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CATALYTIC PRE-WAVE OF NICKEL(II) AND FORMATION OF NICKEL SULFIDE IN THIOSULFATE SOLUTIONS AT MERCURY ELECTRODES

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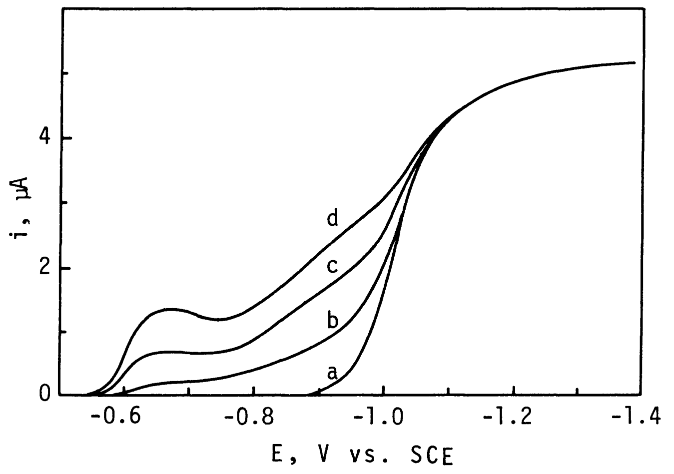
It was found that nickel(II) in thiosulfate solutions at mercury electrodes gave a catalytic pre-wave, and NiS was produced in the electroreduction process of nickel(II). The electrode reaction which is proceeded by the formation of $Ni(S_2O_3)$ from $Ni(H_2O)_6^{2+}$ is retarded by the adsorption of NiS at higher concentrations of $S_2O_3^{2-}$. It has been proposed that the formation of NiS is due to the chemical reduction of $S_2O_3^{2-}$ bound to $Ni(0)S_2O_3^{2-}$ by the electroreduced metallic nickel.

The electroreduction of nickel(II) in thiocyanate solution is quite complex, because in the electroreduction process of nickel(II) the reduction of thiocyanate ion also proceeds with the formation of cyanide and sulfide ions.[1-4] The present author[1-3] has proposed that the reduction of SCN^- in the presence of Ni(II) is due to the chemical reduction of SCN^- by the electroreduced metallic active nickel, while Galus et al.[5] have argued against such a possibility and reported that thiocyanate ion coordinated to nickel(II) was directly reduced at the mercury electrode, but they[6] have recently presented a similar mechanism to that described previously.[3]

It would be worthwhile to investigate the electrode reaction of nickel(II) in the presence of other sulfur-containing inorganic ligands other than thiocyanate ion. This communication deals with the electrode reaction of Ni(II) in thiosulfate solutions at dropping as well as stationary mercury electrodes. Very little work has been reported on the electrochemistry of metal ions in thiosulfate solutions.[7]

Upon the addition of $S_2O_3^{2-}$ to the perchlorate solutions containing nickel(II), nickel(II) gave a polarographic pre-wave with the half-wave potential of -0.62 V vs. SCE, as shown in Fig. 1. The effect of thiosulfate concentration on the current-time(i-t) curve for the pre-wave during the life of a mercury drop is shown in Fig. 2. The value of the exponent of the i-t curve obtained in the presence of 0.05 M $S_2O_3^{2-}$ was found to be 0.62. The pre-wave increases in height with increasing thiosulfate concentration, however, the diffusion-controlled current level is not reached even at concentrations as high as 1.0 M $S_2O_3^{2-}$. This behavior is quite different from that of the catalytic pre-waves of nickel(II) in the presence of SCN^- and other compounds. Koutecký treatment[8] was applied to determine the electroactive species involving in the pre-wave. For the thiosulfate concentration from 0.03 to 0.1 M at an ionic strength of 0.5 M ($NaClO_4$) and the controlled drop time of DME of 4.95 s, the plot of $\log[i_k/(i_d-i_k)]$ against $\log[S_2O_3^{2-}]$ gave a straight line with a slope close to unity, indicating that one thiosulfate ion participates in a slow kinetic wave.



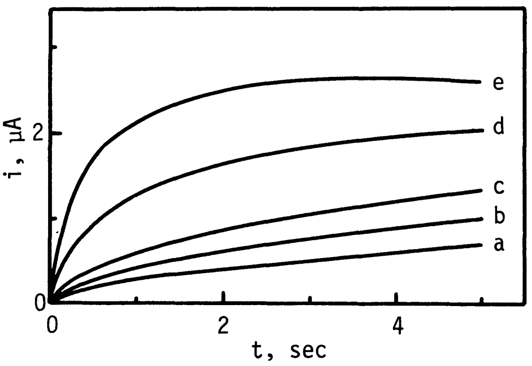


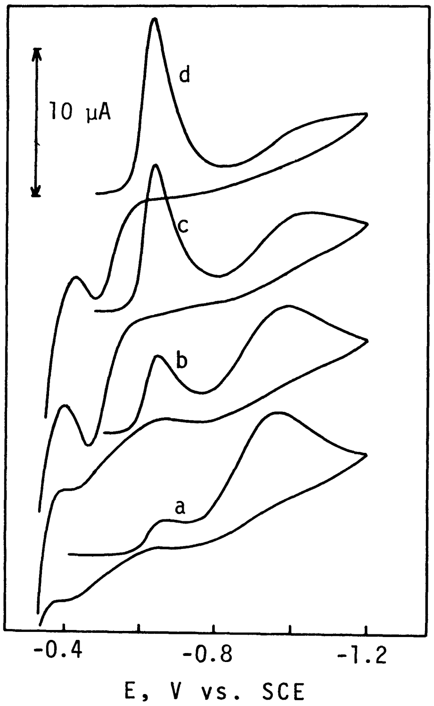
Fig. 1. Effect of $Na_2S_2O_3$ on the reduction waves of 1 x 10^{-3} M Ni(II) at *t*=4.95 s, I=0.5 M($NaClO_4$), and 25°C. [$S_2O_3^{2-}$]: a, 0; b, 0.02; c, 0.05; d, 0.1 M.

Fig. 2. Effect of $S_2O_3^{2-}$ on the *i-t* curves for the reduction of 1 x 10^{-3} M Ni(II) at DME, E=-0.70 V vs. SCE, and *t*=4.95 s. At thiosulfate concentrations below 0.1 M, an ionic strength was maintained at 0.5 M with $NaClO_4$. [$S_2O_3^{2-}$]: a, 0.05; b, 0.07; c, 0.1; d, 0.2; e, 1.0 M.

The cyclic voltammograms and chronoamperometric curves of nickel(II) in thiosulfate solutions are shown in Figs. 3 and 4, respectively. With increase in thiosulfate concentration, the cathodic peak corresponding to the polarographic pre-wave increases in height, while the opposite effect is observed on the second peak for the reduction of hydrated nickel(II). The reduction current, at low thiosulfate concentration, remains almost unchanged with the electrolysis time after charging the electrical double layer, as shown in curves a and b of Fig. 4. This result also suggests that the electrode reaction of the cathodic wave near -0.7 V is kinetic-controlled mechanism.

With further addition of $S_2O_3^{2-}$ above 0.2 M, the polarographic pre-wave as well as the voltammetric wave increase in height, but the *i-t* curves at both DME and HMDE are unsual in their shapes, as shown in Figs. 2 and 4. The *i-t* curve obtained with the DME exhibits a maximum, as shown in curve e of Fig. 2. The reduction current obtained with the HMDE decreases rapidly and drops off to an almost zero level within several seconds. These results suggest that some reduction products of the electrode reaction inhibit further reduction of nickel(II)-thiosulfate complex at the mercury electrode.

Controlled potential reduction of nickel(II) at a mercury pool electrode was carried out in order to identify the reduction products for the electrode reaction. Electrolysis was performed with the solution containing 2 x 10^{-3} M Ni(II) and 0.5 M $Na_2S_2O_3$. With the electrode potential controlled at -0.70 and -0.85 V, respectively, the surface of the mercury pool in each case was covered with the precipitate of nickel sulfide. The analysis of nickel sulfide was carried out by the procedure previously reported.[3]



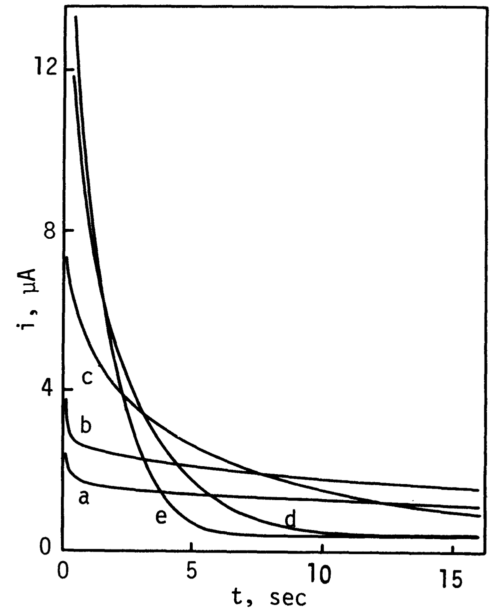


Fig. 3. Effect of $S_2O_3^{2-}$ on the cyclic voltammograms of 1 x 10^{-3} M Ni(II) at scan rate of 0.05 V s^{-1} and the surface area of HMDE of 0.047 cm^2. [$S_2O_3^{2-}$]: a, 0.1; b, 0.2; c, 0.5; d, 1.0 M.

Fig. 4. Effect of $S_2O_3^{2-}$ on the chronoamperometric curves for the reduction of 1 x 10^{-3} M Ni(II) at -0.70 V vs. SCE. [$S_2O_3^{2-}$]: a, 0.07; b, 0.1; c, 0.2; d, 0.5; e, 1.0 M.

The formation of nickel sulfide during the electroreduction of nickel(II) in thiosulfate solution might be explained by taking into account the electrolytic reduction of $S_2O_3^{2-}$ adsorbed at the surface of the mercury covered with the electrodeposited metallic nickel, as has been proposed by Galus et al., in the case of the formation of nickel sulfide during the electroreduction process of nickel(II) in thiocyanate solution at mercury electrodes.$^{5)}$ Such a possibility seems to be improbable because SCN^- as well as $S_2O_3^{2-}$ react rapidly with an active nickel such as Raney nickel to yield nickel sulfides.$^{9)}$ Moreover, nickel(II) in acidic thiocyanate solution exhibits a catalytic current resulting from the cyclic regeneration of the electroactive nickel(II),$^{3)}$ although attempts to obtain a catalytic current involving the cyclic regeneration of nickel(II) in acidic thiosulfate solution were unsuccessful because thiosulfate ions decomposed in acidified solution. If the chemical reactivity of the electrodeposited metallic nickel is the same as that of Raney nickel, the electrodeposited metallic nickel could also react with thiosulfate ion to produce nickel sulfide, although the thermodynamic data on the chemical reactions of SCN^- and $S_2O_3^{2-}$ with metallic nickel are not presently available in the literature. It is therefore reasonable to postulate that the formation of nickel sulfide is attributable to the chemical reaction of $Ni(0)S_2O_3^{2-}$ adsorbed at the mercury electrode.

On the basis of these experiments, the reduction of nickel(II) in thiosulfate solution at the mercury electrode can be explained by the following reactions of sequence:

$$\mathrm{Ni(H_2O)_6^{2+}} + [\mathrm{S_2O_3^{2-}}]_{ads} \xrightarrow[\text{slow}]{} [\mathrm{Ni(S_2O_3}]_{ads} \qquad (1)$$

$$[\mathrm{Ni(S_2O_3)}]_{ads} + 2\,e^- \xrightarrow[\text{fast}]{} [\mathrm{Ni(0)S_2O_3^{2-}}]_{ads} \qquad (2)$$

$$[\mathrm{Ni(0)S_2O_3^{2-}}]_{ads} \longrightarrow \begin{cases} \rightarrow \mathrm{Ni(0)metal} + \mathrm{S_2O_3^{2-}} & (3a) \\ \rightarrow \mathrm{NiS_{ads}} + \mathrm{SO_3^{2-}} & (3b) \end{cases}$$

This elucidation is similar to that for the catalytic reduction of thiocyanate ions in the presence of nickel(II)[1-3] and cobalt(II).[10,11] The rate of the chemical reaction of $\mathrm{Ni(0)S_2O_3^{2-}}$ seems to be more rapid than that of $\mathrm{Ni(0)SCN^-}$. If the electrode surface is to a large extent covered with nickel sulfide, reaction (2) is strongly inhibited. Therefore, the diffusion-controlled current level is not reached even at concentrations as high as 1.0 M $\mathrm{S_2O_3^{2-}}$.

References and Notes

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9) Raney nickel-aluminum alloy(Ni:50 wt.%) was developed using the procedures given in the literature(H. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, 1955, p. 176). The resultant catalyst was washed with distilled water untill the washing became neutral, and then stored in distilled water. The Raney nickel, ca 0.2 g, was added to the solution containing 25 ml of 0.2 M $\mathrm{Na_2S_2O_3}$. The solution was shaken for several times. The qualitative analysis of the precipitate was carried out by polarographic method.[1]
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