Zr, takes place very rapidly in alkaline solutions. The fuel cells based on this electrochemical system, therefore, appear very promising. Some further investigations may, however, be required towards more efficient use of folmaldehyde as the fuel, particularly electro-oxidation of $HCOO^-$ and H_2, and technical problems possibly associated with the use of alkaline solutions.

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References

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