Studies of the Nickel-Sulfur Electrodeposited Cathode

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Nickel electrodeposit containing sulfur (Ni-S) as a low hydrogen overvoltage cathode in NaOH solutions was studied. The hydrogen overvoltage was related to the conditions of electroplating of Ni-S such as the solution composition and the current density. The Ni-S electrodeposited cathode deactivated gradually and the physico-chemical properties of the electrodeposited layer changed with time during an accelerated life test in concentrated NaOH solution at high current densities: 150 A/dm². However, the material is expected to work well for more than 6 months if the current density is low, say 25 A/dm².

1 Introduction

Low carbon steel plate or screen is used as cathode of the water electrolyzer and of the diaphragm-type chlor-alkali cells because iron and steel are corrosion resistant to concentrated alkali and the hydrogen overvoltage (h.o.v. hereafter) of iron is low enough¹⁾, say 0.4V at 20 A/dm² in 2.5N NaOH at 90°C. However, a number of materials as cathode are being studied to minimize the cathode overvoltage and to save the energy consumption for electrolysis^{2~5)}.

Of these, electrodeposited nickel containing sulfur, termed "Ni-S", was employed as a low h.o.v. cathode in an industrial water cell after World War II in this country. The patent claims use of Ni(CNS)₂ as an electroplating bath^{6~8)}. Of course, the same deposit can be obtained from nickel sulfate solutions containing a certain amount of KCNS, whereas formation of double salts such as K₂Ni(SO₄)₂·6H₂O is a problem. Therefore, the modified Watt-type bath containing an adequate amount of KCNS was mostly examined because it was cheap compared to Ni(CNS)₂.

Since the patent and the related papers^{6~8)} have not described details of the Ni-S cathode, experiments have been conducted to obtain optimum conditions for preparation. The paper deals with the physico-chemical properties of the materials obtained, and the polarization

characteristics of the Ni-S cathode in NaOH solutions. Deactivation as cathode with time under service conditions is also discussed. For this purpose, an accelerated life test at high current densities has been conducted for several months.

2 Experimental Procedure

2.1 Electroplating

A typical composition of the Watt bath is shown in the footnote of Table 2. The electroplating solution was prepared with analytically pure chemicals and doubly distilled water. The solution was agitated by a magnetic stirrer or air-bubbling electrolysis. Thick electrolytic nickel plate was used as anode. Low carbon iron sheet cathodes in adequate sizes were degreased with hot NaOH solution, pickled with HCl, and rinsed enough prior to experiment. Platinum and copper sheets were also employed in some cases.

A small cathode of 5 mm wide and 10 mm long was prepared for polarization measurements because of limitation of capacity of the current interrupter as power source. A Luggin-Haber probe connecting with a KCl saturated calomel electrode (SCE) was located near the working cathode. The IR-drop between the Luggin and the cathode was calibrated by the current interruption technique.

An electronic coulometer was employed to determine the current efficiency for electroplating. The deposited material was dissolved with concentrated HCl containing a small amount of oxidation agent such as NaClO₃, and

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chemical analyses of Ni and S were conducted by the methods shown in Japan Industry Standards (JIS), G 1216 for Ni and G 1215 for S (see Appendix).

A simple handmade contractometer was used to determine the internal stress of the electrodeposit. One end (20 mm long) of a copper sheet cathode of 10 mm wide, 120 mm long, and 0.2 mm thick was cramped by a Lucite resin holder, and was positioned horizontally in a cell, also Lucite, of 15 cm wide, 20 cm long, and 5 cm deep. The back side of copper sheet was lined with soft Silicone plastic for electric insulation. Therefore, the working cathode was 10 cm² area. A thick nickel plate anode of 10 mm wide and 100 mm long was located 10 cm far the cathode in parallel. The current distribution on the cathode was confirmed to be uniform. Deviation of the free edge of cathode was observed by a microscope with an accuracy of 1/100 mm. Although the internal stress could be calculated with some assumptions for simplification⁹, only deviation of the free edge in mm was plotted in Fig. 4.

2.2 Hydrogen overvoltage measurements

Polarization measurements of the Ni-S cathode in hydrogen saturated 2.5 N NaOH solution at 90°C were conducted by the galvanostatic steady state method. The Ni-S cathode of 1 cm² area was positioned in a polyethylene cell of about 0.5 l in volume. A Pt foil was used as anode. Caustic soda solution was pre-electrolyzed under hydrogen saturated conditions with large Pt electrodes, both anode and cathode, in a separate polyethylene cell for a day or more to remove trace impurities and was brought to the measurement cell. Such procedure was confirmed to be very important to avoid troubles with contamination and to obtain reproducible results.

The cathode potential was measured by a Luggin-Haber probe in connection with a hydrogen reference electrode (HE) consisting of a platinized platinum sheet in hydrogen saturated solution of 2.5 N NaOH at 90°C. The solution IR drop between the working cathode and the Luggin probe was calibrated by the current interruption technique. Therefore the cathode potential determined is equal to the hydrogen overvoltage directly. The differential

capacitance of the working cathode was calculated from the oscilloscope trace of the decay curve of the potential *vs.* time curve.

The surface of the Ni-S electrodeposited specimens was observed by the scanning electron microscope (SEM), and was also examined by the X-ray diffraction equipment.

2.3 Service life test

A number of specimens to be tested was positioned in a plastic cell of about 5 l in volume containing 2.5 N NaOH solution. A large Ni plate (10 cm wide and 20 cm long) was used as an insoluble anode. The Ni-S cathode was strong at low current densities. For example, no significant failure was found after 6 months of electrolysis at 25 A/dm². Therefore, the accelerated life test was conducted at 150 A/dm² in general to shorten the time of experiment. Preliminary experiment showed that the service life time or the time-to-failure (TTF) was related to the ampere-hours of electrolysis. The solution temperature was in the range 35~40°C during electrolysis by joule heat, whereas it was not controlled.

The test specimen was picked out from the life test cell at adequate intervals, and the potential *vs.* current density curve was measured by the preceding method. Since the data fluctuated, five specimens at least were prepared and examined under each condition so as to avoid erroneous conclusion.

3 Results and Discussion

3.1 Conditions for electroplating

The cathode potential or the current density during electroplating is an important factor for preparation of the Ni-S. At low current densities, bright nickel free of sulfur was obtained even the plating bath contained enough KCNS, and its h.o.v. in NaOH solution was high. The cathode potential became less noble when the current density increased, and gray deposit containing sulfur was obtained. The h.o.v. of such materials in NaOH solution was considerably low compared to a plain Ni or Fe. At high current densities more than 10 A/dm², powdered deposit was obtained. The current density suitable for preparation of the Ni-S electrodeposition was in the range 1~5 A/dm²

depending on the solution composition, temperature, and agitation of solution. Consequently, most experiments were conducted at 2 A/dm² for 1 hour, thereafter. The thickness of Ni deposit was about 25 μ m.

Further experiments were took place under various conditions of the Ni²⁺ concentration [Factor A], the KCNS concentration [B], the solution pH [C], and the temperature [D]. Of these, only Factor B could be changed in a wide range (0~30 g/l), otherwise suitable electrodeposition could not be obtained. The h.o.v. in 2.5 N NaOH at 90°C and 20 A/dm² was measured to evaluate the cathode performance as shown in Table 1. The larger the KCNS concentration in the plating solution the lower was the h.o.v. in NaOH solution. Three other factors were not significant in

the range of experiment.

The sulfur content in the deposited layer increased significantly when the KCNS concentration in the plating solution was high as shown in Table 2. The material obtained from a solution containing 30 g/l KCNS contained more than 5% of S to Ni, and the h.o.v. in NaOH solution was very low. The current efficiency for Ni deposition was around 95% in the modified Watt-type bath in comparison with almost 100% of the Watt-type bath. A problem of the modified Watt-type bath was formation of double salt precipitate such as K₂Ni(SO₄)₂·6H₂O when the KCNS concentration was higher than 40 g/l. With those results, the solution composition of modified Watt-type bath and the operating conditions have been established as follows:

Table 1 Statistical analysis of conditions of electroplating of Ni-S

KCNS concentration g/l	NiRO ₄ ·6H ₂ O concentration, g/l				
		263 (A ₁)	132 (A ₂)	66 (A ₃)	33 (A ₄)
	(Sequence of experiment)				
30 (B ₁)	pH	2 (C ₁)	3 (C ₂)	4 (C ₃)	5 (C ₄)
	temp., °C	25 (D ₁)	40 (D ₂)	55 (D ₃)	70 (D ₄)
3 (B ₂)	pH	3 (C ₂)	2 (C ₁)	5 (C ₄)	4 (C ₃)
	temp., °C	55 (D ₃)	70 (D ₄)	25 (D ₁)	40 (D ₂)
0.3 (B ₃)	pH	4 (C ₃)	5 (C ₄)	2 (C ₁)	3 (C ₂)
	temp., °C	70 (D ₄)	55 (D ₃)	40 (D ₂)	25 (D ₁)
0.03 (B ₄)	pH	5 (C ₄)	4 (C ₃)	3 (C ₂)	2 (C ₁)
	temp., °C	40 (D ₂)	25 (D ₁)	70 (D ₄)	55 (D ₃)
	(Hydrogen overvoltage in mV)*				
30 (B ₁)		C ₁ D ₁ 375	C ₂ D ₂ 225	C ₃ D ₃ 185	C ₄ D ₄ 185
3 (B ₂)		C ₂ D ₃ 350	C ₁ D ₄ 475	C ₄ D ₁ 330	C ₃ D ₂ 290
0.3 (B ₃)		C ₃ D ₄ 505	C ₄ D ₃ 510	C ₁ D ₂ 485	C ₂ D ₁ 350
0.03 (B ₄)		C ₄ D ₂ 510	C ₃ D ₁ 530	C ₂ D ₄ 530	C ₁ D ₃ 540

* In 2.5 N NaOH at 90°C and 20 A/dm²

Table 2 Chemical composition of Ni-S electrodeposit and current efficiency at 2 A/dm² and 40°C

KCNS conc. g/l	Coulombs	Weight, mg			S/Ni (×100)	C.E. for Ni (%)
		Total	Ni	S		
0	1221	371.0	371.0	0	0	100.0
0.03	1288	379.6	378.8	0.8	0.21	97.1
0.3	1300	379.1	373.1	6.0	1.61	94.6
3.0	1275	376.5	365.8	10.7	2.93	94.5
30.0	1161	354.8	336.9	17.9	5.31	95.6

Basic composition of plating solution: 263 g/l NiSO₄·6H₂O, 47.5 g/l NiCl₂·6H₂O, 30 g/l H₃BO₃, pH=4.0

Fig. 1 Polarization curves of Ni rotating disk cathode (2200 RPM) in various solutions at room temperature

Solution composition = 130~260 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 40~50 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ + 30 g/l KCNS + 30 g/l H_3BO_3 , pH=4.0. Temperature = 40~50°C. Current density = 2~5 A/dm².

The polarization curves of a Ni rotating disk cathode in NiSO_4 solutions with and without KCNS are shown in Fig. 1. A typical Tafel line with the slope of 130 mV/decade was obtained at low current densities, and was independent of the solution composition. Bright Ni deposit was obtained from the Watt-type bath (1.2N NiSO_4) even at high current densities (50 A/dm², for example), if the rotating speed of the cathode was high (2200 RPM). On the other hand, the cathode in dilute NiSO_4 solutions free of KCNS was polarized greatly at relatively low current densities (closed points in Fig. 1). The current density at a given potential, -1.2V vs. SCE, for example, increased with increase of the NiSO_4 concentration and the rotating speed of the cathode.

It is well-known that Ni^{2+} forms its complex ions of several forms with CNS^- depending on the CNS^- concentration. With the stability constant¹⁰⁾, most probable form of cations in the modified Watt-type bath is estimated to be $\text{Ni}(\text{CNS})^+$. The polarization curves in solutions containing KCNS were almost independent of the NiSO_4 concentration in the range of experiment (0.04~1.2 M Ni^{2+}) as shown by the open points in Fig. 1.

Figure 2 shows the potential sweep curves of Pt and Ni electrodes in 1M KCl with and without KCNS . The polarization curve of Ni

Fig. 2 potential sweep curves of Pt and Ni electrodes in KCl solutions (pH=5). Sweep rate = 120 s/V, Mixed solution = 1 M KCl + 30 g/l KCNS

cathode was close to that of Pt cathode, and was not affected by addition of KCNS . The top curve in Fig. 2 shows the polarization curve of a Pt anode in KCl solution where chlorine evolution takes place. The Pt anode was depolarized greatly when KCNS was added (Curve 2). A Ni anode dissolved with almost 100% current efficiency in KCl solutions (Curves 3 and 4). Black film of NiS formed on a Ni anode in a solution containing KCNS . Small deviation of Curve 4 from Curve 3 is probably due to the IR drop through the film. Franklin *et al.* studied formation of sulfide layer on various metal anodes in solutions containing CNS^- .¹¹⁾

The results in Fig. 2 are important for control of the solution composition. KCNS is oxidized or consumed when an insoluble anode is employed, and undesirable CN^- forms. As a confirming experiment, electrolysis of a mixed solution of 1M KCl and 3.44 g/l KCNS in a divided cell having a diaphragm composed of KCl saturated agar-gel with Pt anode and cathode was conducted. The anolyte volume was 88 cm³. The current was kept constant at 5 mA and the amount of electricity was 190 coulombs (about 10.5 hrs). The KCNS content in anolyte decreased to 1.44 g/l, whereas KCNS in the catholyte was unchanged. The anolyte

contained CN^- of 0.129 g/l after experiment, also some SO_3^{2-} and SO_4^{2-} were found.

Another experiment showed that the catholyte of a divided cell containing the modified Watt-type solution contained some CN^- , and the KCNS concentration decreased after electrolysis. Therefore, CNS^- free of Ni^{2+} seems to be stable to cathodic reduction, but it is oxidized to SO_3^{2-} and SO_4^{2-} at the insoluble anode. On the other hand, CNS^- in the modified Watt-type bath is reduced cathodically with Ni^{2+} to form Ni-S electrodeposit, and CN^- is left behind in the solution.

Table 2 shows the chemical composition of Ni-S obtained from the modified Watt-type baths containing KCNS of different concentrations. The sulfur content in the electrodeposited layer increased with increase of the KCNS concentration. But the mole ratio of S to Ni is small: 1/10 even in a case of 30 g/l KCNS. According to the phase diagram of the Ni-S system¹²⁾, the mole ratios x as NiS_x are 2/3, 5/6, 6/7, 1, 4/3, and probably 2. A sulfur rich deposit was obtained from a Watt-type bath containing 40 g/l Na_2SO_3 (pH=4) at 2 A/dm² for 1 hour. The deposited layer consisted of 211.3 mg Ni and 39.4 mg S, which corresponded to Ni_3S . But the phase diagram indicates no existence of such a composition.

Sulfur in the electrodeposited layer comes from CNS^- in the plating bath. Apart of CNS^- is oxidized at the anode to form SO_3^{2-} and SO_4^{2-} . Of these, SO_3^{2-} is also a source of S for Ni-S electrodeposition. Thus, NiS_x might be co-deposited with Ni, and the mole ratio of Ni to S in the deposited layer varies with conditions of electroplating. We assume that

On the other hand, Ni anode is dissolved to form NiCNS^+ as follows:

Also a part of CNS^- is oxidized into CN^- at the anode:

[6]

$$E^\circ = 0.55\text{V vs. SHE at } 25^\circ\text{C}^{(13)}$$

3.2 Physical properties

The surface morphology of the deposited layer is closely related to the conditions of electroplating such as the solution composition and the current density. The SEM photograph (Fig. 3) shows large crack on the surface obtained from the solution containing an amount of KCNS, whereas a plain Ni electroplated layer is crack-free.

Figure 4 shows the results of experiment with the contractometer. The free end of the cathode moved greatly with time when a small amount of KCNS was added in the plating solution, say 0.38 g/l. On the other hand, the electrodeposited Ni from a plain Watt-type bath was stress-free (the data are not shown in the figure). The stress of deposited material re-

Fig. 3 SEM photograph of Ni-S electrodeposited from the modified Watt-type bath containing 30/1 KCNS at 2 A/dm² (×1800)

Fig. 4 Deviation of contractometer and the cathode potential as functions of time

Solution=Watt bath+30 g/l KCNS (pH=4.0), Temperature=30°C, Current density=2 A/dm²

duced again with increase of the KCNS concentration (see the results of 3.2 g/l KCNS), and the cathode in the solution containing 30.2 g/l of KCNS did not move during electrolysis. The cathode potential was also stable as shown by the open points.

Now it is interesting that the free end of the cathode moved greatly when the polarizing current was interrupted. Of course, the electrode potential jumped to the static potential, and it changed gradually with time to the noble direction. Why the tensile stress appears after current interruption is unclear as yet. Time lag for crystallization or orientation of the deposited material would be a reason. The specimen is relieved of stress after many hours (see dotted line) because of cracking.

The X-ray diffraction chart showed a large background with the highest, but wide, peak corresponding to Ni (Fig. 5A), but it crystallized with heating at the temperature more than around 250°C. The material heated at 800°C for 1 hr in argon atmosphere decomposed to Ni and Ni_3S_2 as shown in Fig. 5B. A number of small pits on the surface of the crystal grain were observed by SEM. The h.o.v. of those material in NaOH solution was very high.

Fig. 5 X-ray diffraction chart of Ni-S (powered)

Fig. 6 Hydrogen overvoltage of Ni-S and iron cathodes in 2.5 N NaOH at 90°C and 20 A/dm² as a function of the time of electrolysis in 2.5 N NaOH at high current densities at 35~40°C

3.3 Electrochemical properties

The accelerated life test was carried out with 2.5 N NaOH (35~40°C) at 150 A/dm² for 9 months. Also some experiments were conducted at different current densities such as 25 and 50 A/dm². The test specimen was taken from the cell at adequate intervals, say every week, and the h.o.v. characteristics were determined in a separate cell containing purified 2.5 N NaOH at 90°C for evaluation. Figure 6 shows the h.o.v. at 20 A/dm² as a function of the service time in the life-test cell. A fresh Ni-S cathode showed preferably low h.o.v.: 0.2 V compared to 0.4 V of a common iron. But the h.o.v. became large with time due to deactivation of the Ni-S deposited layer. Similar experiments were conducted at different current densities. The data at 50 A/dm² are shown in Fig. 6. According to those accelerated tests, the TTF was shortened with increase of the current density. No significant failure of the Ni-S cathode tested at 25 A/dm² was found after 6 months, for example.

According to the X-ray analysis, the material was unchanged by electrolysis. But the SEM photographs showed that a part of the deposited layer of a degraded

cathode flaked off, and small spots appeared on the surface of grains.

It is interesting why the Ni-S cathode has a low hydrogen overvoltage compared to the plain Ni cathode as shown in Fig. 7. Two reasons can be considered: catalytically active and a

Fig. 7 Hydrogen overvoltage curves of electroplated Ni-S and Ni cathodes in 2.5 N NaOH at 90°C

large surface area, whereas separate estimation of those factors is difficult. Therefore, we obtained the differential capacitance of the cathode and the amount of electricity for hydrogen adsorption on the cathode so as to estimate the activity of the cathode material.

The differential capacitance C of the cathode polarized by more than 20 mV from the reversible potential is represented as follows:⁽¹⁴⁾

$$C = i / [d\eta/dt]_{t=0} \quad [14]$$

where i is the current density and η is the overvoltage. $[d\eta/dt]_{t=0}$ in this equation can be obtained from the potential decay curve of the oscilloscope trace with the interruption method.

The decay curve of the fresh Ni-S cathode is flat as shown in Fig. 8A, due to very large differential capacity. Figure 8B illustrates the decay curve of the same material after electrolysis for 150 days at 150 A/dm², which shape differs from that of the fresh specimen.

The differential capacitance of various cathodes are listed in Table 3. A fresh Ni-S had a very large capacity of around $10^4 \eta F/cm^2$, but the capacity decreased greatly to $10^3 \eta F/cm^2$ after prolonged electrolysis. No significant change of the surface was found. The specimens heated also showed decrease in capacity. As reference,

Fig. 8 Oscilloscope traces of potential vs. time curve

Interruption 1 m sec, Current density 10 A/dm² Potential scale 20 mV/div, The decay curve is shown by arrow

Table 3 Differential capacitance in 2.5 N NaOH at 90°C and 30 A/dm²

Specimen	[h.o.v.] _{t=0} V	[dV/dt] _{t=0} V/sec	C 10³ ηF/cm²
Fresh Ni-S	0.143	17	18
Heated at 150°C	0.264	45	6.7
Heated at 200°C	0.318	78	3.8
Life test for 150 days	0.257	360	0.83
Commercial iron, fresh	0.376	890	0.34

an iron cathode had the capacity of the magnitude of $10^2 \eta F/cm^2$.

The potential sweep curves with the Ni-S cathode in 1 N NaOH at 90°C under high sweep rate (10 sec/V) showed a large area of the amount of electricity for stripping hydrogen absorbed: 147 mC/cm². It is said that a plain nickel electrode shows the amount of electricity of about 320 μC/cm².⁽¹⁵⁾

Recently, Nidola and the co-workers have described degradation of the Ni-S electrode in concentrated KOH solutions at 70°C⁽⁶⁾. NiS_x decomposed into sulfate when the material was polarized anodically. On the other hand, the

material deactivated gradually during cathodic polarization, and a significant change in morphology was observed. However, its mechanism is still unclear.

4 Conclusion

The Ni-S electrodeposited layer is active as a low hydrogen overvoltage cathode in concentrated NaOH solution. The h.o.v. of the deposited material is related to the plating conditions, especially the KCNS concentration in the plating solution and the current density. The sulfur content in the deposited layer increased with increase of the KCNS concentration. A large tensile stress induced in the deposited layer after the polarizing current was turned off, so that a number of cracks appeared on the surface.

The materials just obtained by electroplating is amorphous somewhat, but it crystallizes with heat treatment at the temperatures more than 250°C. At very high temperatures such as 800°C, it decomposes to Ni and Ni₃S₂. Those specimens showed very high h.o.v. in alkali solutions because of deactivation.

The Ni-S cathodes deactivated and/or degraded gradually with time during electrolysis of NaOH solution at very high current densities such as 150 A/dm². The cathode surface changed somewhat, but its differential capacitance decreased greatly from 10⁴ μF/cm² to 10³ μF/cm² after 150 days. However, degradation of the active cathode is related to the current density, and hence the Ni-S cathode is expected to work well for long time, say 6 months, as a low h.o.v. cathode if it is used at relatively low current densities such as 25 A/dm² or less.

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Appendix:

Procedure of chemical analysis of Ni and S is as follows. Sulfur in the sample solution is oxidized by KClO₃. Excess KClO₃ is decomposed by mixture of HNO₃ and HCl, the solution is evaporated, and the residue is dissolved in HCl acidified water. Zinc pellets are added into the solution to reduce Fe³⁺. Sulfate is precipitated by BaCl₂, and is filtrated. Barium sulfate is measured by gravimetry. Tartalic acid is added into the filtrate, the solution is neutralized with ammonia, and nickel is precipitated as nickel glyoxim.

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