

Properties of Ni-S_x electrodes for hydrogen evolution from alkaline medium

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Active layers for hydrogen evolution were prepared electrolytically from nickel-plating baths containing various amounts of thiourea. The sulphur content of the deposited layers, which is dependent on the thiourea content of the electroplating bath, ranged between 10 and 20 wt %. X-ray photoelectron spectroscopic (XPS) analysis revealed that sulphur was present in the layers not only in the form of sulphide, but also in the forms of thiourea and sulphate entrained from the nickel-plating bath. X-ray diffraction analysis showed that the coatings were poorly crystalline. Nickel sulphide, which produces an X-ray diffraction pattern, was present only in coatings deposited from baths with higher amounts of thiourea. The surface layers of such coatings contained a maximum of 10 at % nickel in the form of Ni₃S₂. When the Ni-S_x electrodes were under load in 1 M KOH over a long period, the hydrogen overpotential was found to vary with time. On the basis of XPS measurements, the initial decrease in hydrogen overpotential was ascribed to the washing-out of adsorbed residues of thiourea. The subsequent increase in the overpotential was due to the deposition of iron on to the surface of the layers from the electrolyte used.

1. Introduction

Cathodes exhibiting long periods of low overpotential for hydrogen evolution have recently been the subject of very intensive research. A number of materials have been tested and, with varying degree of success, also commercially employed for this purpose. In addition to pure metals, especially nickel for alkaline media, many metal–non-metal compounds have been studied and applied in practice, primarily those of nickel with sulphur, phosphorus and boron. Of these, Ni-S_x has received special attention as a potential material for hydrogen evolution in alkaline medium [1–7]. Apart from its catalytic properties, its advantage is the ease with which it is prepared; for example, by electro-deposition from aqueous solution. As quoted in a Norsk Hydrox patent [8], Ni-S_x layers exhibit a hydrogen overpotential of 60–110 mV at 0.1 A cm⁻² (80°C, 25 wt % KOH). The overpotential remains stable for at least 4 months. In contradiction to this, Nidola *et al.* [3] observed an increase in the cathode potential by about 350 mV after 1000 h of operation at a current density of 1.0 A cm⁻². These workers attributed the increase to dissolution of hydrogen in the active Ni-S_x layer and subsequent mechanical disintegration of the layer. During on-load conditions in acidic medium, Power [9] observed a non-oxidative dissolution of Ni₃S₂ with the formation of H₂S and nickel metal. An extensive dissolution of hydrogen in

the Ni-S_x layer has also been reported by Vandendorre *et al.* [7]. Their electrode exhibited an increased activity for hydrogen evolution, which the workers ascribed to the existence of a hydride layer.

The aim of this work was to obtain a deeper understanding of the properties of Ni-S_x electrodes. We investigated the effect of thiourea on the composition of the final layer, and the effect of prolonged polarization on the sulphur content of the layers.

2. Experimental details

2.1. Preparation of Ni-S_x layers

Ni-S_x-coated cathodes were prepared by electro-deposition from solutions of NiSO₄ · 7H₂O (200 g dm⁻³), H₃BO₃ (40 g dm⁻³), NaCl (20 g dm⁻³) and various amounts of thiourea as a source of sulphur [8]. The solutions were made up in triply distilled water. The base material was a nickel roll (99.6% Ni, 0.05% Fe, 0.05% Cu, 0.005% Mn, 0.1% Mg and 0.008% Al) of diameter 6 mm, press fitted into a Teflon holder and nickel-coated to improve the adhesion of the Ni-S_x layer. The geometrical area of the cathodes was 0.283 cm².

The active Ni-S_x layer was deposited for 30 min at a temperature (*t*) of 45°C and a cathodic current density (*j_c*) of 0.03 A cm⁻². A length of nickel wire with a geometrical area of about 5 cm² was used as the

anode. Four Ni-S_x electrodes (further designated as Ni-S_x No. 1–4) were prepared, using thiourea concentrations in the activating electroplating bath of 10, 50, 100 and 250 g dm⁻³.

After activation the electrodes were washed thoroughly with distilled water. The morphology of the layers was examined by scanning electron microscopy (SEM) using a Philips PSEM 500 instrument.

2.2. Ni-S_x layer composition and polarization curves

The layer composition was examined by quantitative analysis, XPS analysis and X-ray diffraction. In the quantitative analysis, nickel was determined chelatometrically, and sulphur by gravimetry as BaSO₄. XPS analysis was carried out on an ESCA III Mk II instrument (VG Scientific Ltd, UK), and X-ray diffraction analysis was performed on a Philips PW 1140 instrument. Samples for the analyses were prepared by mechanically removing the deposited layers from the base material and pulverizing in an agate mortar. In order to remove sticking residues of the electroplating bath, we washed part of the samples by decantation with a large excess of distilled water. Dried samples treated thus are designated by the symbol P.

In addition, surface analysis of the compact deposited Ni-S_x layers (without their removal and pulverization) was carried out by the energy-dispersive X-ray analysis (EDAX) method, using a Camebax-Micro instrument (Cameca, France) and an analyzer from Kevex (USA). However, the surface of the samples was too rough for the method to be suited to quantitative determination, and therefore the results obtained were used only to assess qualitatively the presence of impurities on the surface of the Ni-S_x layers.

In polarization measurements, the electrodes immersed in 1 M KOH in glass cells at $t = 25^\circ\text{C}$ were loaded for various periods (up to 1100 h) with a constant current density of 0.8 A cm⁻² (or 0.5 A cm⁻²). The cathode chamber was closed by a water seal and was separated from the anode chamber by a ceramic diaphragm. A length of platinum wire (with a surface area of about 2 cm²) coiled into a helix was used as the anode. The activity of the electrodes was determined by repeated measurements of polarization curves under the same conditions as above. The overpotential for hydrogen evolution was measured by the conventional method of current interruption [10]. The source and the electronic current interrupter were of our own

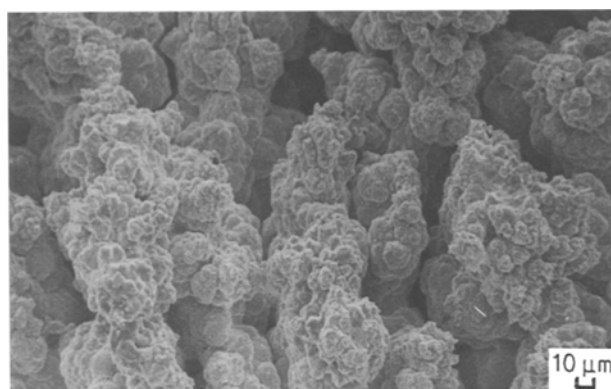


Fig. 1. Appearance of a typical porous Ni-S_x layer, 192 × magnification. The segment at the bottom of the figure represents 10 μm.

design. The potential gradient in the electrolyte between the working electrode and the tip of the Haber–Luggin capillary was read off from a Tektronix T912 oscilloscope. The reference electrode was a hydrogen electrode in the same medium as the working electrode. Before the measurement of polarization curves, the solution was bubbled with nitrogen freed from traces of oxygen by passage through a column packed with BTS catalyst (Fluka) at $t = 150^\circ\text{C}$.

The 1 M KOH electrolyte was prepared from triply distilled water and solid KOH · H₂O purified by zone melting. The composition of the KOH monohydrate used is given in Table 1.

3. Results and discussion

3.1. Surface and composition of Ni-S_x layers

The porous and wrinkled character of the layers is shown by SEM photographs in Figs 1 and 2. Figure 1 illustrates complex 'cauliflower' formations responsible for the porosity of the layer. Figure 2 shows the transition between the nickel support from which part of the layer was removed mechanically and the Ni-S_x layer. The adhesion of the deposited layer to the support can be markedly enhanced by nickel-plating. Table 2 lists specific surface areas of Ni-S_x samples obtained from baths with various thiourea concentrations. The values were measured by the method of Nelssen and Eggertsen [11] using a Geotest Brno instrument. For comparison, the table includes the

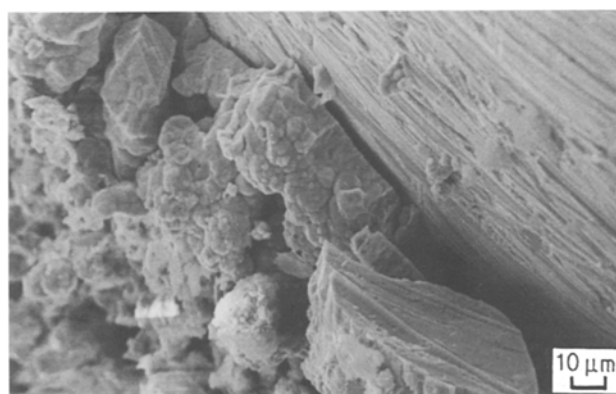


Fig. 2. A 'sectional view' of Ni-S_x layer, 384 × magnification. The segment at the bottom of the figure represents 10 μm.

Table 1. Composition (in wt %) of KOH · H₂O

KOH	min. 75
Fe	max. 5×10^{-5}
Na	1.3×10^{-3}
Pb	5×10^{-6}
CO ₃	5×10^{-3}
Mg, Ca	1×10^{-5}
Ni, Ag, Cu, Mn, Zn, Cd	max. 1×10^{-6}

Table 2. Specific surface areas of Ni-S_x powder samples as determined by the method of Nelssen and Eggertsen [11]

Sample	Concentration of thiourea in electroplating bath (g dm ⁻³)	Specific surface area (m ² g ⁻¹)
Ni-S _x No. 1	10	0.88
Ni-S _x No. 2	50	1.15
Ni-S _x No. 3	100	2.00
Ni-S _x No. 4	250	3.00
Ni-S	—	55.90
chemically precipitated		

value for nickel sulphide prepared by precipitation of nickel sulphate with sodium sulphide.

The specific surface area increases with increasing thiourea content of the nickel-plating bath. Compared with Raney nickel electrodes, however, the specific surface areas of Ni-S_x are rather small [12]. Results of a chemical analysis are summarized in Table 3.

The sulphur content of Ni-S_x layers increases with increasing thiourea content of the nickel-plating bath.

3.2. XPS and X-ray analyses

Bonding energies (BE) were measured for Ni 2p_{3/2}, O 1 s, and S 1 p. The values for nickel span a rather wide range (860.9–861.5 and 854.9–856.1 eV), without showing a dependence on the method of sample preparation or the subsequent treatment. The results are difficult to interpret, for it is known from the literature [13] that values of the bonding energy, as well as the appearance of satellite bands, depend on the method of surface treatment and that the BE varies from 852.2 eV for pure nickel through 854.0 eV for NiO to 857.1 eV for NiSO₄. If more nickel components are present on the surface, the resultant spectrum is the sum of the individual spectra, and the contributions from the components cannot be resolved. The mean value of the bonding energy for

O 1 s in the electrochemically prepared samples is 530.85 ± 0.41 eV, in good agreement with the tabulated value [14, 15] for oxygen bound to nickel in an oxidation state between NiO (529.6 eV) and Ni(OH)₂ (531.2 eV). The BE value for oxygen in chemically precipitated Ni₃S₂ is 529.6 eV, indicating that the oxidation state of nickel in chemically precipitated sulphide is higher than that in electrochemically prepared layers.

The analysis of spectra in the energy region for S 1 p showed that all of the samples analysed contained sulphur in at least two forms; namely as sulphate with BE = 167.7–169.4 eV and as sulphur with BE = 161.3–162.5 eV. The latter bonding energy corresponds to sulphur in the forms of both sulphide and thiourea. Since the samples contained a large amount of sulphur in the form of sulphate which could get into the electroplated layers only from the bath, it is apparent that a considerable amount of sulphur with BE = 162 eV had its origin in thiourea from the solution. Integral intensities of peaks due to the individual elements suggested that a large amount of sulphur, bound both as sulphide and as sulphate, could be washed out with water. However, even a thorough washing left residues of SO₄²⁻ and thiourea adsorbed on the electrode surface. Evaluation of the S²⁻/Ni ratios indicated that the surface layer of the coatings contained sulphide sulphur at a level of 6.5 at % at most. With the composition Ni₃S₂, this implies that the maximum content of nickel in the form of sulphide in the surface layer was 10.4 at %.

X-ray diffraction analysis showed that the degree of crystallinity in the Ni-S_x samples was very low. The primary crystallites were best developed in Ni-S_x No. 1 (largest grains) and least developed for Ni-S_x No. 4 (smallest grains). Apart from nickel, no other compounds could be detected in unwashed samples. This was probably because solution components producing no X-ray diffraction lines were adsorbed on the grain surface. For washed samples diffraction lines of Ni₃S₂ appeared starting from Ni-S_x No. 3P, and became more intense for Ni-S_x No. 4P.

3.3. Polarization curves

Figure 3 shows an example of a polarization curve for hydrogen evolution for the electrode with the highest content of sulphur (Ni-S_x No. 4). It is seen that the dependence $\eta = f(\log j_c)$ is not linear over the range of the current densities measured and therefore, cannot be described by the Tafel equation. At intermediate current densities the porous character of Ni-S_x apparently plays a role, and the increase in the overpotential at $j_c \approx 0.3$ A cm⁻² arises, presumably, because part of the surface is blocked by hydrogen bubbles. Also, a change in the mechanism of the electrode reaction with changing current density cannot be completely discounted. In agreement with the results of Vandenberg *et al.* [7], the electrode activity at the beginning of polarization is distinctly lower than that measured after a period of cathodic current load.

Table 3. Composition (in wt %) of Ni-S_x layers

Sample Ni-S _x	Concentration of thiourea in electroplating bath (g dm ⁻³)	Ni	S	O*	Ni:S
1	10	84.00	10.39	5.61	8.08
1 P	10	83.25	10.50	6.25	7.92
2	50	82.12	12.36	5.52	6.64
2 P	50	82.47	12.47	5.06	6.62
3	100	73.08	17.87	9.05	4.08
3 P	100	73.23	18.15	8.62	4.02
4	250	69.75	19.06	11.19	3.65
4 P	250	72.36	19.61	8.03	3.68
Chemically precipitated	—	39.32	10.40	50.28	3.78

*Calculated as 100-(Ni + S).

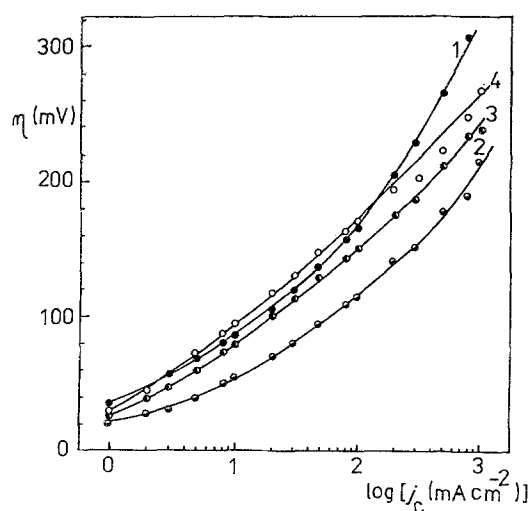


Fig. 3. Polarization curves of Ni-S_x No. 4 electrodes. $j_c = 800 \text{ mA cm}^{-2}$ (long-term load), $t = 25^\circ \text{C}$, 1 M KOH; 1 (●) new electrode; 2 (●) after 25 h polarization; 3 (●) after 290 h polarization; 4 (○) after 554 h polarization.

The variation in the activity of Ni-S_x electrodes with time depends strongly on the sulphur content of the layer. In Fig. 4 the hydrogen evolution overpotential is plotted as a function of time (long-term electrode load at 0.8 A cm^{-2}), and the insert (Fig. 4b) shows the same plot for the very beginning of polarization (prepolarization at 0.5 A cm^{-2}). The greatest decrease in the overpotential is seen to occur for the electrode with the largest sulphur content. In contrast, no minimum in the $\eta = f(t)$ curve is found for the electrode with the lowest sulphur content. As seen from Fig. 4, the drop in the overpotential is not permanent. After some time of polarization, the overpotential increases again at a slower or faster rate. In an attempt to clarify the causes of the increase in overpotential we analysed the layers by the EDAX method. The analysis was made for the region of minima in the $\eta-t$ curves—that is, after 75 h of cathodic load at a current density of 0.5 A cm^{-2} —and when steady-state conditions had been reached—that is, after 1100 h of load at 0.8 A cm^{-2} . The results are listed in Table 4.

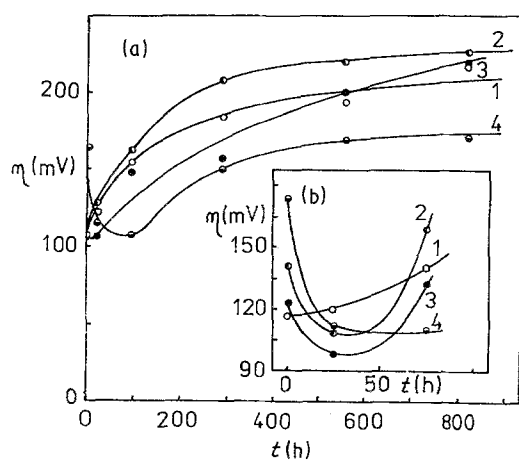


Fig. 4. Plot of hydrogen overpotential against electrolysis time. (a) Long-term polarization at $j_c = 800 \text{ mA cm}^{-2}$; (b) polarization at $j_c = 500 \text{ mA cm}^{-2}$; 1 (○) Ni-S_x No. 1; 2 (●) Ni-S_x No. 2; (●) Ni-S_x No. 3; 4 (○) Ni-S_x No. 4.

Table 4. Results of EDAX analysis of Ni-S_x electrodes after prolonged polarization (the values are given in wt %)

Ni-S _x	Electrode condition	Ni	S	Fe	Ni:S
1	A	85.4	6.6	0	12.9
	B	76.0	2.5	1.1	26.0
	C	44.9	1.2	24.9	37.4
2	A	91.1	2.5	0	36.4
	B	78.5	5.1	0.8	15.3
	C	45.0	1.1	29.9	40.9
3	A	87.7	7.0	0	12.5
	B	76.0	5.2	0.5	14.6
	C	49.3	1.3	22.2	37.9
4	A	88.7	9.0	0	9.8
	B	83.7	6.1	0.2	13.7
	C	44.2	1.2	14.5	36.8

A, after preparation (before loading); B, after 75 h of load at $j_c = 0.5 \text{ A cm}^{-2}$; C, after 1100 h of load at $j_c = 0.8 \text{ A cm}^{-2}$.

Although the results of EDAX analysis are subject to substantial error ($\pm 40\%$), one can discern certain trends in the composition of the surface layer of Ni-S_x electrodes. Two important changes occur. First, despite precautions taken to preclude contamination of the solution with iron (the use of extraordinarily pure starting lye and separation of the vessel space from the atmosphere by a water seal), the iron concentration in the electrode surface increases markedly on prolonged polarization. Secondly, as shown by analyses of the sulphur content of the layers and by the Ni:S ratio, the sulphur content of the Ni-S_x layer decreases considerably in the course of cathodic polarization. From the results of XPS analysis it may be concluded that the decrease in the overpotential is associated with the washing-out or reduction of adsorbed sulphur and exposure of the surface active for hydrogen evolution. The increase in the overpotential, on the other hand, is apparently due to the iron deposited on the surface of the Ni-S_x electrode [16]. The activity of Ni-S_x electrodes depends on the concentration of thiourea in the plating bath. The most active electrodes were formed, in accordance with results of Hine *et al.* [17], who instead of thiourea used thiocyanate in the bath with the greatest thiourea content.

Comparison of the polarization curve of the most active electrode (No. 4) with the polarization curves given in [9, 18] shows that the activities of all of these electrodes at current densities $j_c \lesssim 100 \text{ mA cm}^{-2}$ are approximately the same. Data given in [18] show that these electrodes exhibit lower overvoltage at higher current densities as the polarization curves do not curve to higher potentials.

3.4. Use in a membrane electrolytic cell

A cathode of high surface area (about 100 cm^2) with Ni-S_x No. 4 supported on an expanded steel gauze was placed in a laboratory membrane zero-gap cell made of Teflon (depicted schematically in Fig. 5). After activation of the cathode, the cell was operated for a

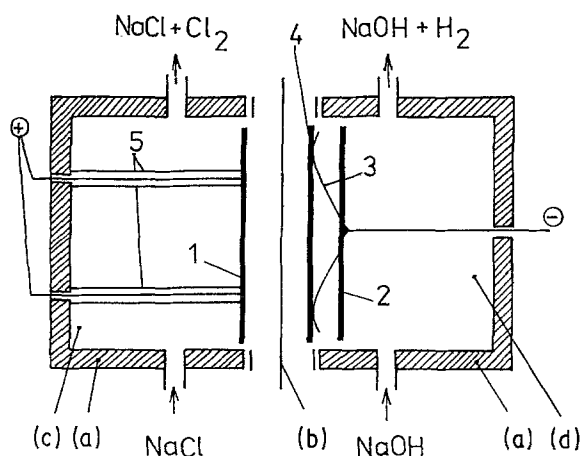


Fig. 5. A schematic representation of the laboratory membrane zero-gap cell. a, Teflon jacket; b, Nafion NX961 membrane; c, anode chamber; d, cathode chamber. 1, Titanium anode with a layer of $\text{RuO}_2\text{-TiO}_2$ (mass proportion of metals, 1:1); 2, pressure plates; 3, springs; 4, cathode activated by Ni-S_x No. 4 layer; 5, Teflon bridges.

long period (7 months) under the following conditions: c_{NaOH} (catholyte) $\approx 420 \text{ g dm}^{-3}$, c_{NaCl} (anolyte) $\approx 230 \text{ g dm}^{-3}$, temperature $t = 90^\circ \text{C}$. The current density (the same on the cathode, anode and membrane) was 0.3 A cm^{-2} , and an ST 132 selenium rectifier was used as the current source. The membrane used was a Nafion NX961, and the anode was made of titanium activated by a $\text{RuO}_2\text{-TiO}_2$ layer to lower the chlorine overpotential. The contamination level (Ca^{2+} and Mg^{2+}) in the salt brine was less than 0.05 ppm. Figure 6 shows plots of the voltage (measured by an RFT, G 1001.500 multimeter, DDR) and the electric energy consumption against time. The current efficiency was 95%. The average voltage on the cell was 2.882 V, and the electric energy consumption ranged between 1980 and 2050 $\text{kWh/t}_{\text{NaOH}}$.

Linear regression of the measured values of voltage yielded a value of $-5.8 \times 10^{-5} \text{ V day}^{-1}$ for the slope of the line $U = a + b\tau$. Compared with an unactivated iron cathode [19], the cathode activated by an Ni-S_x porous layer saves 250 mV in the voltage and about $200 \text{ kWh/t}_{\text{NaOH}}$ in the electric energy con-

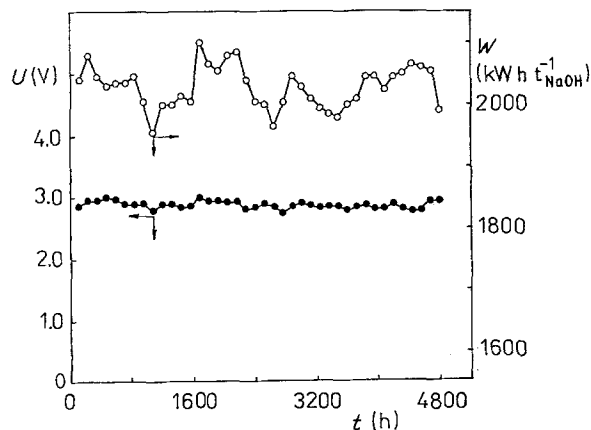


Fig. 6. Electric energy consumption (○) and voltage (●) on zero-gap electrolytic cell during long-term polarization ($i_c = 300 \text{ mA cm}^{-2}$).

sumption. The above discussed increase in hydrogen overpotential with time manifested itself by a slight increase in the voltage of the cell at the beginning of the experiment. During 7 months of continuous operation of the cathode, no changes were observed in the voltage of the cell.

4. Conclusion

The results of the study may be summarized as follows.

(1) The prepared Ni-S_x electrodes have a very irregular surface, whose area increases with increasing concentration of thiourea in the activating bath. The most extended surface area ($3 \text{ m}^2 \text{ g}^{-1}$) was obtained by depositing an Ni-S_x coating 250 g l^{-1} $(\text{NH}_2)_2\text{CS}$ (saturated solution).

(2) The sulphur content of the Ni-S_x layer increases with increasing concentration of thiourea in the activating bath, and ranges between 10 and 20 wt %.

(3) Sulphur is present in the layer in the form of Ni_3S_2 , and in the forms of sulphate and thiourea, which can, for the most part, be washed out by water.

(4) The hydrogen overpotential is least for the Ni-S_x No. 4 electrode. On prolonged cathodic polarization, the sulphur content of the layer decreases and iron is deposited on the electrode surface, with the result that the overpotential increases with time.

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