



Electrochemical behaviour of cadmium in NaOH solution

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Abstract

The electrochemical behaviour of cadmium in 1 M NaOH solution was studied. Different electrochemical methods such as potentiodynamic measurements, polarization techniques and electrochemical impedance spectroscopy (EIS) were used. During the course of polarization, several characteristic features were observed, including prepassivation and a relatively wide passive range extending over 1.4 V. Equivalent circuit models for the electrode–electrolyte interface under different applied potentials were proposed. The impedance data measured at steady state were fitted to calculated data according to proposed equivalent circuits. The relevance of the proposed equivalent circuits to the different phenomena occurring at the electrode–solution interface was discussed. The passive film formed on Cd is composed of two layers: a barrier layer in contact with metal and a deposit on the barrier layer. The barrier layer appears to form directly from the metal through a solid state reaction, rather than by a dissolution–precipitation mechanism. For an applied potential $>+0.7$ V the relative passive film thickness and resistance decrease to lower values indicating transpassive dissolution at this potential.

1. Introduction

In spite of previous studies of the cadmium electrode in alkaline solutions there is uncertainty concerning the nature of the dissolved cadmium species and its relationship to the formation of the passive film. There is also uncertainty concerning the character of the passive film and the mechanism whereby it is produced [1, 2]. In the past a dissolution–precipitation [3–8] and a solid-state mechanism [9–11] have both been proposed.

Several authors [1–3, 12] have suggested that the formation of a layer of $\text{Cd}(\text{OH})_2$ is responsible for the inhibition of metal dissolution. Nevertheless, some experimental evidence suggests the formation of CdO films as the cause of passivation [13–16]. Lately, Arvia, Vilche and coworkers have [17–20] studied the electrochemical oxidation and reduction of cadmium in alkaline solutions. They have suggested that anodization in alkaline solutions comprises the formation of a passivating layer consisting of $\text{Cd}(\text{OH})_2$ and CdO and the simultaneous generation of soluble Cd(II) species going into solution.

In this contribution, the electrochemical behaviour of cadmium in 1 M NaOH solution is studied using potentiodynamic and potentiostatic polarization techniques, with the specific goal of identifying the probable mechanism of the corrosion and passivation processes taking place at the electrode–electrolyte interface in alkaline solution.

2. Experimental details

The working electrode was made from cadmium rod, mounted into a glass tube using epoxy resin leaving a surface area of 0.0314 cm^2 to contact the solution. A stout copper wire was employed as the electrical contact. A three-electrode, all-glass, double-walled cell with a large area platinum counter electrode and saturated calomel reference electrode (SCE) was used. The solutions were prepared from analytical-grade chemicals and triple-distilled water. Electrochemical measurements were carried out in 1 M NaOH solution. Before each experiment, the working electrode was polished mechanically using successively finer grades of emery paper up to 1000 grit, and then polished with alumina powder down to $1 \mu\text{m}$. The electrode was rubbed with a smooth polishing cloth, washed with triple distilled water and transferred quickly to the electrolytic cell containing the NaOH solution.

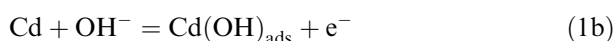
The electrochemical impedance investigations and polarization measurements were performed using a Zahner Elektrik IM5d system. The excitation amplitude was 10 mV peak-to-peak in a frequency domain 10^5 – 10^{-2} Hz. Potential control of the cadmium electrode was achieved by using the same system. Before the passive film was formed, the working electrode was maintained at a potential of -1.8 V vs SCE for about 5 min. Potentiodynamic polarization measurements were carried out using a voltage scan rate of 10 mV s^{-1} . Steady

state polarization data were obtained potentiostatically by holding the potential at the desired value for about 24 h. Using a water thermostat and the double walled cell all experiments were carried out at a constant temperature of 25 ± 0.1 °C. Potentials are referred to the saturated calomel electrode. Details of the experimental procedures are described elsewhere [21, 22].

3. Results and discussion

3.1. Potentiodynamic measurements

A typical potentiodynamic curve, as measured on cadmium at 10 mV s^{-1} in 1 M NaOH after initially polarizing the electrode at -1.8 V vs SCE for about 5 min, is shown in Figure 1. The potential scan was initiated at -1.8 V , where a considerable cathodic current is observed due to hydrogen evolution (HER). After commencing the positive-going sweep, the cathodic current density rapidly diminishes as the potential is made less negative. There is then a transition region before the active region for metal dissolution, in which the current density levels out with potential. Sanghi et al. [5] have suggested that this transition region is due to the change in the adsorbed layer on the cadmium surface. This plateau is most probably due to the formation of adsorbed species such as $\text{Cd}(\text{OH})_{\text{ads}}^-$ and/or $\text{Cd}(\text{OH})_{\text{ads}}$ at the electrode surface [13, 17] via the reactions:



This adsorbed layer impedes both the hydrogen evolution reaction (HER) and anodic dissolution of the metal

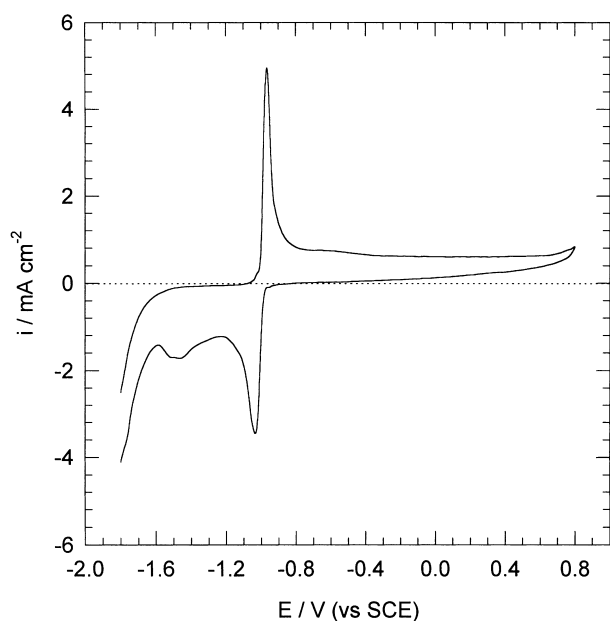
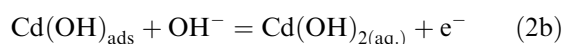
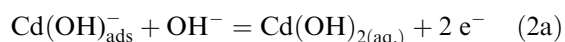


Fig. 1. Potentiodynamic curve for cadmium in 1 M NaOH. Sweep rate 10 mV s^{-1} .

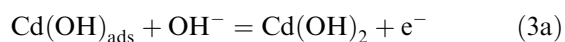
leading to the observed current arrest. In other words, the metal acquires a type of passivity, prepassivation, due to the formation of the adsorbed layer of the intermediate species.

The $\text{Cd}(\text{OH})_{\text{ad}}$ and/or $\text{Cd}(\text{OH})_{\text{ads}}^-$ species is an adsorbed intermediate for both active dissolution and passivation. In the anodic active region cadmium goes into solution as Cd^{2+} ions [17, 19], the current density rapidly increasing with potential until it reaches a maximum value. The presence of the anodic peak can be attributed to a dissolution process followed by a passivation process. Thus,

- (i) Dissolution of the adsorbed layer according to Reactions 2:

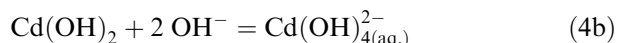


- (ii) Formation of a passive film of $\text{Cd}(\text{OH})_2$ [1–3, 12] and may be CdO [13–16], according to Reactions 3:



The passive film appears to form directly from the metal, rather than by precipitation, as will be discussed later. The presence of $\beta\text{-Cd}(\text{OH})_2$ in the passive film has been confirmed by X-ray measurements, electron diffraction and i.r. spectra [2]. Although $\text{Cd}(\text{OH})_2$ is favoured as the more stable species [12], the formation of CdO cannot be completely eliminated [12–15].

Several authors [1, 2, 8, 12] have studied the kinetics of cadmium dissolution in alkaline solutions, including the determination of Tafel constants and reaction orders with respect to the concentration of OH^- for the beginning of the active region. Substantial experimental evidence points to the fact that the predominant species in concentrated alkaline solutions is largely $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ [12, 23]. It may be suggested that the outer layer of the passive film is dissolved in the passive region through the following chemical reactions:



A small anodic peak was observed at about -0.6 V which can be attributed to cadmium dissolution through the passive film and a concomitant growth of a passive layer on the metal [22]. Alternatively, it may be a result of metal dissolution and ageing of the passive film [17]. In general the measured anodic current can be attributed to passive film growth, metal dissolution through the passive film and reformation of the passive film [24]. For passive cadmium the dissolution is mostly a chemical process (Reactions 4(a) and (b)). The positive-going scan is continued up to $+0.8 \text{ V}$, which is

about 0.1 V more positive than the transpassive dissolution potential. The passive state is seen to extend over a wide range of potential from about -0.7 to $+0.7$ V. The reverse scan exhibits two cathodic current peaks, at about -1.0 and -1.4 V, which can be attributed to electrochemical reduction of $\text{Cd}(\text{OH})_2/\text{CdO}$ and soluble species, respectively [17]. A net cathodic current contribution is recorded at potentials more negative than -1.6 V due to HER.

3.2. Steady state polarization measurements

The steady state polarization curve obtained for Cd in 1 M NaOH is shown in Figure 2. The points on this curve indicate the polarization potentials at which the electrode impedance measurements were performed. In the following, only some will be shown which illustrate typical features of the impedance diagram and its change with potential.

The steady state curve obtained in 1 M NaOH solutions shows similar features to the positive-going scan of the potentiodynamic curve measured in the same solution (cf. Figure 1). The steady state cathodic current decreases with potential until a current arrest observed near -1.0 V. This arrest is mostly related to a prepassivation process occurring at the electrode surface due to the formation of the adsorbed layer of intermediate species as described above. Similar results were reported for iron dissolution in acidified 1 M Na_2SO_4 [25]. The further current increase corresponds to the active dissolution and then the passivation process starts beyond the anodic current maximum. The critical passivation potential is located at about -0.7 V vs SCE and the passive current density diminishes to about $6 \mu\text{A cm}^{-2}$. As recorded in the potentiodynamic curve a small anodic peak was observed at about -0.5 V. The

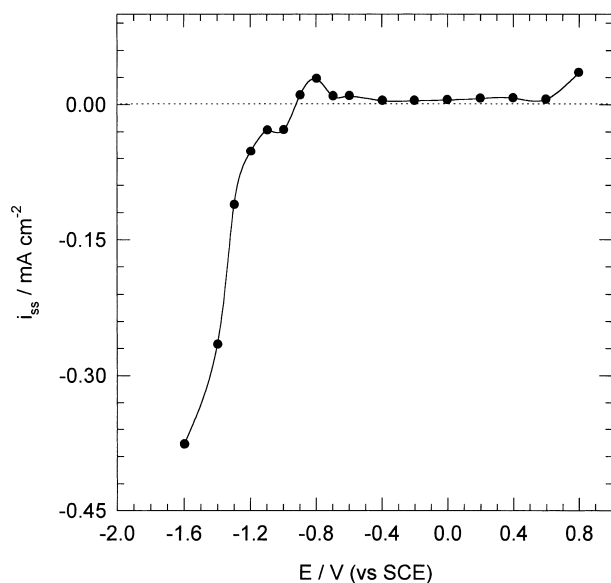


Fig. 2. Steady state polarization curve for a cadmium electrode in 1 M NaOH solution.

steady state current density remained more or less constant as the potential was raised from -0.7 to $+0.7$ V, and hereafter the transpassive anodic current region was observed.

3.3. Potentiostatic transient measurements

A typical potentiostatic transient recorded after sweeping the potential from -1.8 V to -0.4 V is shown in Figure 3. The current rapidly decayed with time followed by a moderate current decrease and ultimately reached a steady state. A pseudo-steady state was observed after a very short time, about 20 min, a true steady state was recorded after about 20 h. This indicates that the interfacial processes (e.g., passive film growth and metal dissolution) are of very low relaxation frequencies, that is they are very slow processes. At longer times a steady state condition is reached with dissolution of the outer layer of the passive film balanced by its rate of formation. The steady state current is generally related to the rate of electrochemical dissolution of the metal through the passive film or 'chemical dissolution' and reformation of the passive film [24].

3.4. EIS measurements

The impedance measurements were carried out at various polarization potentials: hydrogen evolution, prepassivation, anodic dissolution, passivation, transpassive and oxygen evolution range. Figures 4–6 show the impedance diagrams obtained for Cd in 1 M NaOH at various polarization potentials.

To investigate the impedance characteristics of the Cd electrode in 1 M NaOH solution, a constant potential was applied to the electrode until a steady state was

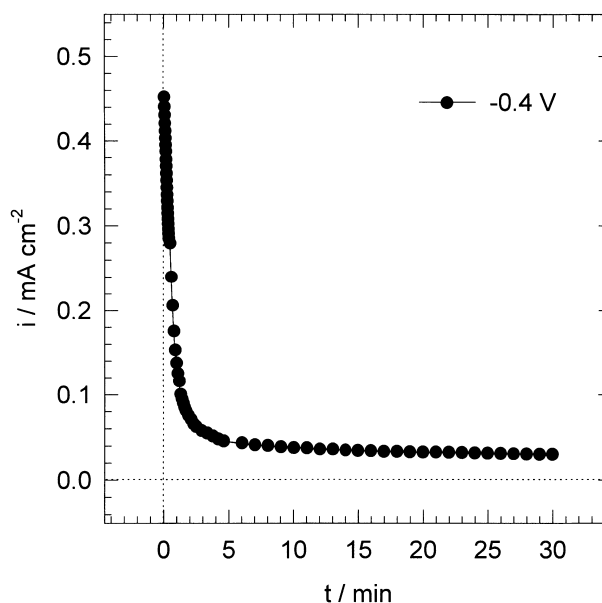


Fig. 3. Potentiostatic transient for cadmium in 1 M NaOH solution, on holding the potential at -0.4 V vs SCE.

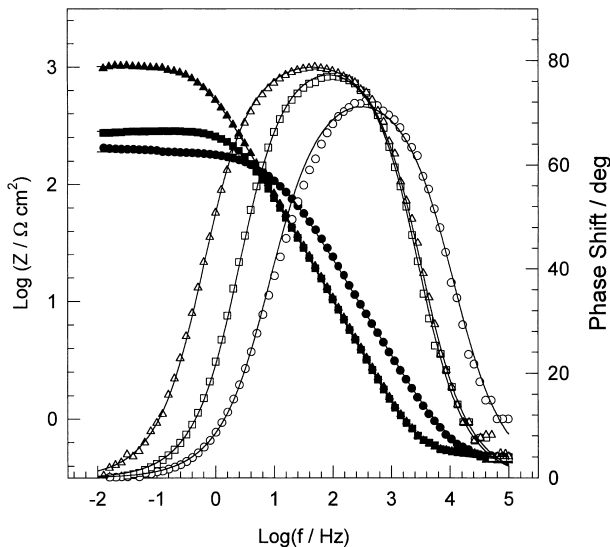


Fig. 4. Bode plots of cadmium in 1 M NaOH solution at steady state in the hydrogen evolution range. Key: (●) -1.6, (■) -1.4 and (▲) -1.3 V; (—) simulated.

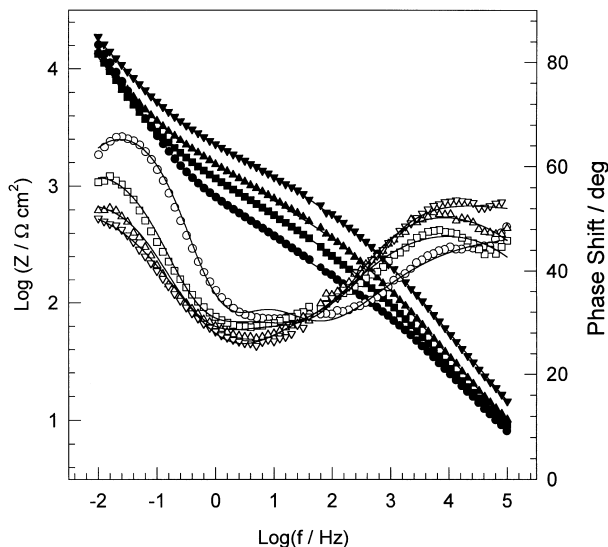


Fig. 6. Bode plots of cadmium in 1 M NaOH solution at steady state in the passive range. Key: (●) -0.2, (■) +0.2, (▲) +0.4 and (▼) +0.6 V; (—) simulated.

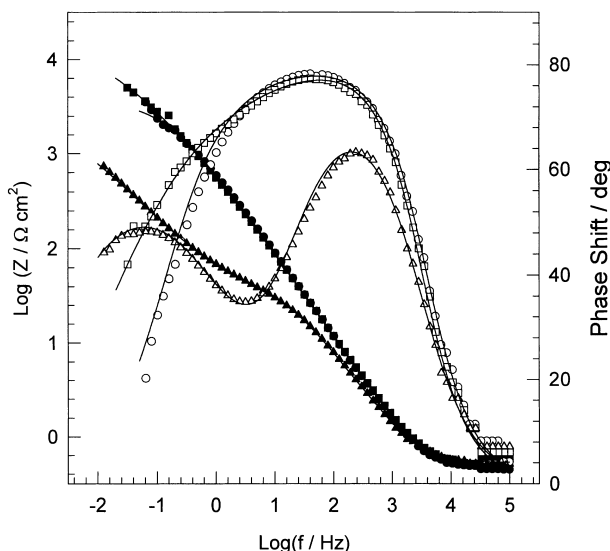


Fig. 5. Bode plots of cadmium in 1 M NaOH solution at steady state in the prepassivation range. Key: (●) -1.2, (■) -1.1 and (▲) 1.0 V; (—) simulated.

reached, which normally took about 20 h; then the impedance spectra were recorded. The steady state was considered when the measured impedance and current did not change with time at the particular potential values. The recorded impedance and current are somewhat changed during 20 h of polarization at a constant d.c. bias. After that period of time, there are no further changes in the recorded data. Figure 4 shows the impedance diagrams obtained at various polarization potentials in the hydrogen evolution domain. The Bode plots show resistive regions at the high and low frequencies and only one phase maximum at intermediate frequencies indicating the presence of only one time constant due to the electrical double layer.

The impedance at different potentials in the hydrogen evolution domain was analysed using the equivalent circuit shown in Figure 7(a), where R_s is the solution resistance, C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The dispersion formula for electrode impedance of this combination is used, where the empirical exponent, α , is introduced:

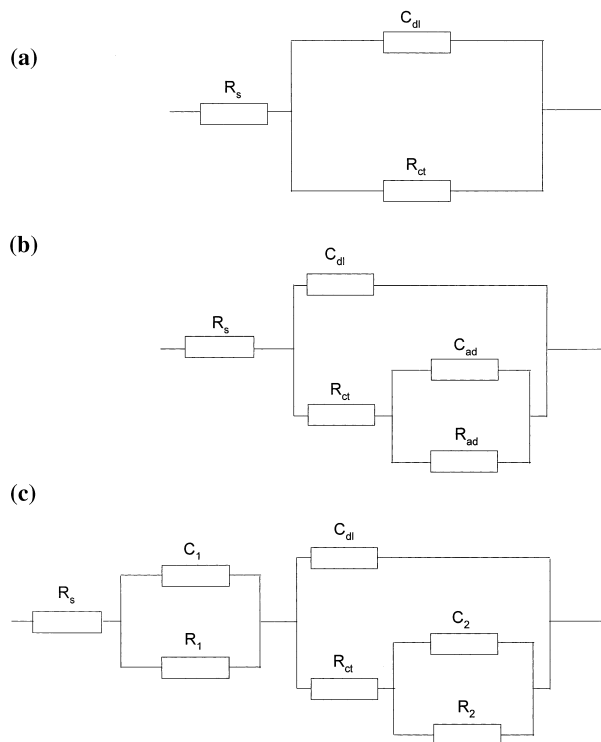


Fig. 7. Equivalent circuits used in the fitting of the impedance data of cadmium at different conditions; (R_s) solution resistance, (C_{dl}) double layer capacitance, (R_{ct}) charge transfer resistance, (R_{ad}) and (C_{ad}) adsorbed layer resistance and capacitance in the prepassivation domain ($R_{1,2}$ and $C_{1,2}$) outer and inner layer resistance and capacitance in the passive range.

Table 1. Equivalent circuit parameters for Cd after 20 h of electrode immersion in 1 M NaOH solution at different applied potentials in the hydrogen evolution range at 25 °C

E_{app}/V	R_s/Ω	$C_{\text{dl}}/\mu\text{F cm}^{-2}$	α	$R_{\text{ct}}/\Omega \text{ cm}^2$
-1.6	13.7	47.0	0.86	188.3
-1.5	13.7	67.6	0.88	380.6
-1.4	14.9	127.7	0.91	285.3
-1.3	14.4	120.4	0.90	1017.7

$$Z = R_s + \frac{R}{1 + (2\pi fRC)^\alpha} \quad (5)$$

where α denotes an empirical parameter ($0 \leq \alpha \leq 1$) and f is the frequency in hertz. The above relation takes into account the deviation from the ideal RC -behaviour in terms of a distribution of time constants due to surface inhomogeneities, roughness effects, and variations in surface layer properties or compositions [26–28].

The calculated equivalent circuit parameters for cadmium at different potentials in the hydrogen evolution domain are presented in Table 1. The double layer capacitance was found to be in the range of 47–127 $\mu\text{F cm}^{-2}$ (cf. Table 1). In the potential range from -1.6 to -1.3 V, almost the entire electrode surface is covered by adsorbed hydrogen, which is probably the reason why the double layer capacitance in this potential range is slightly high. During the transition from hydrogen evolution to prepassivation and active dissolution states, the electrode impedance changes with potential. At less negative potentials, -1.2 to -0.8 V, the phase maximum becomes broader until it splits into two peaks indicating the presence of two relaxation processes due to the electrical double layer and the surface coverage of adsorbed intermediate species, such as $\text{Cd}(\text{OH})_{\text{ad}}$ and/or $\text{Cd}(\text{OH})_{\text{ads}}^-$ (cf. Figure 5). The time constant at high frequencies originates from the $R_{\text{ct}}C_{\text{dl}}$ combination while the one at low frequencies initiates from the $R_{\text{ad}}C_{\text{ad}}$ combination. This finding is consistent with the current arrest observed in the potentiodynamic polarization curve and steady state current–potential measurements. The measured impedance data in the prepassivation and active dissolution range were analysed using the equivalent circuit shown in Figure 7(b)

Table 2. Equivalent circuit parameters for Cd after 20 h of electrode immersion in 1 M NaOH solution at different applied potentials in the prepassivation and active dissolution range at 25 °C

E_{app}/V	R_s/Ω	$C_{\text{dl}}/\mu\text{F cm}^{-2}$	α	$R_{\text{ct}}/\Omega \text{ cm}^2$	$C_{\text{ad}}/\mu\text{F cm}^{-2}$	α	$R_{\text{ad}}/\text{k}\Omega \text{ cm}^2$
-1.2	14.4	107.0	0.91	100.1	2.8	0.56	3.6
-1.1	16.6	103.4	0.92	25.2	4.9	0.54	14.3
-1.0	15.4	130.3	0.83	39.8	293.3	0.65	2.5
-0.8	15.4	30.8	0.65	606.7	719.4	0.84	13.2

where $R_{\text{ad}}C_{\text{ad}}$ was introduced to account for adsorption of the intermediate species, $\text{Cd}(\text{OH})_{\text{ads}}$ and/or $\text{Cd}(\text{OH})_{\text{ads}}^-$. The calculated equivalent circuit parameters for cadmium in this range are presented in Table 2.

Figure 6 shows schematic impedance spectra of Cd at different potentials in the passive potential range from -0.7 to +0.7 V. In this range the phase angle shows three peaks. The impedance at high frequencies represents the relaxation of the electrical double layer. The capacitive impedance at low frequencies is due to a passive film which seems to be duplex in nature, comprising a barrier (inner) layer, CdO and/or $\text{Cd}(\text{OH})_2$, covered with a porous (outer) layer of $\text{Cd}(\text{OH})_2$. In the passive range, R_1C_1 and R_2C_2 denote the resistance and capacitance of the outer and inner layer respectively (cf. Figure 7(c)). The passive film thickness is given by

$$d = \frac{\varepsilon\varepsilon_0}{C} \quad (6)$$

where d is the film thickness, ε the dielectric constant of the passive film, ε_0 the permittivity of free space ($8.85 \times 10^{-14} \text{ F cm}^{-1}$) and C is the capacitance of the passive film. Although the actual value of ε within the film is difficult to estimate, a change of C can be used as an indicator of a change in the film thickness, d . The reciprocal capacitance of the passive film, $1/C$, is directly proportional to the passive film thickness [22, 29]. The porous layer thickness, $1/C_1$, does not show a clear change with potential. Its relative thickness, $1/C_1$, is more or less the same throughout the passive range (cf. Table 3). The outer layer resistance, R_1 , was also found to be more or less the same with different applied potentials (cf. Table 3).

Table 3. Equivalent circuit parameters for Cd after 20 h of electrode immersion in 1 M NaOH solution at different applied potentials in the passive range at 25 °C

E_{app}/V	R_s/Ω	$C_{\text{dl}}/\mu\text{F cm}^{-2}$	α	$R_{\text{ct}}/\Omega \text{ cm}^2$	$C_1/\mu\text{F cm}^{-2}$	α	$R_1/\Omega \text{ cm}^2$	$C_2/\mu\text{F cm}^{-2}$	α	$R_2/\text{k}\Omega \text{ cm}^2$
-0.7	1.0	10.3	0.60	680	3.75	0.69	78	624	0.86	54
-0.6	1.0	11.1	0.61	280	1.98	0.76	117	219	0.73	63
-0.4	30.1	17.9	0.68	7470	2.41	0.60	87	242	1.00	66
-0.2	8.5	20.6	0.75	760	1.89	0.52	7450	94	0.83	125
0.0	81.8	42.8	0.80	940	2.48	0.52	476	48	0.77	121
0.2	53.5	11.8	0.67	1600	1.70	0.56	393	50	0.76	244
0.4	117.3	5.3	0.66	1270	1.33	0.64	275	33	0.75	475
0.6	143.4	3.9	0.66	2570	0.79	0.65	238	9	0.62	265
0.8	6.9	2.64	0.50	2.76	0.70	0.67	274	67	0.79	26.9

According to the fitting results, the capacitance values of the inner layer (C_2) are remarkably high and decrease with potential shift in the positive direction (cf. Table 3). This tendency can be explained assuming that the passive film thickness increases with increasing applied potential, provided that the same type of passive film is growing at different potentials, because capacitance is inversely proportional to the passive film thickness [22, 29]. The inner layer resistance, R_2 , was also found to increase with applied potential (cf. Table 3). In general, the impedance measurements show passivation behaviour for applied potentials from -0.7 to $+0.7$ V, where the barrier layer formed on cadmium is thin and of high resistance (cf. Table 3). Above $+0.7$ V anodic polarization leads to significant decay in the thickness and resistance of the barrier layer. This remarkable change in film thickness and resistance at this potential is attributable to transpassive dissolution and/or oxygen evolution.

A comparison of the resistance and thickness of the outer and inner layer reveals that the inner layer is thinner and more resistive than the outer layer. Thus, under most conditions in the passive state, the metal is covered by a duplex film, comprising a barrier layer (CdO and/or Cd(OH)₂) covered with a porous layer of Cd(OH)₂. The barrier layer appears to form directly from the metal, rather than by precipitation, and its formation is considered to be responsible for the transition from active to passive state.

The absence of a diffusion contribution may indicate that the passive film formation does not proceed through a dissolution–precipitation mechanism [21, 22, 30]. Therefore, the formation of a very thin, very resistive film and the absence of a diffusion process may indicate that the passive film formation under potentiostatic conditions proceeds through a solid state mechanism.

4. Conclusions

Using different electrochemical techniques, several characteristic features of the behaviour of Cd in NaOH solutions were recorded, including prepassivation and a relatively wide passive range extending over 1.4 V from about -0.7 to $+0.7$ V. An adsorbed layer represents the intermediate species for both active dissolution and passivation. The passive film formed on cadmium is duplex in nature, consisting of an inner barrier layer and an outer porous layer. The passive film formation under

potentiostatic conditions is believed to occur through a solid state mechanism.

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