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Short communication

Electrochemical oxidation of hydrazine and its derivatives on the surface of metal electrodes in alkaline media

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ABSTRACT

Electrochemical oxidation of hydrazine and its derivatives on the surface of various metal electrodes in alkaline media was investigated. A comparison of various polycrystalline metal electrodes (Ni, Co, Fe, Cu, Ag, Au, and Pt) showed that Co and Ni electrodes have a lower onset potential for hydrazine oxidation than the Pt electrode. The onset oxidation potential of APA (aminopolyacrylamide), a hydrazine derivative (−0.127 V vs. reversible hydrogen electrode, RHE), was similar to that of hydrazine hydrate (−0.178 V vs. RHE) in the case of the Co electrode. APA oxidation was possible because of hydrazine desorption that was caused by APA hydrolysis. The hydrolysis reaction was brought about by a heat treatment. This result suggests that the hydrazine hydrolysis reaction of hydrazine derivatives makes it possible to store hydrazine hydrate safely.

1. Introduction

In the 1960s and 1970s, a hydrazine–air fuel cell was investigated intensively in order to gain more information about an alkaline fuel cell using a liquid alkaline electrolyte [1]. Then, a hydrazine fuel cell using a polymer electrolyte was investigated [2–5]. Hydrazine is one of the most popular reduction agents. Therefore, hydrazine oxidation on platinum [6–10], palladium [11–13], nickel [11,14–16], cobalt [13], gold [10], mercury [17–20], and silver [19] electrodes in alkaline media was investigated intensively from the 1960s to the 1980s. In recent times, the research work in this field has been investigated on of hydrazine oxidation on platinum [21] and Ag/Ti [22] electrodes in alkaline media.

Hydrazine is toxic and probably even mutagenic. Some hydrazine derivatives have lower toxicity and mutagenicity than hydrazine itself. Furthermore, some hydrazine derivatives exist as solids. This decreases the risk of hydrazine diffusion in the environment. However, there are few papers on electrochemical oxidation of hydrazine derivatives [23,24]. In this study, electrochemical oxidation of hydrazine derivatives, which has not been reported anywhere else, on the surface of various metals (Ni, Co, Fe, Cu, Ag, Au, and Pt) has been investigated in alkaline media.

2. Experimental

2.1. Preparation of hydrazine derivatives and KOH aqueous solutions

The hydrazine derivatives used in this study were methyl carbazate ($N_2H_3COOCH_3$, MW = 90.08), carbodihydrazide ($N_2H_3CON_2H_3$, MW = 90.09), hydrazine carbonate ($(N_2H_4)_2CO_2$, MW = 108.1), and aminopolyacrylamide (APA, $-[CH_2CH(CONHNH_2)]_{0.8}-[CH_2CH(CONH_2)]_{0.2}-$, MW/unit = 83.09). All hydrazine derivatives and hydrazine hydrate (60 wt.%) were obtained from Otsuka Chemicals Co., Ltd. Potassium hydroxide (85 wt.%) was purchased from Hayashi Junyaku K.K.

All hydrazine derivatives except APA were dissolved in 1 M KOH aqueous solution. APA was suspended in 1 M KOH aqueous solution. This suspension was heated at 60 °C for 15 min because APA exhibited very less solubility at room temperature. As a reference, an aqueous solution of hydrazine hydrate ($N_2H_4 \cdot H_2O$, MW = 50.06) in 1 M KOH was prepared. The concentration of hydrazine hydrate and hydrazine derivatives in KOH aqueous solutions was 5 wt.%; these solutions were used for carrying out electrochemical measurements.

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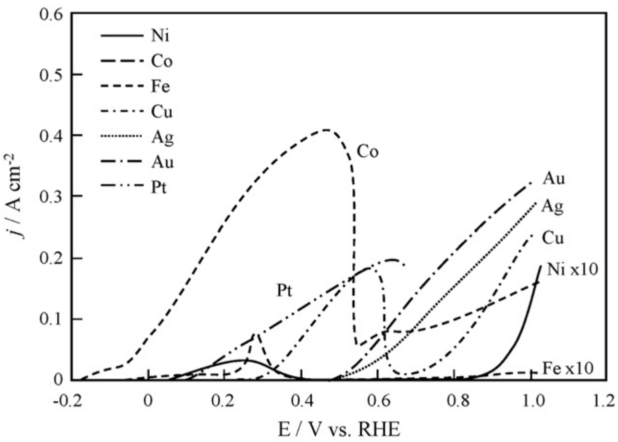

Fig. 1. Oxidation of hydrazine on a metal disk electrode in 5 wt.% hydrazine hydrate in 1 M KOH aqueous solution. Sweep rate was 20 mV s^{-1}.

2.2. Characterization of electrochemical oxidation on the surface of metals

Electrochemical oxidation performances were measured using cyclic voltammetry (CV), and the data were measured during the second cathodic half cycle. The scan speed of the potential sweep was 20 mV s^{-1}. A single component of the three-electrode glass cell was operated at 30 °C. The apparent area of the disk electrodes was 1.77 mm^2 for Fe, 0.79 mm^2 for Co, 1.77 mm^2 for Ni, 2.01 mm^2 for Cu, 2.01 mm^2 for Ag, 7.07 mm^2 for Pt, and 2.01 mm^2 for Au. The metal disk electrodes were polished with alumina. A Pt coil was used as a counter electrode, and an Ag/AgCl-saturated KCl solution electrode was used as a reference electrode. Note that all the potentials given in this paper are quoted on the reversible hydrogen electrode (RHE) scale. All metal disk electrodes, the counter electrode, and the reference electrode were purchased from BAS Japan. Before each experiment, all solutions were deoxygenated by purging with pure argon for at least 15 min and then, potential sweep voltammetry was carried out using a solution without hydrazine until the waves were sufficiently stable for electrode conditioning.

3. Results and discussion

The voltammograms obtained for each electrode in hydrazine hydrate solution are shown in Fig. 1. The onset potential for each electrode was 0.654 V for Fe, −0.178 V for Co, −0.108 V for Ni, 0.193 V for Cu, 0.378 V for Ag, 0.384 V for Au, and 0.062 V for Pt. The onset potential for the hydrazine oxidation on the Pt electrode was similar to that mentioned in a previous work [21]. The onset potentials for hydrazine hydrate oxidation on the Co and Ni electrodes were lower than the onset potential for oxidation on the Pt electrode at 30 °C. The voltammograms showed that in the low overpotential region (<0.2 V), Co and Pt exhibited high catalytic activity during hydrazine oxidation. In particular, Co exhibited higher catalytic activity than Pt in this region. This result is similar to that given in a previous report by Fukumoto et al.; in their study, Fukumoto et al. used electrodes prepared by chemical plating. However, the result obtained in the present study shows the difference in the catalytic activities of Co and Pt more clearly.

Oxidation current in the case of the Fe electrode was observed at oxidation potentials between −0.1 and 0.4 V. This current was observed in the case without hydrazine. Therefore, it could be concluded that the Fe electrode itself was oxidized. In contrast, the oxidation current in the case of the other metal electrodes without hydrazine was insignificant and thus not considered.

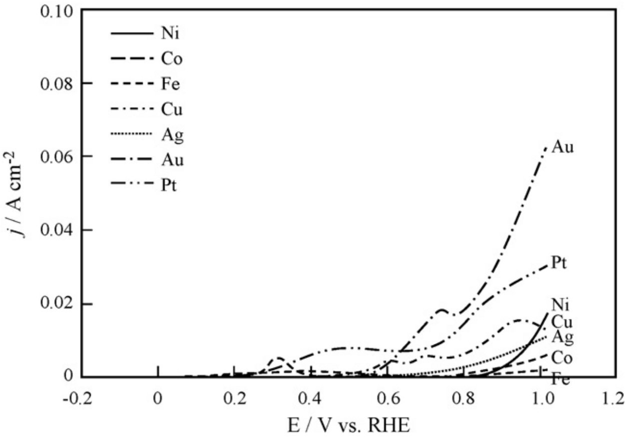

Fig. 2. Oxidation of carbozihydrazide on a metal disk electrode in 5 wt.% hydrazine derivative in 1 M KOH aqueous solution. Sweep rate was 20 mV s^{-1}.

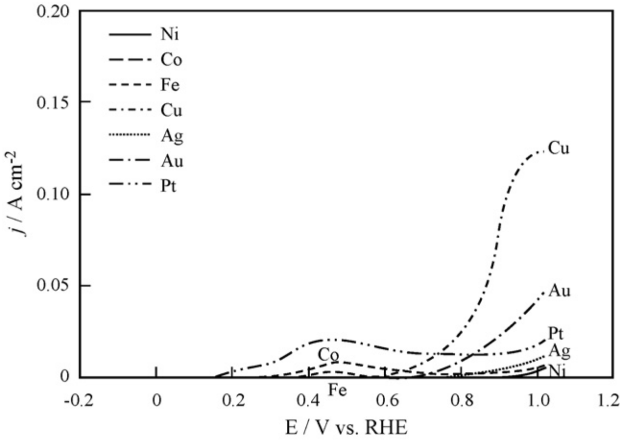

Fig. 3. Oxidation of methyl carbazate on a metal disk electrode in 5 wt.% hydrazine derivative in 1 M KOH aqueous solution. Sweep rate was 20 mV s^{-1}.

The electrochemical oxidation of hydrazine in alkaline media can be expressed by the following equation [3,5]:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \qquad (1)$$

The voltammograms for each electrode in the solution or suspension of derivatives are shown in Figs. 2–4. All derivatives exhibited a lower current density than hydrazine hydrate.

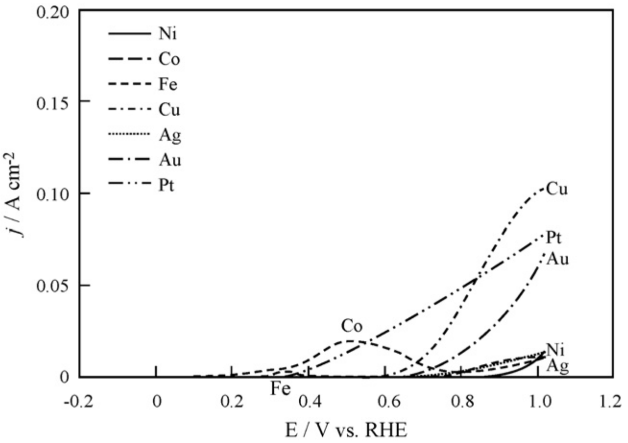

Fig. 4. Oxidation of hydrazine carbonate on a metal disk electrode in 5 wt.% hydrazine derivative in 1 M KOH aqueous solution. Sweep rate was 20 mV s^{-1}.

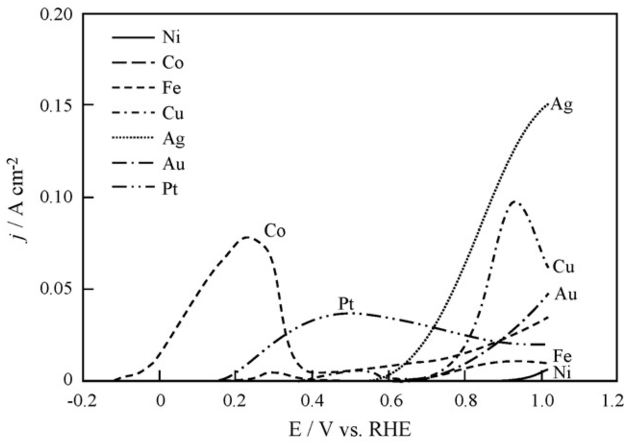

Fig. 5. Oxidation of APA on a metal disk electrode in 5 wt.% hydrazine derivative in 1 M KOH aqueous solution. Sweep rate was 20 mV s^{-1}.

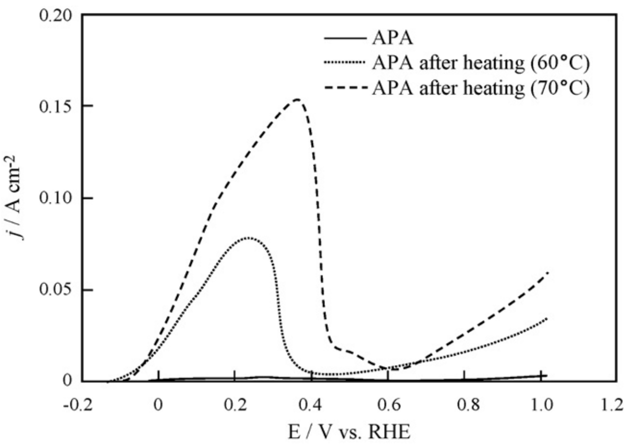

Fig. 6. Change in oxidation of 5 wt.% APA on the Co disk electrode at 30 °C after heat treatment at 60 °C and 70 °C. Sweep rate was 20 mV s^{-1}

As observed from Figs. 2–4, the voltammograms for the hydrazine derivatives showed that these derivatives were not oxidized in the presence of any of the catalysts in the low overpotential region (<0.2 V). This implied that the hydrazine derivatives did not get oxidized because of the presence of strong and stable N–N bonds. In particular, carbodihydrazide exhibited a low current density (Fig. 2). This suggested that the N–N bonding was strong and stable.

By using a suitable catalyst, the strength of the N–N bonds in the hydrazine derivatives could lower. Pt showed higher catalytic activity than Co during the oxidation of both carbodihydrazide (Fig. 2) and methyl carbazate (Fig. 3). In particular, Co showed no catalytic properties during the oxidation of carbozihydrazide. Further, these results suggest that Co exhibited extraordinary catalytic activity during the oxidation of the N–N bonds of free hydrazine. The N–N bonding of hydrazine carbonate was similar to that of free hydrazine. In fact, Co exhibited considerable catalytic activity during the oxidation of hydrazine carbonate.

Fig. 5 shows the oxidation of APA on the electrodes. APA exhibited a relatively higher current density than the other derivatives. Moreover, APA was oxidized in the low overpotential region (<0.2 V). The onset potential of APA was similar to that of hydrazine hydrate. Furthermore, the electrochemical behavior of APA was very similar to that of hydrazine hydrate because APA exhibited catalytic activity in the low overpotential region (<0.2 V) and Co showed higher catalytic activity during the oxidation of APA oxidation than did Pt. However, before the measurement, in order to prepare an aqueous solution, APA was heated at 60 °C. Therefore, APA might have decomposed partially and desorbed free hydrazine. From the result of ion chromatography, we detected 0.735% of hydrazine in the APA suspension after the measurement. Therefore, it was suggested that APA underwent hydrolysis and desorbed hydrazine in water. The hydrolysis reaction can be expressed as follows:

$$-[CH_2CH(CONHNH_2)]- + H_2O \rightarrow -[CH_2CH(COOH)]- + N_2H_4 \qquad (2)$$

Results of the electrochemical measurements and ion chromatography suggest that the hydrazine desorbed as given in Eq. (2) was oxidized.

Ag exhibited higher catalytic activity during the oxidation of APA than Au in the high potential region (>0.6 V). In contrast, Au exhibited slightly higher catalytic activity during the oxidation of hydrazine than Ag. One of the possible reasons for these higher values is the direct oxidation of hydrazine derivatives in the high overvoltage region.

In order to understand the APA hydrolysis better, APA was oxidized at 30 °C. Voltammograms recorded before and after the heat treatments at 60 °C and 70 °C for 15 min were used for comparison and are shown in Fig. 6. Hydrolysis proceeded strongly with the heat treatment. In contrast, hydrolysis was not observed before the heat treatment. When heat treatment was carried out at 70 °C rather than at 60 °C, a higher current density was observed. The current density was 68 times higher than without thermal history at 70 °C. This result showed that APA hydrolysis could be controlled by temperature and that the hydrolysis reaction proceeded faster at 70 °C than at 60 °C. APA did not react directly on the electrode. However, it is applicable to fuel cell using hydrazine desorption from APA when it is heated up. These results suggest that the hydrazine hydrolysis reaction of hydrazine derivatives makes it possible to store hydrazine hydrate safely.

4. Conclusions

The electrochemical oxidation of hydrazine and hydrazine derivatives on the surface of various metals was investigated in alkaline media. The experimental results are summarized as follows:

1. Co and Ni showed lower onset potentials than Pt for the hydrazine electrochemical oxidation. Co showed higher catalytic activity than Pt in the low overpotential region.
2. Onset potential for the APA oxidation was similar to that for hydrazine oxidation owing to the hydrazine desorbed from APA upon hydrolysis. All catalysts aided the oxidation of hydrazine derivatives in the low overpotential region. However, oxidation reactions of carbozihydrazide and methyl carbazate differed from that of the oxidation of hydrazine because Pt exhibits a higher catalytic activity than Co.
3. Hydrolysis of APA occurred with the heat treatment. The reaction could be controlled by temperature.

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