

# Nature and stability of anodic oxide films formed on molybdenum in chloride solutions

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The formation and stability of anodic oxide films on molybdenum in chloride solutions was tested using impedance and polarization measurements. The efficiency of oxide formation increases as the acidity of the formation medium increases. The film is highly stable and resistive to attack and dissolution regardless of the chloride concentration, pH or film thickness. The corrosion potential did not vary with variation of immersion time, solution composition or film thickness and recorded  $\approx 0.000$  V vs SCE indicating the high insulating properties of the film. Polarization measurements on previously anodized molybdenum electrode showed that the electrode is ideally polarized over a potential region not less than 2 V. The magnitude of that potential region increases as the film thickness increases. The anodic film cannot be reduced or removed by galvanostatic cathodic polarization. The impedance behaviour of the anodized molybdenum electrode was found to be purely capacitive and the oxide film may be treated approximately as a perfect dielectric material.

## 1. Introduction

Previous work on the electrochemical behaviour of pure molybdenum indicated that the metal passivated easily and that the end product of its electrochemical oxidation is hexavalent molybdenum [1-9]. In aqueous media, the passivation film consists mainly of  $\text{MoO}_2$  [8-13]. Hull [14, 15] studied the anodic dissolution of molybdenum in  $\text{H}_2\text{SO}_4$  and KOH solutions using linear sweep voltammetry. He identified three different films in alkaline solutions ( $\text{MoO}_2$ ,  $\text{MoO}_3$  and  $\text{Mo}(\text{OH})_3$ ) and two films in acid solutions ( $\text{MoO}_2$  and  $\text{MoO}_3$ ). Johnson *et al.* [16, 17] also proposed a mechanism for the anodic dissolution of molybdenum in chloride and sulphate solutions of different pHs involving the further oxidation of the passivation film,  $\text{Mo}_2\text{O}_5$ , to  $\text{MoO}_3$  which hydrolyses and dissolves.

Studies on the kinetics of open-circuit oxide film formation on molybdenum in HCl, NaOH [18] and salt solutions [19] were reported. Quite recently, the galvanostatic anodization of molybdenum and the electrical breakdown of the formed oxide were investigated in detail [20-22]. The aim of this work is to investigate the nature and the stability of anodic oxide film formed on molybdenum in chloride solutions.

## 2. Experimental details

Details of the experimental method employed here have been given elsewhere [23, 24]. The electrode was cut from a spectroscopically pure molybdenum rod (Johnson-Matthey, London). The molybdenum was fitted in a suitable glass tube using an epoxy resin, with a small copper wire for electrical contact. The exposed surface area was  $0.125\text{ cm}^2$ . All chemicals were AnalaR grade or chemically pure. Triply distilled water was used for preparation of all solutions. The

electrode potential was measured against a saturated calomel electrode (SCE). The normal working frequency was 1 kHz. The measurements were carried out in an air thermostat at  $30 \pm 0.2^\circ\text{C}$ .

### 2.1. Procedure

Before each experiment, the electrode was mechanically polished using successively finer grades of metallographic emery papers down to 4/0 until silvery bright surfaces were obtained, then rubbed with a soft cloth and rinsed with triply distilled water before immersion in the formation medium. The galvanostatic polarizations were started after about 1 h at a constant current density of  $0.8\text{ mA cm}^{-2}$  until the desired formation voltage (FV). The current was then interrupted and the electrode was transferred to the test solution after being washed quickly and gently with triply distilled water, where the measurements were carried out immediately. The polarization measurements were carried out after about 5 h immersion in the test solution.

## 3. Results and discussion

### 3.1. Anodic oxide film formation

The molybdenum electrode was anodized in various electrolytes at different constant current densities; some potential-time curves were selected and are illustrated in Fig. 1. Generally, polarization curves are similar to those reported in the anodization of valve metals; each curve consists of a gradual potential rise followed by a potential arrest. The arrest is followed by another potential rise (not observed in highly acidic solutions).

The first potential rise is connected mainly with

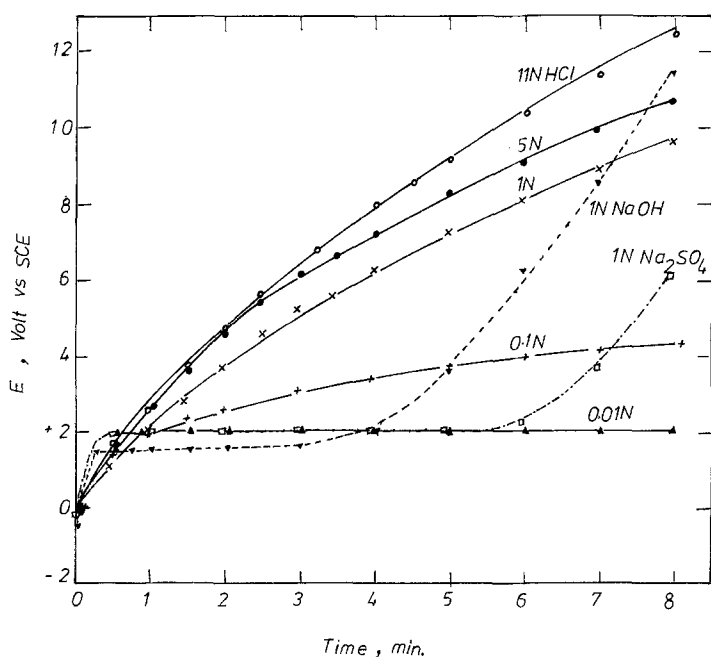


Fig. 1. Anodic polarization curves of molybdenum in various naturally aerated solutions. — HCl solutions, c.d. =  $0.2 \text{ mA cm}^{-2}$ ; --- 1 N NaOH, c.d. =  $2.0 \text{ mA cm}^{-2}$ ; - · - 1 N  $\text{Na}_2\text{SO}_4$ , c.d. =  $0.8 \text{ mA cm}^{-2}$ .

oxide film formation and thickening [25, 26]. The efficiency of oxide formation decreases with time where other anodic processes occur. The arrest is connected mainly with  $\text{O}_2$  evolution and halogen may also be liberated [27]. After the arrest the metal surface becomes reactive towards oxide formation, again probably due to oxidation of the metal surface during the arrest [28] or oxide film crystallization [29]. The results show that the efficiency of oxide film formation increases with increase of formation medium acidity (see Appendix 1).

### 3.2. Anodic oxide film stability in chloride solutions

3.2.1. *Effect of pH.* As described in the experimental details the electrode was anodized in 1 N  $\text{H}_2\text{SO}_4$  solution to 20 V vs SCE and then transferred to the test solution where potential, capacitance and resistance were traced for about 4 h. The tested solutions were normal chloride solutions of different pHs; their compositions were: 1 N HCl +  $x \text{ M H}_2\text{SO}_4$  (pH 0.7), 1 N NaCl +  $x \text{ M Na}_2\text{SO}_4$  (pH 5.5) and 1 N NaCl +  $x \text{ M Na}_2\text{SO}_4$  + 1 N NaOH (pH 12.2), where  $x$  rep-

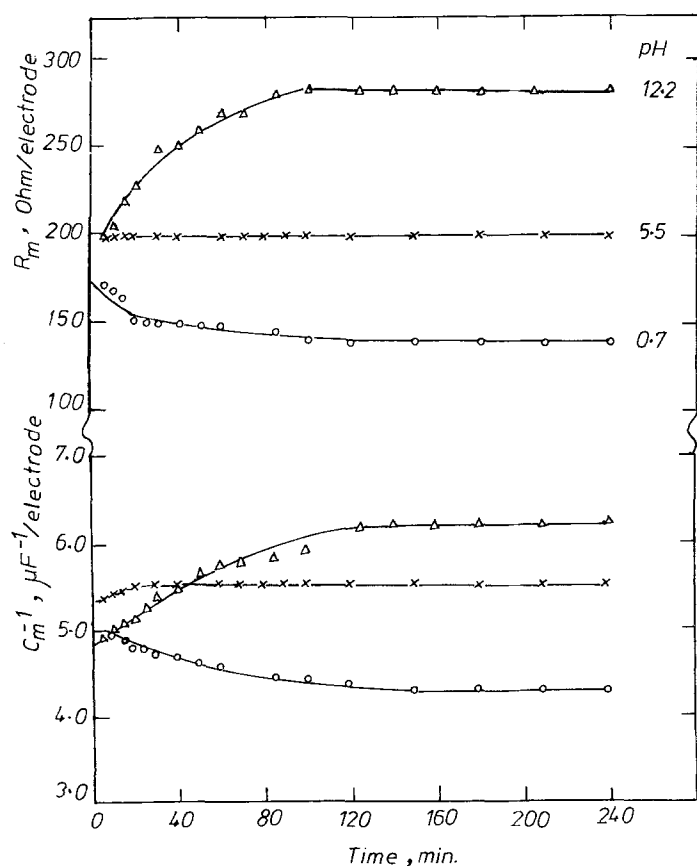


Fig. 2. Variation of reciprocal capacitance and resistance with time for anodized molybdenum electrodes (to 20 V) in chloride solutions of different pH values.

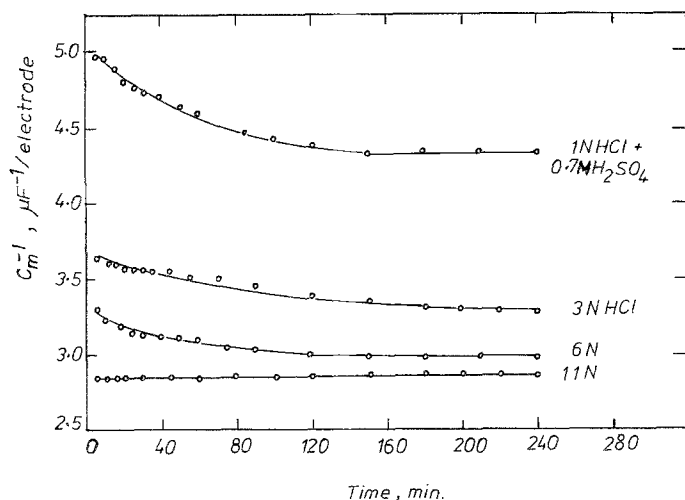


Fig. 3. Variation of reciprocal capacitance of anodized molybdenum electrodes (to 20 V) with time in acid chloride solutions of different concentrations.

resents the number of moles required to make the ionic strength equal to 3.

The corrosion potential did not vary with time and was independent of the solution pH. The recorded potential values were  $\approx 0.000$  V. Replacement of the SCE by other reference electrodes did not affect the previous recorded value. This finding indicates the high insulating properties of the oxide film [30].

The variation of reciprocal capacitance,  $C_m^{-1}$ , and resistance,  $R_m$ , of the anodized molybdenum electrode with time is shown in Fig. 2. As can be seen, both  $C_m^{-1}$  and  $R_m$  behave similarly. Stable values of both  $C_m^{-1}$  and  $R_m$  were reached after about 2 h. The results show that the film is highly stable and does not suffer attack or dissolution. The slight decrease of  $C_m^{-1}$  in the case of pH 0.7 before attainment of the stabilized value, about 15% decrease, may be attributed to an increase in the film conductivity [31] probably by the penetration of  $H^+$  ions from the defects in the film. Also, the increase of  $C_m^{-1}$  in the case of pH 12.2 may be attributed to the film thickening as a result of  $OH^-$  ion adsorption onto the oxide film surface [32]. The resistance measurements support the capacitance measurements as can be seen in Fig. 2.

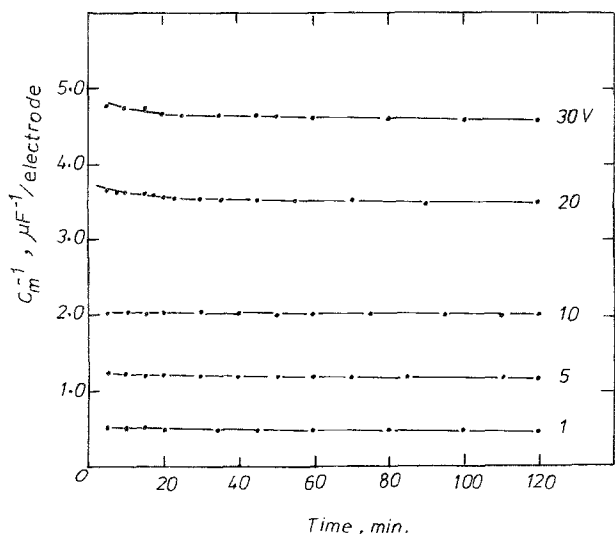


Fig. 4. Variation of reciprocal capacitance of anodized molybdenum electrodes (to 1, 10, 20 and 30 V) with time in 3N HCl solutions.

**3.2.2. Effect of acid chloride concentration.** The stability of the anodic oxide film was tested in HCl solutions of different concentrations up to 11 N. Here also, the corrosion potential was found to be independent of the solution composition and, as previously, was  $\approx 0.000$  V.

The variation of  $C_m^{-1}$  with time is shown in Fig. 3. The results show the high stability of the anodic film in all cases. The slight decrease of  $C_m^{-1}$  before the stabilization becomes less pronounced as the acid concentration increases.

**3.2.3. Effect of formation voltage.** The variation of  $C_m^{-1}$  of the anodized electrode (to 1, 5, 10, 20 and 30 V) with time in 3.0 N HCl solution is illustrated in Fig. 4. As can be seen,  $C_m^{-1}$  does not vary with time and stable values are quite distinct. The initial slight decrease of  $C_m^{-1}$  can be observed only for thick films (high formation voltage). Extrapolation of  $C_m^{-1}$  to zero time gives  $C_m^{0-1}$  which corresponds to the oxide film thickness at the respective FV. As shown in Fig. 5,  $C_m^{0-1}$  increases linearly with FV which indicates that  $C_m^{-1}$  is directly proportional to the oxide thickness [33]. Also, the electrode resistance,  $R_m^0$ , increases linearly with FV (cf. Fig. 5). The corrosion potential of the anodized electrode  $\geq 5$  V was independent of FV and did not vary with time and recorded a value of  $\approx 0.000$  V. At FV < 5 V, the electrode does not seem to have the

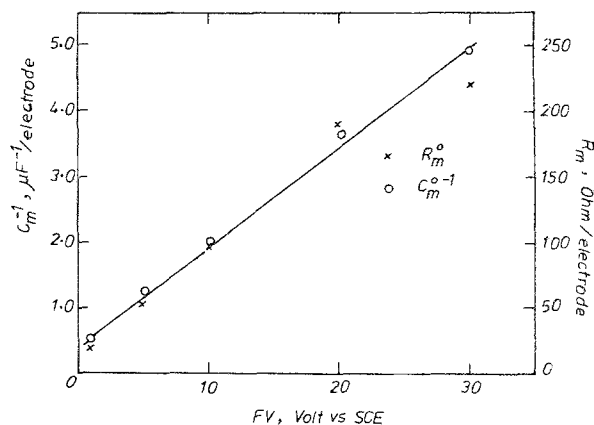


Fig. 5. Variation of initial reciprocal capacitance,  $C_m^{0-1}$ , and resistance,  $R_m^0$ , with formation voltage, FV.

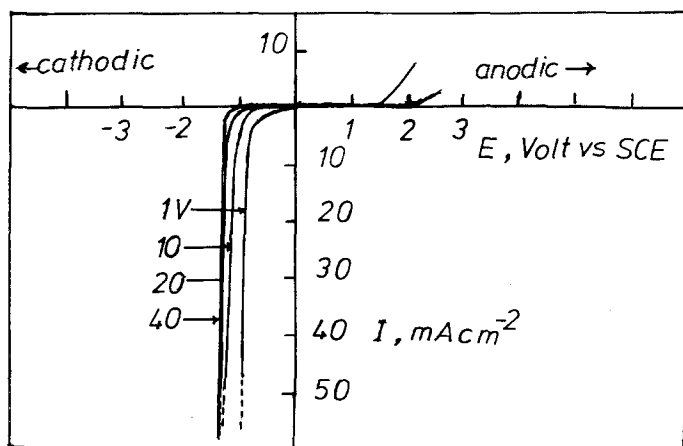


Fig. 6. Potentiostatic polarization curves of anodized molybdenum electrodes (to 1, 10, 20 and 30 V) in naturally aerated 1 N HCl solutions.

required oxide film thickness to cause the corrosion potential to be independent of the solution composition.

### 3.3. Polarization measurements

Potentiostatic  $i$ - $E$  curves of the anodized molybdenum electrode (to 1, 10, 20 and 30 V) in 1 N HCl solutions are illustrated in Fig. 6. As can be seen, the anodized electrode is ideally polarized over a potential region not less than 2 V. The potential at which the cathodic processes (mainly  $H_2$  evolution and  $O_2$  reduction) start to proceed with a measurable rate shifts towards more negative values with increase of FV.

The measured  $C_m$  and  $R_m$  before and after the cathodic polarizations (potentiostatic and galvanostatic) were identical regardless of the duration time of polarization or the current densities used. This means that the anodic oxide film cannot be reduced or removed by cathodic polarization.

Cathodic polarization curves of anodized molybdenum electrodes in HCl solutions are shown in

Fig. 7. As can be seen, two linear Tafel regions can be identified; the slope in the low polarization region (region I) is nearly double that of the high polarization region (region II). Corrosion potentials, Tafel slopes and exchange current densities calculated from Fig. 7 are presented in Table I. The previously reported Tafel slope values for cathodic polarization of molybdenum in acid solutions, either aerated or deaerated, are close to those corresponding to region II [8, 17].

### 3.4. Impedance characteristics of the anodized electrode

The effect of frequency on the impedance behaviour of the anodized electrode was studied when the values of  $C_m$  and  $R_m$  were more or less constant. An impedance diagram of an anodized electrode for different FVs in 3 N HCl solutions is shown in Fig. 8. As can be seen,  $\theta$  is less than  $90^\circ$  which means that the anodized metal/solution interface cannot be considered as a perfect capacitor [34]. The slopes  $d \log Z_m / d \log F$  are approximately equal to  $-1$ , confirming the assumed electrical model shown in Fig. 8. Although the increase

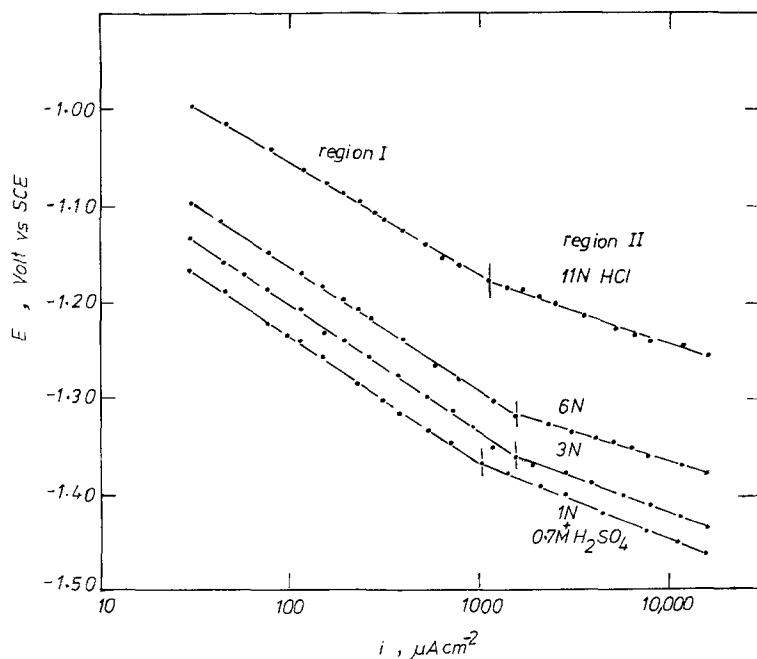


Fig. 7. Galvanostatic cathodic polarization curves of anodized molybdenum electrodes (to 20 V) in acid chloride solutions of different concentrations.

Table 1. Corrosion potentials, Tafel slopes and exchange current densities for polarization of anodized molybdenum in naturally aerated chloride solutions at 30°C

Electrolyte	$E_{\text{corr}}$ (mV)	Region I		Region II	
		$b_c$ (mV)	$i_0$ ( $A\text{ cm}^{-2}$ )	$b_c$ (mV)	$i_0$ ( $A\text{ cm}^{-2}$ )
1 N HCl + 0.7 M $\text{H}_2\text{SO}_4$	000	125	$9.6 \times 10^{-6}$	70	$1.9 \times 10^{-18}$
3 N HCl	000	124	$15.2 \times 10^{-6}$	65	$1.2 \times 10^{-19}$
6 N HCl	000	120	$16.8 \times 10^{-6}$	63	$2.0 \times 10^{-19}$
11 N HCl	000	110	$18.4 \times 10^{-6}$	58	$3.3 \times 10^{-19}$

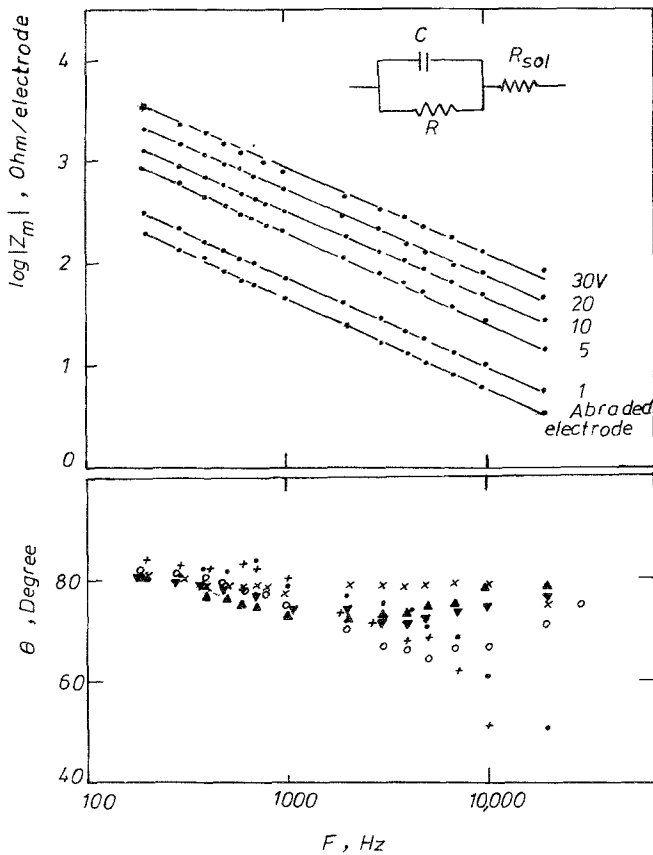


Fig. 8. Impedance diagram of anodized molybdenum electrodes in 3 N HCl solutions: (O) 30 V; (v) 20 V; (A) 10 V; (x) 5 V; (●) 1 V; (+) abraded electrode.

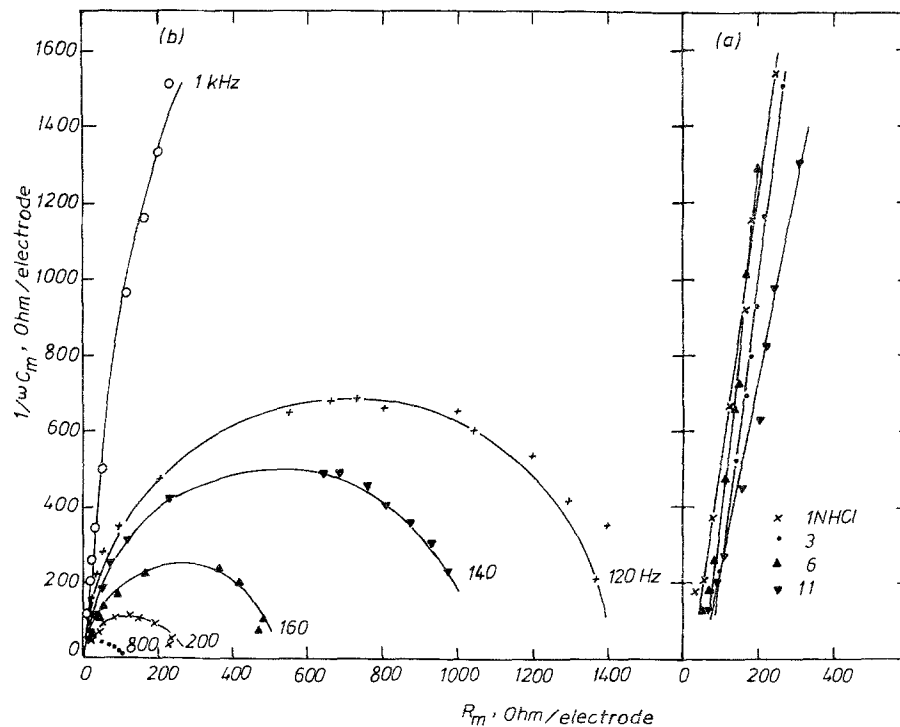


Fig. 9. (a) Complex plane impedance of anodized molybdenum electrodes (to 20 V) at the corrosion potential in acid chloride solutions. (b) Complex plane impedance plots of anodized molybdenum electrodes (to 20 V) at different cathodic current densities: (●) 8.00 mA  $\text{cm}^{-2}$ ; (x) 4.00 mA  $\text{cm}^{-2}$ ; (A) 2.00 mA  $\text{cm}^{-2}$ ; (v) 1.00 mA  $\text{cm}^{-2}$ ; (+) 0.80 mA  $\text{cm}^{-2}$ ; (O) 0.08 mA  $\text{cm}^{-2}$ .

Table 2. Amount of electricity,  $Q$  ( $mC\ cm^{-2}$ ) necessary to form an oxide film of a thickness  $132\ \text{\AA}$

Electrolyte	$Q$ ( $mC\ cm^{-2}$ )
11 N HCl	48.0
5 N HCl	57.6
1 N HCl	69.6
0.5 N HCl	84.0
0.1 N HCl	210.0
1 N $Na_2SO_4$	450.0
1 N NaOH	774.0

of FV (i.e. film thickness increases) increases the electrode impedance, the phase shift,  $\theta$ , does not vary noticeably.

Representation of the electrode impedance in the complex plane yielded straight lines regardless of the solution composition or the film thickness; some results are shown in Fig. 9a. This behaviour has been reported previously for many passive metals [35–38]. The extension of the frequency range to lower values, or application of cathodic polarization, shows that the straight lines are, in fact, parts of large semicircles or arcs as can be seen in Fig. 9b.

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#### Appendix I

Although the efficiency of oxide film formation varies with time as can be seen in Fig. 1, we can compare, approximately, the efficiency of oxide formation in different electrolytes by calculating the amount of electricity (charge density) necessary to form an oxide film of a certain thickness. The thickness is determined by using capacitance measurements, assuming a dielectric constant of 29.4 [39]. From the relations between the thickness and charge density the following Table 2 is produced.

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