ELECTROCHEMICAL BEHAVIOUR OF COBALT IN NaOH SOLUTIONS

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The electrochemical behaviour of cobalt in 0.001 – 1 M NaOH was investigated by voltammetric techniques coupled with ESCA examination. The anodic polarization curve exhibits a well defined peak which corresponds to the formation of $Co(OH)_2$ or CoO. Further peaks in the transpassive potential region correspond to the electrooxidation of Co(II) species to Co_3O_4 and CoOOH, respectively. The heights of the anodic peaks increase with the increase of NaOH concentration, temperature and scan rate. In cyclic voltammetry, the reverse scan consistently shows three cathodic peaks which are ascribed to the reduction of CoOOH, Co_3O_4 and CoO oxides, respectively. ESCA examination confirmed the presence of these oxides in the passive film.

Compared to the large number of work on iron and nickel electrodes only few studies have been devoted to the electrochemical behaviour of cobalt. The results of these studies are, however, contradictory. The electrochemical oxidation and passivation of cobalt was first reported by Grube et al.[1], Besson et al.[2] and El Wakkad and Hickling[3].

The anodic polarization of cobalt anode in NaOH solutions has been studied under potentiostatic and galvanostatic conditions[4]. Only two stages in oxidation were reported. It is suggested that these stages correspond to the transition $Co/Co(OH)_2$ and $Co(OH)_2/Co(OH)_3$. The nucleation and growth of passivation layer of $Co(OH)_2$ are studied by analysis of current–time curves at various constant potentials.

Behl and Toni[5] used cyclic voltammetry with rotating cobalt ring disc electrodes to study the anodic behaviour of cobalt in KOH solutions. They have concluded that the electrochemical oxidation of cobalt leads to the formation of $Co(OH)_2$ which is oxidized at more positive potentials to Co_3O_4 and CoOOH. Jayaraman et al.[6,7] have investigated the anodic behaviour of cobalt (plated on nickel substrate) in NaOH solutions

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potentiostatically. The anodic process is attributed to the formation of $Co(OH)_2$ and CoO. These species are further oxidized to higher oxides at more positive potentials.

The present work is devoted to gain more light on the electrochemical behaviour of cobalt in NaOH solutions and the effect of alkali concentration, scan rate and temperature on this behaviour using voltammetric techniques complemented by ESCA measurements.

EXPERIMENTAL

The working electrodes were made of specpure cobalt rodes (99.99%, Johnson and Matthey) axially embedded in Araldite holders to obtain exposed circular area of 0.5 cm^2. Prior to the experiments, each electrode was polished with successively finer grades emery paper and then with high purity alumina powder, degreased with ethyl alcohol and finally rinsed with running double distilled water. The counter electrode was 0.5 cm^2 platinum sheet. Potentials were measured against a saturated calomel reference electrode (SCE). In order to avoid contamination, the reference electrode was separated by an electrolyte bridge with Luggin capillary tip, filled with solution under test. The three electrodes were mounted in Pyrex glass cell.

Electrochemical measurements were performed using a potentiostat (Forschungsinstitut Meinsberg, type PS 2,3) in 0.001 – 1 M NaOH (Merck) solutions freshly prepared in double distilled water, at constant temperature in the range of 25 – 75 °C ± 0.5 °C.

Electron spectroscopy for chemical analysis (ESCA) was applied on the electrode surfaces after potential sweeping up to the oxygen evolution potential at scan rate of 400 mV min^{-1} in 1 M NaOH at 25 °C. The ESCA examinations were performed after removing the electrodes from the electrolyte and rinsing them with double distilled water. A spectrometer provided with X-ray radiation (1 253 eV) and a pass energy of 25 ± 0.5 eV was used.

RESULTS AND DISCUSSION

Figure 1 shows the voltammetric curves of cobalt in 0.001 – 1 M NaOH at 25 °C, scanned from –2 000 mV up to oxygen evolution potential with scan rate of 400 mV min^{-1}. Each anodic curve exhibits a well defined dissolution peak I followed by a passive and a broad transpassive regions prior to oxygen evolution reaction. The electrodissolution of cobalt corresponding to the peak I can be explained as an adsorption reaction involving catalysis by OH^- ions only at active surface sites, and formation of soluble intermediate complex according to the following equations[8].

$$Co + OH^- \longrightarrow Co(OH)_{ads} + e \qquad (A)$$

$$Co(OH)_{ads} \xrightarrow{rds} CoOH^+ + e \qquad (B)$$

The surface concentration of the active sites increases with increasing the anodic potential. Accumulation of the intermediate complex $CoOH^+$ formed precipitates $Co(OH)_2$ and/or CoO on the metal surface according to the following reactions.

$$CoOH^+ + OH^- \longrightarrow Co(OH)_2 \qquad (C)$$

and/or

$$CoOH^+ + OH^- \longrightarrow CoO + H_2O \qquad (D)$$

The equilibrium potentials of the system $Co/Co(OH)_2$ and Co/CoO at pH 14 are –0.442 and –0.513 V, respectively (ref.[3]) indicating that they are close enough that it appears to be difficult to distinguish between anodically formed $Co(OH)_2$ and CoO. When the surface is entirely covered with a passive film, the anodic current drops to a very small value i_{pass} denoting the onset of passivation. Cowling and Riddiford[4] have assumed that the passivation film consisted of $Co(OH)_2$ while Behl et al.[5] attributed passivity to the compact CoO layer formed from $Co(OH)_2$ close to the metal surface.

The transpassive region displays two anodic peaks II and III. These two peaks can correlate to the electrochemical formation of Co_3O_4 and CoOOH, respectively, from $Co(OH)_2$ according to the reactions:

$$3\,Co(OH)_2 + 2\,OH^- \longrightarrow 4\,H_2O + 2\,e \qquad (E)$$

$$Co(OH)_2 + OH^- \longrightarrow CoOOH + H_2O + e\ . \qquad (F)$$

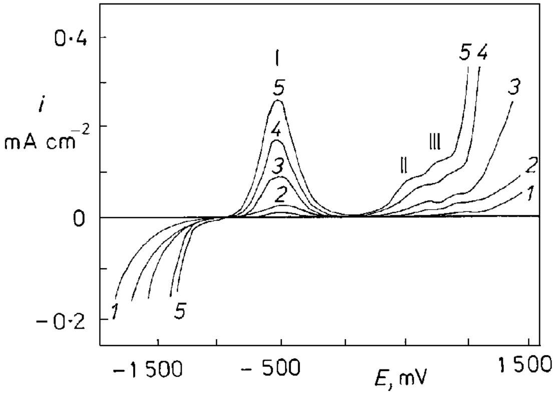

FIG. 1
Voltammetric curves of Co at scan rate of 0.4 V min^{-1} and 25 °C and various concentrations of NaOH: *1* 0.001, *2* 0.01, *3* 0.1, *4* 0.5, *5* 1.0 mol l^{-1}

Despite the fact that ESCA results prove the absence of $Co(OH)_3$, still the conditions of its formation in solution at very positive potential are met. At high vacuum in ESCA measurements, however, the decomposition of $Co(OH)_3$ can occur. Alternatively, as stated by Besson[2], the hydroxide of trivalent cobalt is CoOOH and not necessarily $Co(OH)_3$. The nature of the passive film formed on the cobalt surface after application of potential sweep up to the oxygen evolution potential was examined by ESCA. Figure 2*a* shows the binding of O 1*s* bonds in the film. The data reveal various types of bonded oxygen. The low binding energy signal at 530 eV corresponds to oxygen in the metal–O bond[9]. The broad signal at the binding energy 532 eV relates to oxygen in the metal–OH bond while the signal at 533 eV correlates to oxygen in H_2O probably physically adsorbed on the surface. Figure 2*b* shows the spectrum of electron for $2p^{3/2}$ orbital of cobalt. The spectrum is complex and if we take into account the spectra of oxygen and those of the known cobalt compound[9], we can resolve the total electron peak of $2p^{3/2}$ into three peaks at the binding energies of 777.9, 779.5 and 780.0 eV. The first peak is assigned to Co metal, the value of the binding energy of 780.0 eV can be correlated to CoO, while the binding energy of 779.5 eV can be attributed to the presence of the higher oxides Co_3O_4 and CoOOH, since the binding energies of these two oxides are very close to 779.59 eV. Thus we can conclude that the passive film formed potentiodynamically is composed of CoO, Co_3O_4 and CoOOH.

Inspection of the data of Fig. 1 reveals that the heights of the peaks I, II and III increase with increasing concentration of NaOH. The results could be attributed to the dissolving power of OH^- ions on the anodically formed cobalt oxides.

The influence of sweep rate v (20 – 1 212 mV min^{-1}) on the potentiodynamic behaviour of cobalt was examined in 0.1 M NaOH at 25 °C. It was found that the peak current i_{p1} of peak I increased and the corresponding peak potential E_{p1} shifted slightly

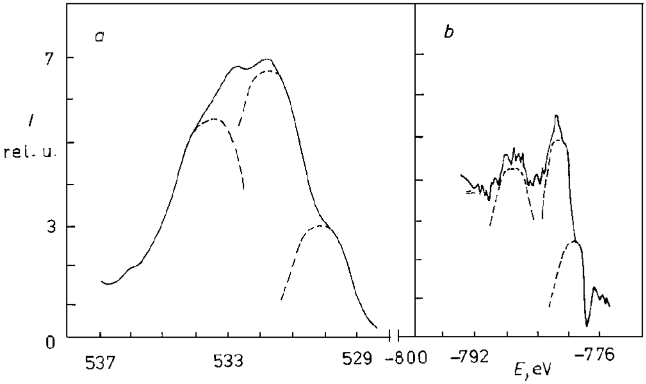

FIG. 2
ESCA examination of Co after potential sweeping in 1.0 M NaOH at 25 °C and scan rate of 0.4 min^{-1}; *a* O 1*s* level, *b* Co $2p^{3/2}$ level

to the more positive values. The plot of the peak current i_{p1} vs $v^{1/2}$ gives straight line extrapolated to the origin as shown in Fig. 3. The plot of E_{p1} vs log v also exhibits linear relation with a slope of 150 mV per decade of sweep rate (Fig. 4). These relationships indicate that the anodic dissolution of cobalt corresponding to peak I is controlled by the diffusion of OH^- ions towards the metal surface. At high scan rates, the amount of OH^- ions is not sufficient to exceed the solubility product of CoO and/or $Co(OH)_2$ and dissolution enhances. It seems that nucleation and growth of the passive film are more significant than the solubility. Thus at high scan rates the time needed to nucleate CoO at its reversible potential is very short and passivation is delayed until the nuclei have grown to the critical size required for passivation. According to the theory of Berzins and Delahay[10], the anodic dissolution current i_{p1} can be described by the equation

$$i_{p1} = a\, b\, z^{1/2}\, C\, D^{1/2}\, v^{1/2} \ , \qquad (1)$$

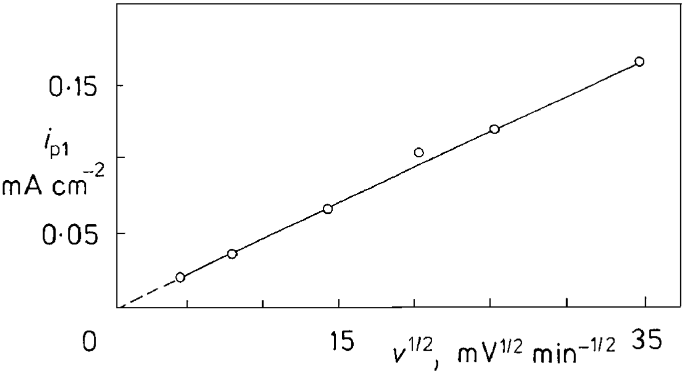

FIG. 3
Dependence of i_{p1} on $v^{1/2}$ in 0.1 M NaOH at 25 °C

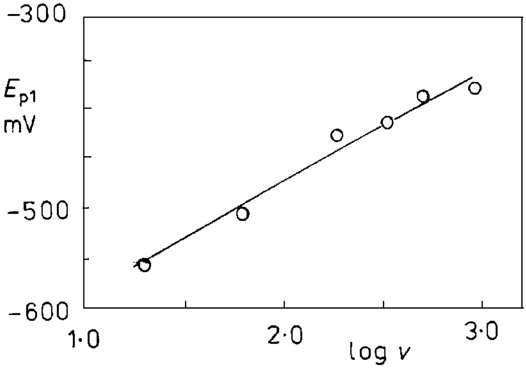

FIG. 4
Dependence of E_{p1} on log v in 0.1 M NaOH at 25 °C

where a and b are constants, z is the number of exchanged electrons, C is the bulk concentration, D is the diffusion coefficient of the OH^- ions and v is the scan rate. Furthermore, present data depict that the multiplicity of the transpassive region into the two peaks II and III becomes sharper with increasing the scan rate. It is probable that at low scan rates ($v < 66$ mV min^{-1}) the two peaks coalesce with each other and appear as one peak.

The influence of temperature on E–i curves was also examined. Increasing the temperature enhances the heights of the three anodic peaks and shifts the peak potential of peak I to the more negative values. Arrhenuis plot of log i_{p1} vs T^{-1} is given in Fig. 5. The slope of this line gives an apparent activation energy value equal to about 6.27 kJ mol^{-1} for the dissolution reaction.

Figure 6 represents cyclic voltammograms recorded for cobalt in 0.1 M NaOH at 25 °C starting from –2 000 mV with scan rate of 400 mV min^{-1}, where the sweep was

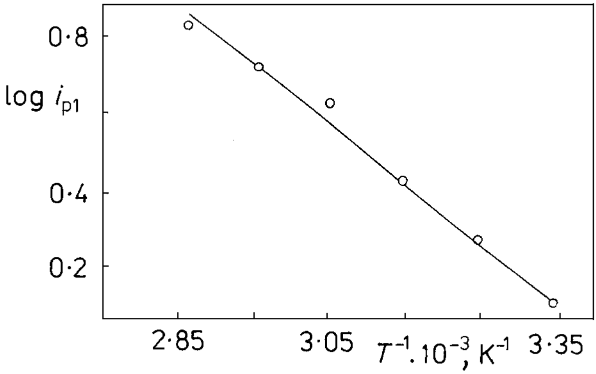

FIG. 5
Dependence of i_{p1} on temperature in 0.1 M NaOH at scan rate of 0.40 V min^{-1}

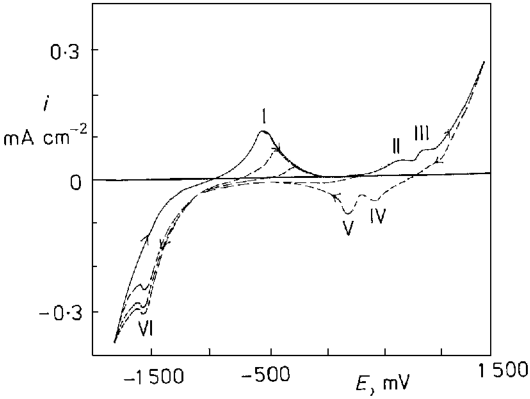

FIG. 6
Cyclic voltammograms of Co in 0.1 M NaOH, started from –2.0 V and reversed at various potentials at scan rate of 0.40 V min^{-1}

reversed at various potentials. Only one cathodic peak VI appears if the anodic potential has been reversed within the potential range of both peak I and passive region. However, the voltammograms exhibit three cathodic peaks IV, V and VI if potential sweep has been reversed at values more positive than potential of oxygen evolution. The cathodic peaks IV and V could be assigned to the electroreduction of CoOOH and Co_3O_4, respectively, to Co(II) species, while the peak VI attributed to the electroreduction of Co(II) to Co. It can be seen that both forward and reverse scans are different denoting irreversible nature of the processes. However, on repetitive cycling at the same scan rate, the currents the three anodic peaks and their conjugated cathodic peaks enhance with increasing the cycle number. The results can be explained in terms of activation of the electrode by cyclic polarization as shown in Fig. 7.

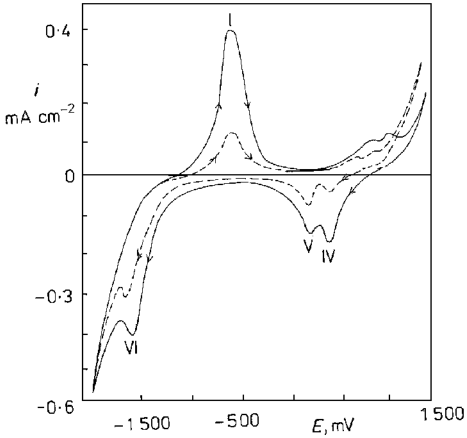

FIG. 7
Repetitive cycling voltammograms of Co in 0.1 M NaOH at 25 °C between –2.0 V and 1.35 V at scan rate of 0.40 V min^{-1} – – – first cycle, —— fifth cycle

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