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Characterization of hydrogen evolution on cobalt electrodeposits in water electrolysis

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The hydrogen evolution reaction (HER) on cobalt electrodes has been investigated in both alkaline (30 wt % KOH) and acid (1 M H_2SO_4) media at 25 °C. The electrocatalytic cobalt materials were produced under different electrodeposition conditions, namely deposition in the absence or presence of bubbling oxygen or nitrogen gas with two gas flow rates (80 and 230 ml min^{-1}) and at different current densities (50–800 A m^{-2}) and deposition in a cobalt powder-containing bath. It has been shown that the electrocatalytic behaviour of the cobalt deposits can be significantly affected by deposition current density via a change of surface area of the cobalt deposits. A considerable HER overpotential decrease (up to 150 mV) has been achieved on the highly porous and active cobalt electrodes deposited in the presence of bubbling oxygen and chloride ions in deposition solution. However, the HER overpotential was increased on the cobalt electrodes deposited with bubbling nitrogen in the bath.

1. Introduction

Cobalt and cobalt-containing materials, beside nickel, have received considerable attention for their electrocatalytic behaviour in water electrolysis. Brossard *et al.* [1, 2] studied both hydrogen and oxygen evolution on cobalt electrodes in 30 wt % KOH at 70 °C in the presence of dissolved metallic impurities such as molybdenum, iron and vanadium, which could significantly affect the surface activity of cobalt. Choquette *et al.* [3] used Raney cobalt and Raney nickel–cobalt composite-coated materials for both hydrogen evolution cathodes and oxygen evolution anodes in alkaline media. They found that the presence of cobalt in the electrode materials was detrimental to hydrogen evolution. However, based on the electrocatalytic behaviour of niobium–cobalt alloys in 25 wt % KOH, Umetsu, Piron *et al.* [4, 5] reported that alloys with more than 70 wt % cobalt enhanced the hydrogen and oxygen evolution reactions in electrolysis.

Jiang *et al.* [6–8] developed a technique, named reactive deposition, for producing highly porous, high-surface area cobalt structures. The process involves the electrodeposition of cobalt in the presence of bubbling oxygen gas and chloride ions in solution. The continuous formation of oxide and/or hydroxide during electrodeposition should interfere with the orderly build-up of the metallic layers and result in a porous metallic structure. In addition, the presence of chloride ions which can activate the dissolution process of the freshly deposited metal or metal oxide also enhances the porosity of the electrodeposits [6]. It was believed that the cobalt produced by reactive deposition is active for oxygen and hydrogen evolution in alkaline solution [9]. However, no systematic research has been reported on the relationships between the electrocatalytic behaviour of such deposited cobalt and the deposition conditions, such as current density and oxygen flow rate.

In the present study, cobalt electrolytic coatings were produced in different ways, namely deposition in the absence or the presence of bubbling oxygen or nitrogen with different gas flow rates and current densities, and deposition in a cobalt powder-containing bath. These cobalt electrodes have been characterized for HER in both 30 wt % KOH and 1 M H_2SO_4 at 25 °C. Comparisons have been made of the electrocatalytic activity on the different cobalt electrodes. The relationships between surface activity of the cobalt electrodes, their surface morphology and deposition conditions have been investigated.

2. Experimental details

2.1. *Fabrication of cobalt electrodes*

The substrates used were rolled copper sheets (0.01 cm thick). Before deposition, the samples (1.0 × 1.0 cm^2) were electropolished in 2 M H_2SO_4 at an anodic current density of 150 A m^{-2} and 25 °C for 10 min. The deposition was carried out in a 1 dm^3 cell [6]. A cobalt anode was placed at a distance of 7 cm to the cathode. For the deposition in the presence of bubbling gas, the cell setup was such that it was continuously purged with gas.

Oxygen or nitrogen gas was fed through a sintered glass plug on to the cathode in the solution for 1 h before and during deposition. The gas flow rate was kept constant and controlled by a gas flow meter. Mechanical agitation was only used for deposition in a cobalt powder-containing bath by a plastic propeller

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Table 1. Bath compositions and electrolysis conditions

$CoCl_2 \cdot 6H_2O$	$48\,g\,dm^{-3}$ (0.2 M)
KCl	$29\,g\,dm^{-3}$ (0.4 M)
Co powder (100 mesh)	0 and $4\,g\,dm^{-3}$
Current density, ($A\,m^{-2}$): (deposition time, min)	50 (240)
	100 (120)
	200 (60)
	300 (40)
	400 (30)
	600 (20)
	700 (17)
	800 (15)
Temperature	25 °C
pH	5.6
O_2 flow rate	0, 80 and $230\,ml\,min^{-1}$
N_2 flow rate	0 and $80\,ml\,min^{-1}$

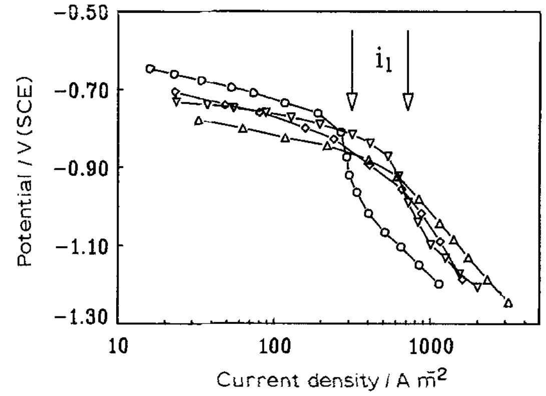

Fig. 1. Polarization curves for cobalt electrodeposition with and without oxygen or nitrogen gas flow, 25 °C, scan rate: $1\,mV\,s^{-1}$. Flow rate, $ml\,min^{-1}$: (○) none; (▽) N_2: 230; (◇) O_2: 80; and (△) O_2: 230.

rotating in the bath in order to keep full powder suspension. The chemicals used in this work were of reagent purity grade. The composition of the deposition baths and the electrolysis conditions are listed in Table 1. The deposition time was selected for different deposition current densities to achieve a cobalt loading of $22\,mg\,cm^{-2}$ on the deposited electrodes, provided that the current efficiency for cobalt deposition was 100%. The real current efficiency of cobalt deposition under different conditions was measured by weighing the electrodes. The cobalt loading on the different electrodes was then determined; it was around $20\,mg\,cm^{-2}$ on the produced electrodes except when the cobalt was deposited in the absence of bubbling gas at a current density of or above $300\,A\,m^{-2}$. The amounts of cobalt deposited without bubbling gas at a current density of 300, 400 and $600\,A\,m^{-2}$ were only about 13, 7 and $2\,mg\,cm^{-2}$, respectively, due to the low current efficiency of the cobalt deposition at the high current densities.

The cathodic polarization for the cobalt depositions was carried out by scanning cathodically the potential ($1\,mV\,s^{-1}$) of the cobalt-coated electrode in the deposition bath.

2.2. *Characterization of the electrolytic cobalt*

Hydrogen evolution on the cobalt electrodes was examined in both 30 wt% KOH and 1 M H_2SO_4 solutions at 25 °C. Cathodic polarization of the cobalt electrodes was performed at a scan rate of $1\,mV\,s^{-1}$ in an electrolysis cell connected to a potentiostat (EG&G Princeton Applied Research, Model 173) which was computer controlled through an interface (EG&G Princeton Applied Research, Model 276). In the cell, a platinum auxiliary electrode was used; a Luggin capillary connected to a saturated calomel electrode (SCE) as a reference, was placed close to the cobalt electrode ($< 2\,mm$) to minimize errors due to ohmic drop, and no correction of residual *IR* was made. Tafel behaviour was observed during the polarizations in the current density range of 10 to $1000\,A\,m^{-2}$, and the Tafel slope (b) of each polarization curve was obtained. The HER overpotential (η) was determined for each cobalt electrode by comparing the HER potential at the current density of $1000\,A\,m^{-2}$ and the calculated hydrogen equilibrium potential ($-1120\,mV/SCE$ in 30 wt% KOH and $-280\,mV/SCE$ in 1 M H_2SO_4). The hydrogen exchange current density (i_{ex}) on each cobalt electrode was deduced from the values of overpotential and Tafel slope.

The time variation effect on the HER overpotential in both 30 wt% KOH and 1 M H_2SO_4 solutions was examined for the cobalt electrodes deposited with bubbling oxygen. With a constant current density of $1000\,A\,m^{-2}$, the potential of HER on the electrodes was monitored for 50 h.

The a.c. impedance measurements were made on the surface (apparent area: $1\,cm^2$) of deposited cobalt electrodes in 30 wt% KOH with an applied potential of $-1.5\,V/SCE$ and at 25 °C. The measurements were performed by using a computer-controlled potentiostat (EG&G Princeton Applied Research, Model 273) in combination with a phase lock-in analyser (EG&G Princeton Applied Research, Model 5208). A small a.c. voltage with an amplitude of 5 mV (peak-to-peak value) was superimposed on the applied potential in a frequency range of 5 Hz–10 kHz. The characteristic behaviour of a single *R–C* combination was found on impedance spectra. The apparent double-layer capacity ($C_{dl,app}$) was evaluated from the impedance response for each electrode. The surface roughness factor for a porous electrode was thus calculated by dividing the $C_{dl,app}$ value by a double-layer capacity ($20\,\mu F\,cm^{-2}$) for a smooth mercury electrode [6].

The surface morphology of the cobalt electrodes was examined using a scanning electron microscope (JEOL, JSM-820).

3. Results

Figure 1 shows the polarization curves of the cobalt electrodepositions in the absence or presence of bubbling oxygen or nitrogen gas in the deposition solution. As the deposition is conducted at a current density well below the limiting current density, the relationship between deposition potential and current density is linear in a semi-log graph, as predicted by

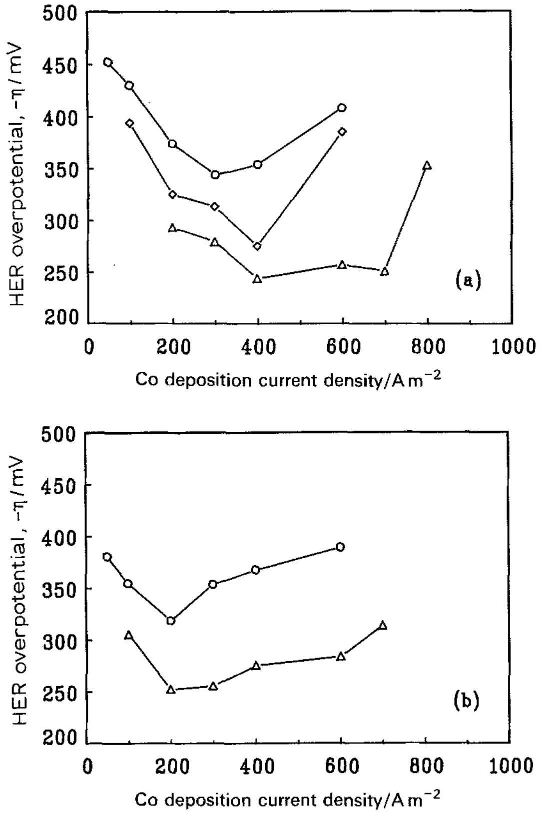

Fig. 2. HER overpotentials in (a) 30 wt % KOH and (b) 1 M H_2SO_4 at 25 °C on cobalt electrodes deposited with or without oxygen gas flow at different current densities and at 25 °C. Flow rate, ml min^{-1}: (○) none; (◇) O_2: 80 and (△) O_2: 230.

Tafel's law for activation-controlled electrodeposition. The limiting current density of the cobalt deposition without bubbling gas and the deposition with bubbling nitrogen can be assessed from the polarizations to be about 300 and 700 A m^{-2}, respectively. As the cobalt deposition was conducted without bubbling gas, the deposition current efficiency was around 90% at a current density ranging from 50 to 200 A m^{-2}. At the limiting current density (300 A m^{-2}), the current efficiency was 60%, and it decreased to 10% at a current density of 600 A m^{-2}. When the cobalt deposition was carried out in the absence of bubbling gas at a current density above the limiting current density, hydrogen evolution was visually observed at the cathode surface in the solution, and the cobalt loading was considerably lowered. When bubbling oxygen was added during deposition, however, the current efficiency was around 90% over the entire current density range used (100–800 A m^{-2}). It seems that hydrogen evolution lessened at high current densities when oxygen was present in the solution.

Table 2. HER overpotentials in 30 wt % KOH at 25 °C on the cobalt electrodes deposited with bubbling oxygen and with or without cobalt powders in the bath, oxygen flow rate: 230 ml min^{-1}

Deposition c.d./A m^{-2}	*$-\eta$/mV*	
	With powders	*Without powder*
200	264	293
300	254	279

η: HER overpotential at polarization current density of 1000 A m^{-2}.

Figure 2 shows the HER overpotentials ($-\eta$) at 25 °C in 30 wt % KOH (Fig. 2(a)) and 1 M H_2SO_4 (Fig. 2(b)) on the deposited cobalt electrodes in the absence or presence of bubbling oxygen at different oxygen flow rates and current densities. For the cobalt electrodes, the HER overpotential first decreases significantly to a minimum value of about 250 mV in both 30 wt % KOH and 1 M H_2SO_4 as the cobalt deposition current density increases in the tested range. Then, as the current density reaches a certain value, the HER overpotential increases with increasing the current density. With a comparable cobalt deposition current density, the HER overpotential on the deposited cobalt electrode in the presence of bubbling oxygen obviously decreases with respect to that on the deposited cobalt without gas bubbling; such an HER overpotential decrease of 150 mV is reached in 30 wt % KOH (Fig. 2(a)). For the cobalt depositions with oxygen gas flow, a decrease in HER overpotential has been achieved by increasing the oxygen flow rate. With the same oxygen flow rate and a deposition current density less than 300 A m^{-2}, the HER overpotential is lower in 1 M H_2SO_4 than in 30 wt % KOH. However, as the deposition current density exceeds 300 A m^{-2}, the HER overpotential is generally higher in 1 M H_2SO_4 than in 30 wt % KOH for the same oxygen flow rate during the deposition. For a high oxygen flow rate of 230 ml min^{-1}, the HER overpotential is almost constant at a low value over a relatively wide deposition current density range of 400 to 700 A m^{-2} in 30 wt % KOH (Fig. 2(a)). Moreover, the HER overpotential can further be slightly reduced on the cobalt electrode produced by reactive deposition in a cobalt powder-containing bath at comparable plating current densities (Table 2).

Table 3 lists the Tafel slope and the exchange current density for the HER in 30 wt % KOH and 1 M H_2SO_4 solutions at 25 °C on the cobalt electrodes deposited without bubbling gas or in the presence of bubbling oxygen with two gas flow rates and at different current densities. The Tafel slopes obtained with the deposited cobalt electrodes are around 100 and 115 mV(decade)$^{-1}$ in 30 wt % KOH and 1 M H_2SO_4, respectively. Since the electrochemically active surface area of the electrodeposited cobalt electrodes can be related to the exchange current density [9], the variation of the exchange current density indicates a significant effect of the deposition conditions on the surface area of the deposited cobalt electrodes. In both 30 wt % KOH and 1 M H_2SO_4, generally, the hydrogen exchange current density on the deposited cobalt initially increases with increasing deposition current density; it then decreases as the deposition current density exceeds a certain value. The surface roughness factor determined by a.c. impedance measurements is 51, 152 and 56 for the cobalt electrodes deposited without bubbling gas at a current density of 100, 300 and 600 A m^{-2}, respectively. With a comparable deposition current density, the surface area

Table 3. Tafel slope and exchange current density for HER on the cobalt electrodes prepared under different conditions

Deposition c.d./A m^{-2}	*b/mV(dec)$^{-1}$*					*i_{ex}/A m^{-2}*				
	in 30 wt % KOH			*in 1 M H_2SO_4*		*in 30 wt % KOH*			*in 1 M H_2SO_4*	
	C	*L*	*H*	*C*	*H*	*C*	*L*	*H*	*C*	*H*
50	106	–	–	108	–	0.054	–	–	0.30	–
100	96	114	–	90	115	0.033	0.35	–	0.11	2.2
200	97	106	106	100	120	0.14	0.86	1.7	0.65	7.8
300	92	102	108	113	122	0.18	0.85	2.6	0.74	8.0
400	90	106	99	120	125	0.12	2.5	3.4	0.86	6.2
600	95	104	104	110	120	0.051	0.20	3.4	0.29	4.3
700	–	–	103	–	127	–	–	3.7	–	3.4
800	–	–	120	–	–	–	–	1.1	–	–

C: Deposition without bubbling gas.
L: Deposition with bubbling oxygen, flow rate: 80 ml min^{-1}.
H: Deposition with bubbling oxygen, flow rate: 230 ml min^{-1}.

increases with increasing the oxygen flow rate. The exchange current density for the deposited cobalt electrodes with 230 ml min^{-1} oxygen is generally one order of magnitude higher than that of the cobalt deposited without flowing oxygen. The surface roughness factor is 152, 352 and 1776 for the cobalt electrodes deposited at 300 A m^{-2} without bubbling gas and in the presence of bubbling oxygen with a flow rate of 80 and 230 ml min^{-1}, respectively. The surface area of the cobalt can be increased by increasing the deposition current density in the range below the limiting current density and by using a high oxygen flow rate.

The deposited cobalt electrodes in the absence of oxygen were grey in colour. However, uniform black cobalt layers were observed on the samples prepared in the presence of bubbling oxygen. The adherence of the reactively deposited cobalt layers to the substrates was very good. The scanning electron micrographs (Fig. 3) show the surface morphology of the deposited cobalt electrodes in the absence and in the presence of bubbling oxygen. For the cobalt deposited without bubbling gas, densely structured electrodeposited coating is observed (Figs 3(a) and (b)). As the deposition current density increases, a higher surface roughness occurs. A distinct difference is revealed in the structures of the cobalt surfaces deposited without bubbling gas and in the presence of bubbling oxygen. Although some cracks can be seen in the cobalt layer deposited in the absence of bubbling gas, those deposited with bubbling oxygen are much more porous (Figs 3(c), (d) and (e)). With a comparable deposition current density, the cobalt electrodes deposited in the presence of bubbling oxygen show much finer crystallites. At higher oxygen flow rates, a needle-like structure appears (Fig. 3(e)). The cobalt electrode reactively deposited from a powder-containing bath has a rough surface. The cobalt powder is imbedded between the crystallites (Fig. 4).

The HER overpotential ($-\eta$) is 374, 293 and 533 mV in 30 wt % KOH at 25 °C on the cobalt electrodes deposited without bubbling gas and in the presence of bubbling oxygen or nitrogen gas with a gas flow rate of 230 ml min^{-1} and a current density of 200 A m^{-2}. With respect to the depositions with bubbling oxygen or without bubbling gas, the cobalt deposition with bubbling nitrogen results in a considerable increase in the HER overpotential. On the cobalt layer deposited with bubbling nitrogen, a dense surface structure has been observed. No significant difference in surface morphology can be seen between the deposited cobalt electrodes with bubbling nitrogen and without bubbling gas (Fig. 5).

The time variation effect on the HER overpotential is shown in Fig. 6 for the reactively deposited cobalt electrodes in both 30 wt % KOH and 1 M H_2SO_4 solutions. In the alkaline medium, the HER overpotential ($-\eta$) decreases during first 10 h operation. Then the overpotential keeps constant in the test range. In the acid medium, although the HER overpotential decreases during the first 15 h and becomes lower than that of the cobalt in the alkaline medium, it increases constantly after the initial decrease, and finally it exceeds the initial value. It was observed that the cobalt deposit partially dissolved in the acid solution.

4. Discussion

The current density of cobalt deposition exerts a significant influence on the electrocatalytic behaviour of the cobalt deposit surface by changing the surface area of the deposits. As the electrodeposition is carried out at a current density well below the limiting current density, it is mainly activation-controlled (Fig. 1). The deposited cobalt surface is relatively smooth. When the current density is increased to around the limiting current density, metal deposition is mainly controlled by the mass transport of the cations towards the cathode. In this case, protruding parts of a size smaller than the thickness of the diffusion layer are privileged from the viewpoint of diffusion and grow faster than recesses or flat parts of the cathode. Under the deposition conditions used in this work, the thickness of the diffusion layer is usually about 0.01–0.3 mm [11], and the roughness of the polished substrate surfaces is much less than these orders of magnitude. However, the substrate surface is normally not perfectly smooth

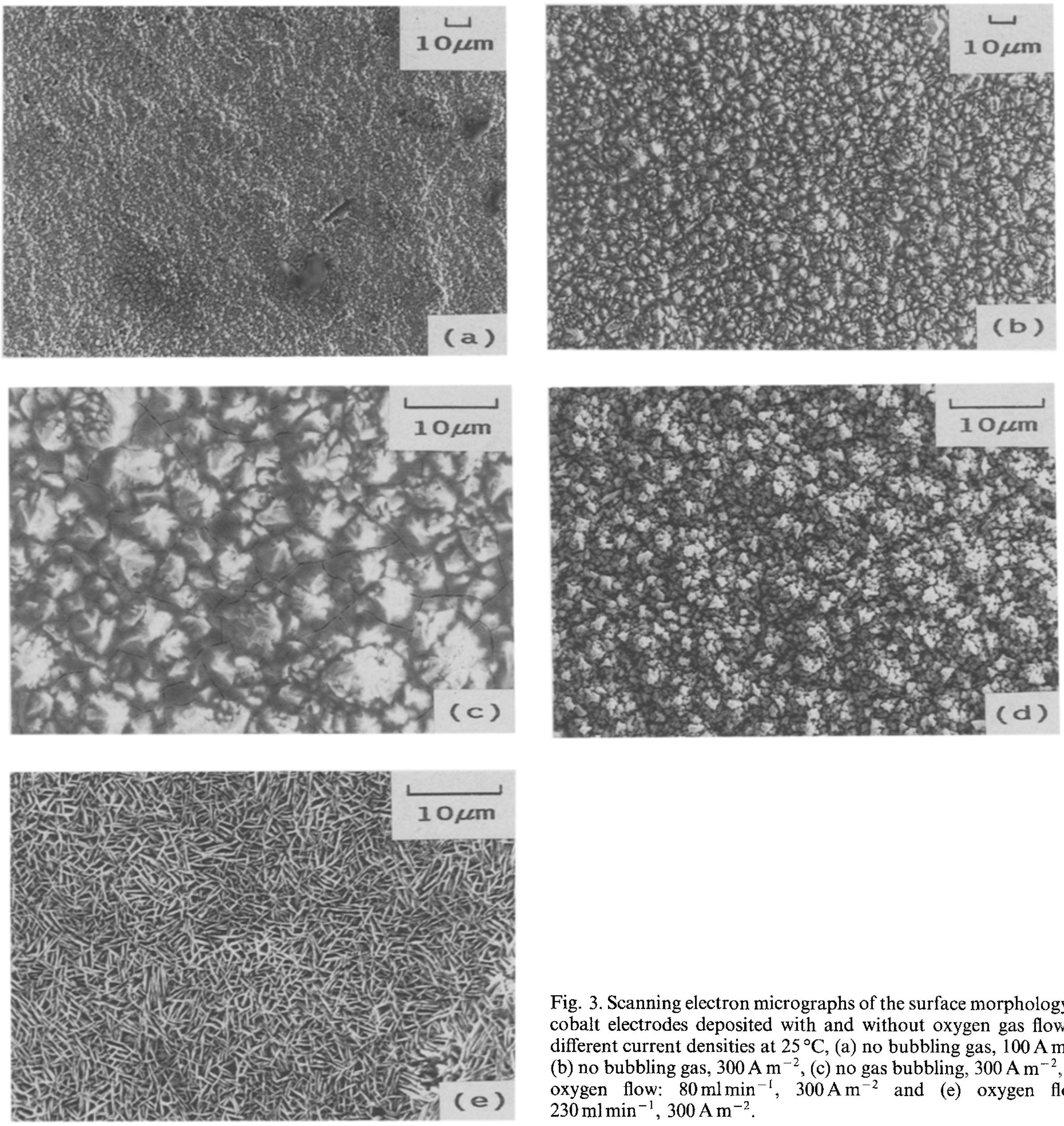

Fig. 3. Scanning electron micrographs of the surface morphology of cobalt electrodes deposited with and without oxygen gas flow at different current densities at 25 °C, (a) no bubbling gas, $100\,\mathrm{A\,m^{-2}}$, (b) no bubbling gas, $300\,\mathrm{A\,m^{-2}}$, (c) no gas bubbling, $300\,\mathrm{A\,m^{-2}}$, (d) oxygen flow: $80\,\mathrm{ml\,min^{-1}}$, $300\,\mathrm{A\,m^{-2}}$ and (e) oxygen flow: $230\,\mathrm{ml\,min^{-1}}$, $300\,\mathrm{A\,m^{-2}}$.

and some initial roughness is usually present. The initial roughness thus tends to be amplified if the rate of metal deposition is controlled by the mass transport; rough and porous deposits should be expected [10, 11]. The deposit real surface area is thus enlarged, and the HER overpotential may be lowered. However, as the plating current density is increased further above the limiting current density, the deposit becomes powdery and fragile, the deposition current efficiency decreases, and the amount deposited is lowered, as in this work. During the characterization of HER on these cobalt deposits, the powdery deposit was detached by gas evolution. The deposit loading was reduced and the deposit surface became smooth. In this case, the deposit surface area was significantly reduced, and therefore, the HER overpotential increased.

The highly porous structure of the cobalt layer produced by the reactive deposition is due to the participation of the oxygen reduction reaction. In the absence of oxygen, electrodeposition of cobalt is the predominant cathodic process. However, parallel processes may be involved in the presence of oxygen in the cobalt solution [6]: i.e. the direct electrodeposition of Co^{2+} ions and the indirect deposition of cobalt via the

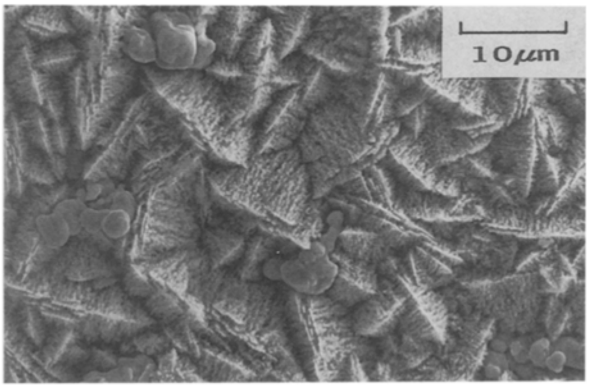

Fig. 4. Scanning electron micrograph of the surface morphology of a cobalt electrode deposited with oxygen gas flow from a cobalt powder-containing bath, cobalt powder: $4\,\mathrm{g\,dm^{-3}}$ $200\,\mathrm{A\,m^{-2}}$, 25 °C, oxygen flow: $230\,\mathrm{ml\,min^{-1}}$.

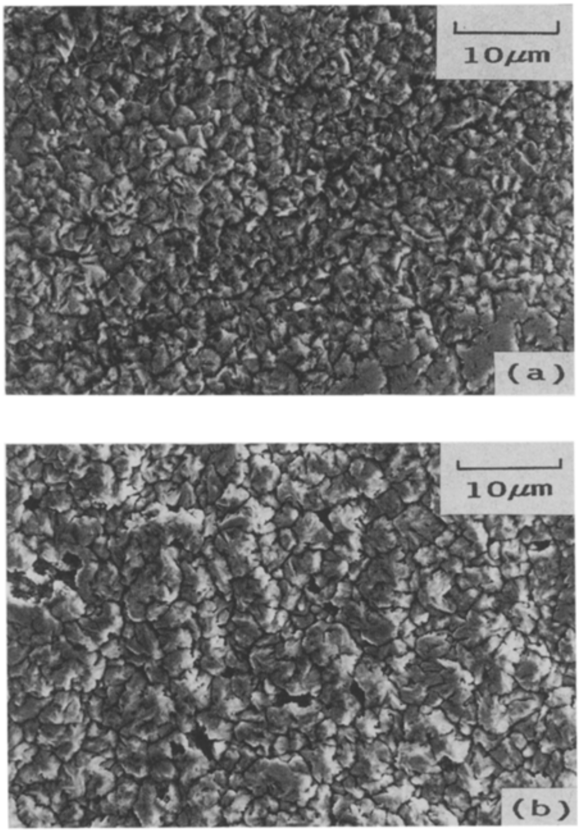

Fig. 5. Scanning electron micrographs of surface morphology of cobalt electrodes deposited with and without nitrogen gas flow at 200 A m^{-2} and 25 °C, (a) nitrogen flow: 230 ml min^{-1} and (b) no gas flow.

reduction of cobalt oxide/hydroxide intermediates. The latter process may be predominant in the reactive deposition. Consequently, the continuous formation and reduction of cobalt oxide/hydroxide interferes with the ordered deposition of cobalt ions. The dissolution of the freshly formed cobalt or cobalt oxides is responsible for the formation of the high-surface-area deposit and highly porous cobalt structure. The presence of Cl$^-$ ions in the solution plays a crucial role in the formation of the unique porous structure produced by reactive deposition. Although Cl$^-$ may not directly influence the metallic dissolution process, it does interfere with the formation and dissolution of metal oxides [12, 13]. In addition, during deposition in the presence of bubbling oxygen, the cobalt oxide and hydroxide layer may be broken as a result of the sparging effect of the bubbling gas [14]. The sparging effect also promotes the generation of the porous cobalt deposit. When the flow rate of the bubbling oxygen was increased during the cobalt deposition, the size of the gas bubbles was increased, as visually observed. In this case, the sparging effect of the bubbling gas was more pronounced, resulting in a more porous cobalt deposit with increased surface area. The HER on such cobalt materials can be further enhanced.

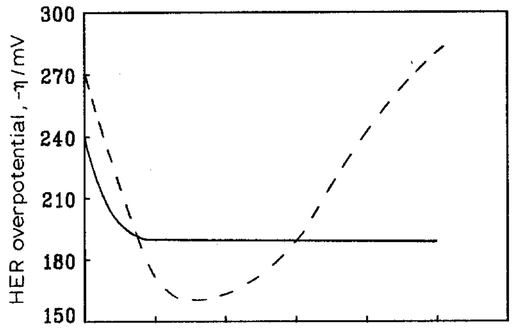

Fig. 6. Time effect on the HER overpotential at 1000 A m^{-2} in both 30 wt % KOH (——) and 1 M H_2SO_4 (- - -) at 25 °C for reactively deposited cobalt electrodes (deposition current density: 400 A m^{-2}, oxygen flow: 230 ml min^{-1}, 25 °C).

The previous study [6] showed that the surface activity of the deposited cobalt in the presence of bubbling nitrogen was lowered for the oxygen evolution reaction. The existence of cobalt and cobalt oxides such CoOOH, Co_3O_4 and CoO was determined on the deposited cobalt electrodes with bubbling oxygen; whereas, only cobalt metal was found on the electrodes prepared with bubbling nitrogen [6]. It was believed that the highly porous structure of cobalt produced by the reactive deposition is not due to the agitation effects of bubbling gases. This is confirmed in the present study using deposited cobalt as a hydrogen evolution electrode. When nitrogen is used instead of oxygen in cobalt deposition, the surface activity of the cobalt electrode for HER in water electrolysis is even lower than that of the cobalt when no gas is used. With the agitation of the bubbling nitrogen, the limiting current density of the deposition can be significantly increased (Fig. 1). The plating current density is then far below the limiting current density. The surface of the cobalt deposit thus obtained, is relatively smooth (Fig. 5) and the surface activity is poor.

When the cobalt reactive deposition is carried out in a powder-containing bath, the powders are codeposited onto the electrode surface and the surface morphology is dramatically changed (compare Figs 3 and 4). The surface activity for HER is then increased. Research on powder-codeposition for preparing surface active electrodes is under way in our laboratory.

Although it can hardly be concluded that the surface performance for HER of cobalt electrodes in acid media is inferior to that in alkaline media based on the electrode characterization without prepolarization, the HER overpotential of the reactively deposited cobalt electrode cannot be maintained at a relative low value with time in the acid medium (Fig. 6); it increases and exceeds the initial value. The surface activity is reduced as gradual dissolution of the cobalt deposit occurs in the acid solution.

5. Conclusions

Electrolytic HER in both 30 wt % KOH and 1 M H_2SO_4 at 25 °C on electrodeposited cobalt electrodes can be enhanced by plating the high-surface area cobalt deposits at a current density close to the limiting current density. The electrocatalytic activity for HER was considerably improved on the highly porous and rough cobalt electrodes deposited in the presence of bubbling oxygen and chloride ions. This is due to the dissolution of the freshly formed oxide layer on the deposit surface during the deposition. A high oxygen flow rate and the presence of cobalt powder in the deposition bath favour the production of cobalt deposits with high surface activity for HER electrocatalysis. However, the surface activity is reduced for the cobalt electrode deposited with bubbling nitrogen. During the first 10 h of cathodic polarization at a constant current density, the HER overpotential on the deposited cobalt electrodes decreases in both 30 wt % KOH and 1 M H_2SO_4 solutions. It is not evident that the surface performance for HER of the cobalt electrodes without prepolarization in 1 M H_2SO_4 is inferior to that in 30 wt % KOH, however, the stability of the cobalt electrodes for HER is much poorer in the acid medium than in the alkaline one.

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