Preparation and modification of hydrous thick cobalt oxide layers: voltammetric characteristics of rough Co_3O_4 -spinel-type electrodes

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The application of a periodic perturbing potential to a cobalt electrode immersed in alkaline solutions at room temperature allows accumulation of a hydrous cobalt hydroxide overlayer which becomes a precursor to the production of a rough Co_3O_4 spinel film through subsequent thermal treatment at 480°C . The optimal working conditions for the application of this procedure are discussed. The properties of the resulting overlayers were determined through voltammetry, X-ray analysis, infrared spectroscopy, thermal gravimetric and differential thermal analysis, and SEM micrography. The explanation of the entire process is given in terms of sequential electrochemical oxidation and reduction reactions involving different Co-containing species. The electroreduction reactions including the HER, play an important role in determining the characteristics of the resulting Co_3O_4 overlayer.

1. Introduction

Hydrous metal oxide layers can be easily produced on several metals by applying periodic potential treatments within certain potential and frequency ranges [1-6]. These layers are electrochemically active under potentiodynamic conditions and exhibit drastic voltammetric changes due to modifications of the layer structure.

It was recently reported that an incipient cobalt oxide spinel-structure overlayer with a relatively large electrocatalytic active surface area can be produced by applying a periodic potential treatment to cobalt electrodes immersed in alkaline solution [5]. The characteristics of the potential routine used in the preparation of the electrode and the composition of the solution determine the electrochemical behaviour of the resulting cobalt oxide layer. These types of cobalt oxide electrodes exhibit a clear electrocatalytic activity for the oxygen evolution reaction [6].

The present work describes the preparation procedure of rough Co_3O_4 -spinel-type electrodes from thick hydrous cobalt oxide layers, the composition of the different cobalt oxide layers resulting either electrochemically or from a thermal treatment, and the probable electrochemical reactions related to these processes.

2. Experimental details

Runs were made in a conventional two compartment/three electrode Pyrex glass electrochemical cell of about 0.1 dm^3 capacity. The working electrodes (0.3 to 0.5 cm^2 apparent area) were made from cobalt wires (Johnson Matthey, specpure quality). The potential of the working electrode was measured against a $\text{Hg}/\text{HgO}/1\text{ M NaOH}$ reference electrode ($E^0 = 0.925\text{ V}$ (against RHE), at 25°C , $dE/dT = 0.00056\text{ V K}^{-1}$) connected to the rest of the cell through a Luggin-Haber capillary tip 0.2 mm dia. located at about 0.1 mm from the working electrode surface. The counter-electrode consisted of a Pt spiral of $\sim 10\text{ cm}^2$ geometric area surrounding the working electrode concentrically. The 1 M NaOH solution was prepared from NaOH (Merck p.a.) and triply distilled CO_2 -free water. The electrolyte solution was kept continuously under nitrogen. The runs were made at 30°C .

Each run comprised the working electrode pretreatment, the hydrous cobalt hydroxide layer preparation through the application of a repetitive square wave potential routine (RSWPR), and the determination of the voltammetric characteristics of the new electrode surface.

The working electrode pretreatment comprised 5 min etching in 50% H_2SO_4 , washing and rinsing

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in triply distilled water, and finally 5 min potential cycling at 0.1 V s^{-1} between -0.32 V and 0.64 V , in 1 M NaOH to attain a stabilized voltammetric profile similar to that reported in the literature [7, 10].

The RSWPR treatment involved the application of either a time-symmetric or time-asymmetric signal between an upper, E_u , and a lower potential, E_l , at the frequency, f , for the time t . For the symmetric signal, $f = 1/(2\tau) = 1/T$, where τ is the half-period and T is the period of the signal, whereas for the asymmetric signal $f = 1/(\tau_u + \tau_l) = 1/T$, where τ_u and τ_l are the half-periods associated with E_u and E_l , respectively. In the present work the following ranges of the potential routine variables were used, $-0.2 \text{ V} \leq E_u \leq 0.8 \text{ V}$; $-2.4 \text{ V} \leq E_l \leq -1.6 \text{ V}$; $0.05 \text{ kHz} \leq f \leq 4.0 \text{ kHz}$; $0 \text{ s} < t \leq 60 \text{ s}$ and $0.4 \leq \tau_u/\tau_l \leq 2.4$. Most of the results reported in this paper correspond to the application of a symmetric wave ($\tau_u = \tau_l$), except otherwise stated. The RSWPR treatment was followed by a triangular potential cycling (RTPS) at 0.1 V s^{-1} between -0.32 and 0.64 V for 5 min. The voltammogram recorded immediately afterwards allowed the electroreduction charge, Q_r , to be obtained, from $Q_r = Q_a - Q_b$, where Q_a and Q_b are the electroreduction charges after and before applying the RSWPS, respectively.

Occasionally, cobalt hydroxide layers, resulting from the electrochemical treatment under the optimal RSWPR conditions, were thermally treated at 480°C for 4 h under air in a quartz furnace, following the procedure recently described [6].

The electrochemical data of cobalt oxide layers resulting from the different treatments were complemented with *ex situ* SEM micrographs, X-ray diffractometry, infrared spectroscopy and thermal analysis data.

3. Results

3.1. Voltammetric characteristics of the treated cobalt electrodes

The base voltammogram of polycrystalline cobalt in 1 M NaOH after 5 min potential cycling at 0.1 V s^{-1} between -0.32 and 0.64 V (Fig. 1a) exhibits the conventional current peaks, namely, I_a/I_c , II_a/II_c and III_a/III_c already described in the literature [7, 8]. The estimated peak potential values in the electro-oxidation scan are 0.07, 0.23 and 0.54 V, whereas in the electroreduction scan they are 0.53, 0.22 and $\sim -0.2 \text{ V}$, the latter appearing only as a small trace. For further details about voltammograms see [7] and [8].

When a cobalt electrode in 1 M NaOH is subjected to RSWPR for 30 s at $E_l = -1.8 \text{ V}$, $E_u = 0.5 \text{ V}$ and $f = 2.5 \text{ kHz}$, a thick hydrous cobalt oxide overlayer is formed. The corresponding stabilized voltammogram at 0.1 V s^{-1} (Fig. 1b) exhibits a large increase in the voltammetric charge of about 30 times that found for the blank. The treated electrode also shows a considerable enhancement of the oxygen evolution reaction

Fig. 1. Voltammograms of Co in 1 M NaOH at 0.1 V s^{-1} , geometric electrode area 0.37 cm^2 , 30°C . (a) Untreated polycrystalline Co electrode (blank) after 5 min potential cycling between -0.32 and 0.64 V ; (b) Co electrode after the application of a symmetric RSWPR for 30 s at $f = 2.5 \text{ kHz}$ between $E_l = -1.8 \text{ V}$ and $E_u = 0.5 \text{ V}$; and (c) Co electrode prepared as described in (b) and subsequently subjected to heating at 480°C for 2 h.

(OER) at 0.65 V , and becomes a precursor for a Co_3O_4 spinel overlayer [11–13].

The characteristics of the first voltammetric scan after the application of the RSWPR depends on E_u . Thus, when $E_u = 0.5 \text{ V}$ the electrooxidation charge of the first scan becomes only slightly greater than that resulting for the stabilized voltammogram, but this

Fig. 2. Q_r against E_u plot. The Co electrodes were subjected for 30 s to a symmetric RSWPR between $E_i = -1.8$ V and different E_u values at $f = 2.5$ kHz, 1 M NaOH, 30°C.

difference increases considerably according to E_u for $0.3 \text{ V} \leq E_u \leq 0.1 \text{ V}$. This charge is probably related to the formation of soluble cobalt species, the electroreduction of the latter taking place simultaneously with the hydrogen evolution reaction (HER).

3.2. The influence of E_u , E_i and f on Q_r

The optimal RSWPR conditions for obtaining a relatively large amount of active material were systematically studied by changing E_u , E_i and f . The amount of active material was taken as directly proportional to Q_r . Thus, the Q_r against E_u plot ($E_i = -1.8$ V, $f = 2.5$ kHz and $t = 30$ s) exhibits three peaked values of Q_r , at 0.1, 0.35 and 0.5 V, respectively (Fig. 2). The potentials corresponding to the three maxima are closely related to those shown in the voltammogram of Fig. 1b. On the other hand, the Q_r against E_i plot

Fig. 3. Q_r against E_i plot. The Co electrodes were subjected for 30 s to a symmetric RSWPR between $E_u = 0.5$ V and different E_i values at $f = 2.5$ kHz, 1 M NaOH, 30°C.

($E_u = 0.5$ V, $f = 2.5$ kHz and $t = 30$ s) shows up only a single peaked value of Q_r at about -1.9 V (Fig. 3).

The value of Q_r depends considerably on both f and E_u (Fig. 4). Thus, for $E_u = 0.1$ V and $f = 0.8$ kHz a broad peaked value of Q_r and the formation of a pink oxide layer can be observed. For $E_u = 0.3$ V the maximum value of Q_r also appears for $f = 0.8$ kHz, but in this case the electrode acquires a yellowish brown tinge. Likewise, the Q_r against E_u relationship becomes narrower and the peaked value of Q_r greater than in the preceding case. Finally, for $E_u = 0.5$ V, two peaked values of Q_r can be observed, the steepest one for $f = 0.15$ kHz, and another, much broader, for $f = 1.2$ kHz. For the latter a black compound is produced at the electrode surface. The colour changes at the electrode surface are, in principle, consistent with the formation of Co(II) oxide-containing layers for $E_u < 0.3$ V, and Co(III) oxide-containing layers for $E_u \approx 0.5$ V [1, 8].

The dependence of Q_r on t , the duration of the RSWPR, is shown in Fig. 5. Initially, Q_r increases linearly with t , independently of E_u , [$(\Delta Q_r / \Delta T)_{t \rightarrow 0} \approx 6 \text{ mC cm}^{-2} \text{ s}^{-1}$]. But for $t \geq 3$ s the rate of increase of Q_r depends on E_u . For $E_u = 0.3$ V, Q_r increases to approach a limiting value, whereas for $E_u = 0.5$ V, Q_r goes through a maximum value for $t \approx 30$ s, and later decreases rather slowly.

For an asymmetric RSWPR with $E_i = -1.8$ V, $E_u = 0.5$ V and $f = 1$ kHz (Fig. 6), the value of Q_r reaches a maximum for $\tau_u / \tau_i = 0.8$, i.e. $\tau_u = 0.44$ ms. From data depicted in Fig. 6 it appears that a threshold value, $\tau_u / \tau_i \approx 0.3$ is related to the increase of Q_r .

3.3. SEM micrographs

The hydrous cobalt oxide layers obtained after 30 s application of the RSWPR between $E_i = -1.8$ V and $E_u = 0.1$ V at $f = 1$ kHz appear as transparent pink tinged layers. SEM micrographs of these layers show a globular spongy-like rough structure (Fig. 7a). On the other hand, the cobalt oxide layers prepared for the same E_i and f values but $E_u = 0.3$ V, acquire a yellowish-brown colour and the corresponding SEM micrographs display a non-uniform granular morphology (Fig. 7b). Finally, for $E_u = 0.5$ V, the resulting black cobalt oxide layers exhibit a rather uniform globular spongy-like structure (Fig. 7c). The particles that constitute the globular structure present sharp edges and angles.

3.4. IR spectroscopy, thermal gravimetric and differential thermal analysis, and X-ray diffractometry

Cobalt oxide samples were prepared from cobalt electrodes by applying the RSWPR for $E_i = -1.8$ V, $f = 1$ kHz, and for $E_u = 0.1$ V (sample I), $E_u = 0.3$ V (sample II) and $E_u = 0.5$ V (sample III). The cobalt oxide removed from the electrode and collected from the bottom of the cell, was filtered, rinsed repeatedly

Fig. 4. Q_r against f plot. The Co electrodes were subjected for 30 s to a symmetric RSWPR between $E_i = -1.8$ V and E_u at different values of f , 1 M NaOH, 30°C. (□) $E_u = 0.1$ V; (Δ) $E_u = 0.3$ V; (○) $E_u = 0.5$ V.

with triply distilled water, and dried at room temperature under nitrogen. Sample I was initially a near transparent solid which, after a few minutes, turned into a brown compound. This spontaneous process was attributed to the oxidation of β -Co(OH)₂ to CoOOH [14–16]. The sample II was also brown, whereas sample III was black.

The IR spectra of samples I and II (Fig. 8a and b) show similar shapes with a well defined absorption band at 590 cm⁻¹. On the other hand, sample III also shows the band at 590 cm⁻¹ in addition to other bands at 320 and 670 cm⁻¹ (Fig. 8c). Besides, a shoulder at 560 cm⁻¹ can be distinguished, that is, an absorption band superposed on that at 590 cm⁻¹. The bands at 560 and 670 cm⁻¹ were assigned to the vibrations of the Co(III)O₆ and Co(II)O₄ polyhedra [17].

The IR spectra of cobalt oxide samples prepared as indicated above, and subsequently subjected to thermal treatment at 480°C for 4 h, show the main absorption bands centred at 390, 570 and 670 cm⁻¹ (Fig. 8d and e) in good agreement with the spectrum

of Co₃O₄ obtained by thermal decomposition of cobalt nitrate [17–19].

The thermal gravimetric analysis (TGA) of samples I and II (Fig. 9a and b) give both a weight loss of about 31% up to 450°C, whereas the corresponding TGA of sample III shows a weight loss of about 25% involving the stripping of different types of water molecules at 50, 85, 100 and probably 200°C (Fig. 9). All the thermograms can be divided into two regions. The first, up to approximately 150°C, is associated with the loss of the adsorbed and interstitial water. The temperature dependence reflects the different ways in which this water is distributed in the bulk of the oxide. In the second region, the transformation of the hydroxides into oxides (dehydroxylation) occurs. Furthermore, both phenomena can be observed in the DTA spectra, which show two endothermic signals, both coinciding with the initial stages of the corresponding regions on TGA. The dehydroxylation process shows an endothermic peak at about 220°C.

The X-ray diffractograms of thermally treated

Fig. 5. Q_r against t plot. The Co electrodes were subjected for different times (t) to a symmetric RSWPR between $E_i = -1.8$ V and different E_u values at $f = 2.5$ kHz, 1 M NaOH, 30°C. (○) $E_u = 0.3$ V; (□) $E_u = 0.5$ V.

Fig. 6. Q_r against τ_u/τ_l plot. The Co electrodes were subjected for 30 s to a symmetric RSWPR between $E_l = -1.8$ V and $E_u = 0.5$ V at $f = 1$ kHz ($\tau_u + \tau_l = 1$ ms), 1 M NaOH, 30°C.

samples (Fig. 10), give diffraction peaks corresponding to the planes (220), (311), (222), (400), (511) and (440), which are typical of Co_3O_4 spinels. Otherwise, the diffractograms of electrochemically prepared cobalt oxide electrodes show, after thermal treatment at 480°C, a progressive change from an amorphous to a crystalline structure in the direction expected for the development of the Co_3O_4 -spinel structure [5].

4. Discussion

The results show a hydrous cobalt oxide layer can be produced by means of the RSWPR applied to Co electrodes in 1 M NaOH. The stabilized voltammetric profile of the electrochemically oxidized cobalt approaches that of a Co_3O_4 spinel electrode although showing a considerable increase in the overall charge which can be attributed to an active surface area much larger than that of the untreated cobalt electrode. The coincidence between the voltammograms of a Co_3O_4 -spinel electrode and that resulting from the electrochemically oxidized cobalt specimen is obtained when the latter is thermally treated at 480°C.

In principle, there is a correlation between the number of voltammetric peaks (Fig. 1), the number of maxima appearing in the Q_r against E_u plot (Fig. 2) and the colours of the surface compounds resulting after the application of the RSWPR. According to the mechanism of Co_3O_4 formation advanced previously [5], each of the three potential ranges distinguishable in Figs 1 and 2 can be associated with a predominant species at the anodised electrode surface. In going from lower to higher potentials these compounds can be related to $\text{Co}(\text{OH})_2$, Co_3O_4 and Co_2O_3 . According to the literature the $\text{Co}(\text{OH})_2$ species acquires a pink colour in an excess of OH^- ions in solution [20] whereas a yellowish-brown colour has been assigned to the hydrated Co_3O_4 [16] and a black colour has been related to hydrated Co_2O_3 [15, 16]. The sequence of colours appearing for the compounds obtained at

Fig. 7. SEM micrographs of the cobalt oxide layer, scale: 1 μm . The Co electrodes were subjected to a symmetric RSWPR in 1 M NaOH, 30°C, for 30 s between $E_l = -1.8$ V and different E_u values at $f = 1$ kHz. (a) $E_u = 0.1$ V, pink tinged transparent layer; (b) $E_u = 0.3$ V, yellowish-brown tinged layer; and (c) $E_u = 0.5$ V, black coloured layer.

different potentials is consistent with thermodynamic predictions [20–23] and with the conclusions derived from studies of the electrochemical kinetics of cobalt in base solutions, particularly for the possible compounds involved in the anodic formation of thick cobalt hydroxide films in the different potential regions corresponding to peaks shown in Figs 1 and 2 [1, 24–26].

The formation of the hydrous cobalt oxide layer under the RSWPR indicated the fundamental role played by the anodic and cathodic half cycles in determining the characteristics of the anodic layer [5]. The present results indicate that the RSWPR treatment promotes the formation of a precursor compound in the cobalt hydroxide layer which, after the thermal

Fig. 8. Infrared spectra of Co oxide samples prepared in 1M NaOH, 30°C, by using a symmetric RSWPR for 30 s between $E_i = -1.8$ V and different E_u values at $f = 1$ kHz. (a) $E_u = 0.1$ V; (b) $E_u = 0.3$ V; (c) $E_u = 0.5$ V; (d) sample prepared as (a) and then thermally treated at 480°C; and (e) sample prepared as (c) and then thermally treated at 480°C.

treatment, furnishes the Co_3O_4 spinel electrode. The precursor compound has a relatively large water content as deduced from TGA and TDA and exhibits amorphous characteristics, as shown by X-ray diffraction [5], in contrast to the Co_3O_4 spinel resulting from the thermal treatment.

Let us then consider the processes occurring in each half cycle during the application of the RSWPR. At potentials lower than 0.3 V, the anodic half cycle should involve the following sequence of reactions:

On increasing E_u one should expect that those species related to Co(OH)_2 , Co_3O_4 , CoOOH , CoO_2 and soluble Co-anionic species be formed at different potentials. The formation of the hydrous Co(OH)_2 layer can be expressed through a reaction involving $\text{Co(OH)}_{\text{ad}}$ species as follows:

where n is the number of particles entering the formation of the 3D cobalt hydroxide layer. This process, which occurs at $E_u = 0.1$ V, can be related to the voltammetric peak I_a .

The following oxidation levels appearing in the potential range of peak II_a can be represented by the reactions such as:

Fig. 9. Thermal gravimetric (TGA) and differential thermal (DTA) analysis run between 25 and 450°C, for Co oxides prepared as described in Fig. 8. (a) $E_u = 0.1$ V; (b) $E_u = 0.3$ V; and (c) $E_u = 0.5$ V.

Fig. 10. X-ray diffractograms for different Co oxide samples with further thermal treatment. (a) Obtained from thermal decomposition of $\text{Co}(\text{NO}_3)_2$; (b) prepared as indicated in Fig. 8, $E_u = 0.1 \text{ V}$; (c) as for (b) with $E_u = 0.3 \text{ V}$; and (d) as for (b) with $E_u = 0.5 \text{ V}$.

Reaction 3a implies the formation of a gel-like compound which can be expressed by the stoichiometry $\text{Co}_3\text{O}_4 \cdot 6\text{H}_2\text{O}$ ($x' = 4$) [5] and regarded as a precursor for the Co_3O_4 formation. Reaction 3b involves the complete electrooxidation of the $\text{Co}(\text{OH})_2$ to CoOOH , for the latter the probable stoichiometry being $\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ($x'' \leq 5$). Reaction 3c corresponds to the electrochemical dissolution of the $\text{Co}(\text{OH})_2$ layer yielding soluble HCoO_2^- . It has been shown that Reactions 3a [5] and 3c [26] are relatively slow processes, so that probably Reaction 3b predominates along the anodic halfcycle, in the potential range of peak II_a. Therefore, $[\text{2CoOOH} \cdot x''\text{H}_2\text{O}]$ is probably the type of compound mainly obtained at $E_u = 0.3 \text{ V}$.

Finally, in the potential range of peak III_a, just preceding the OER, the highest oxidation level of Co is attained through a reaction such as

Reaction 4 is a fast reaction implying the adsorption of OH^- ions on the hydrous cobalt hydroxide layer

($x''' \leq 3$) assisted by the high positive potential applied to the electrode. The stoichiometry of the product in Reaction 4 is consistent with emission Mössbauer spectroscopy data reported for the anodic oxidation of cobalt [24] although it can be formally related to that of a hydrous CoO_2 species [5, 7, 8, 26].

The first reaction occurring in the cathodic half cycle of the RSWPR is related to Reaction 4 in the reverse direction, yielding $[\text{2CoOOH} \cdot x''\text{H}_2\text{O}]$. This is a fast reaction which is followed either by Reaction 3b in the reverse direction or by the following one producing the precursor

Soluble species are formed in the electroreduction process through a reaction such as

coupled to the equilibrium reaction

The product from Reaction 5 is accumulated principally in the electroreduction half cycle and to a lesser extent during the electrooxidation half cycle. Otherwise, the $[2\text{CoOOH} \cdot x\text{H}_2\text{O}]$ species are gradually electroreduced to $[\text{Co}(\text{OH})_2 \cdot x\text{H}_2\text{O}]$, to $\text{Co}(\text{OH})_{\text{ad}}$ and to Co. The Co(O) oxidation state is probably attained only in the HER potential range, although the high local increase in pH may contribute to the precipitation of $\text{Co}(\text{OH})_2$ on the electrode, particularly when soluble cobalt species are formed in the electroreduction Reaction 6a. This explains the fact that the maximum accumulation of precursor appears when the value of E_1 lies in the potential range where the simultaneous HER and complete electroreduction of the cobalt oxide species to Co(O) take place. Hence, as discussed previously [5], the increase in the electrode roughness and the amount of precursor produced in the RSWPR depend principally on the electroreduction conditions, as has been recently described for other metals in different solutions [27, 28].

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