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ELECTROCHEMICAL BEHAVIOR OF MOLYBDENUM ELECTRODE IN ACETIC, FORMIC AND OXALIC ACID SOLUTIONS.

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Abstract

The electrochemical behavior of molybdenum electrode in acetic, formic and oxalic acid solutions is studied. The effect of immersion time, composition medium, applied voltage, applied current density and scanning rate is investigated using potentiodynamic, potentiostatic and galvanostatic polarization measurements.

The stability of the oxide film formed on Mo electrode is affected by both the formation medium and the applied potential. In 0.5N oxalic acid, the critical applied voltage below which the current start to oscillate is equal to -80 mV. The rate of dissolution of anodic oxide film formed on Mo in oxalic acid is very rapid compared with that formed in acetic and formic acids. Also in oxalic acid solutions Mo is notably affected by applied current density in which reciprocal capacitance, C_s^{-1} , decrease with increasing applied current density. On the contrary in acetic and formic acids Mo did not affect. In acetic acid solution, the time of anodization has little or no effect on the dissolution process.

Introduction

Molybdenum has a well known role in improving the characteristics of stainless steels⁽¹⁻³⁾. The metal is a corrosion resistant due to the formation of a passive layer on its surface in aqueous media^(4,5). Several different electrochemical techniques are used to study the redox reaction in aqueous HNO₃, H₂SO₄, H₃PO₄ and HCl⁽⁶⁻¹²⁾. On the other hand, Mo is used in the formation of different complexes in a large scale. Some of which are used in electrochemical applications, e.g. as an indicator electrode which used in potentiometric titration of monohydrogenphosphate ion with barium chloride⁽¹³⁾.

The objective of the present work is to study the anodic behavior of molybdenum electrode in some carboxylic acids such as: formic, acetic and oxalic acids solutions by electrochemical methods. Moreover, investigating the effect of immersion time, composition medium, applied voltage, applied current density and scanning rate on the behavior of molybdenum electrode.

Experiment

The electrical circuit, electrolytic cell and the details of the experimental procedures are essentially the same as those described elsewhere⁽¹⁴⁾. The electrochemical cell is a three- electrodes cell (capacity 50 ml). The working electrode is made of massive cylindrical, spectroscopically pure molybdenum rod

(Aldrich - Chemie). A stout copper wire is employed as electrical contact. The electrode is fitted into glass tubing of appropriate internal diameter with epoxy resin, leaving a cylindrical surface area of 0.196 cm² to contact the electrolyte. A platinum sheet is used as counter electrode. The potentials are measured against a saturated calomel electrode with the aid of digital multimeter (KEITHLEY, model 175, USA). Potentiodynamic polarization measurements are generated using a Wenking Electronic Potentiostat (model 73).

All measurements are carried out at room temperature (30°C). The electrolytic solutions are prepared using analytical grade reagents and bidistilled water.

Before each experiment, the electrode surface is mechanically polished using successive grades of emery paper followed by washing with bidistilled water. In this way, the electrode surface acquired reproducibly silvery bright surface. After this, the electrode is quickly transferred to the test solution where the measurements are carried out immediately.

Results And Discussion

I- Potentiodynamic polarization measurements

I-1- Effect of scanning rate:

The effect of scanning rate on the corrosion of molybdenum can be detected by the polarization in 0.5N acetic acid at various scanning rates as shown in Figure (1). The corrosion kinetic parameters listed in Table (1) show that, increasing the scan rate will increase the corrosion current i_{corr} which is very little with increasing scan rate. This indicates that in acetic acid solution, the time of anodization has a little effect on the dissolution process. Also, molybdenum becomes an active site with increasing scan rate due to the increase in corrosion rate C_R and the decrease in polarization resistance P_R .

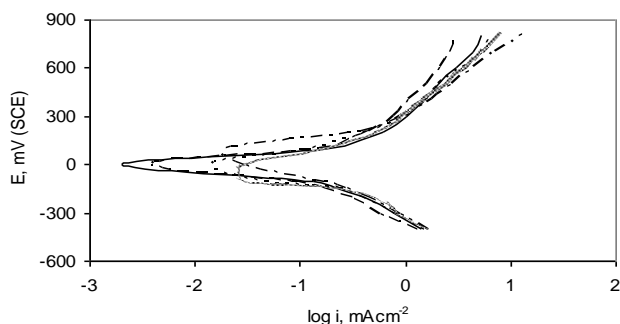


Figure (1): Effect of scanning rate of Mo electrode in 0.5N acetic acid

— 1mV/s - - - 2mV/s ····· 3mV/s - · - · 5mV/s - - - - - 7mV/s

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Table (1): Corrosion kinetic parameters of Mo in 0.5N acetic acid at different scanning rates

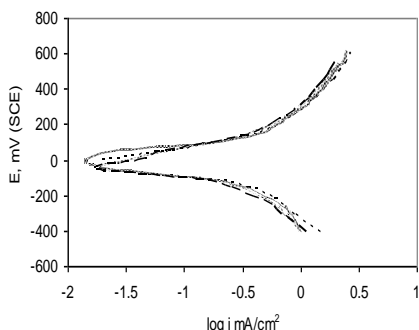
Parameters	Scanning rate (mV/S)				
	1	2	3	5	7
E_{corr} mV(SCE)	10	10	10	100	-50
i_{corr} $\mu\text{A}/\text{cm}^2$	2	4	15	20	30
B_a mV/decade	478	444	427	467	419
B_c mV/decade	503	674	543	453	533
C_R mm/y	12	25	93	125	187
P_R $\text{K}\Omega \text{ cm}^2$	53	29	7	5	3

I-2- Effect of immersion time on the behavior of passive film on Mo electrode:

The results reveal that, the potentiodynamic curves of the passive films formed at different immersion times at scanning rate of 1.7mV/sec in 1 N acetic acid are approximately coinciding together. This indicate that the immersion time do not affect the molybdenum corrosion (Figure 2). The same behavior is observed for formic and oxalic acid solutions. This behavior is due to the high stability of the oxide films formed even at low immersion time. This is illustrated by plotting the open circuit potential of the formed oxide at the end of each period against time (Figure 3). The curves of the three acids indicated that, the oxide layer takes about 10 minutes to be stabilized for all acids. Subsequently, it is logic to observe no change in behavior for oxides formed at 10, 30 and 60 minutes. The potential values of oxides obtained at 5 minutes are not so far from that formed at 10 minutes, and show the same behavior. The passivity of the oxide layers formed under open circuit conditions followed the following order:

acetic > formic > oxalic

The E- log i curves for Mo electrode in 1 N acetic, formic and oxalic acid at scanning rate of 1.7 mV/sec and after 60 second of immersion in the test solution at open circuit potential of (153, 93 and 74 mV respectively) are presented in Figure 4. The corrosion current densities for anodic and cathodic reactions (i_{corr}), the corrosion potential (E_{corr}) and the Tafel slopes (B_a , B_c) are obtained and tabulated in Table (2).



Figure(2) : Effect of immersion time on 1M acetic acid solution

.....5min 10min 30min 60min

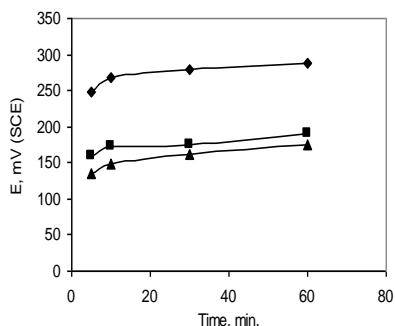


Figure (3): Potential- time curves of the formed oxides at the three studied acids

◆ acetic ■ formic ▲ oxalic

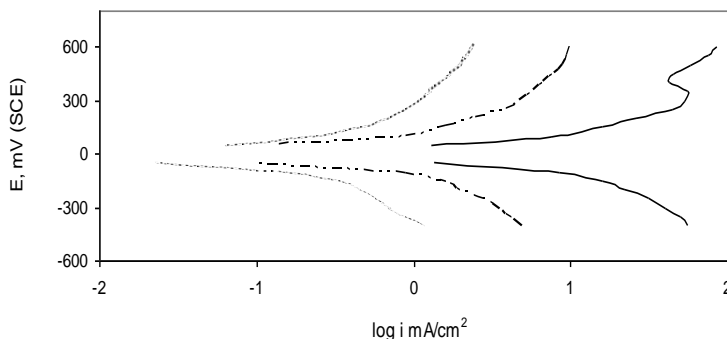


Figure (4): Effect of formation medium at immersion time of 60 sec.

..... acetic formic oxalic

Table (2): Electrochemical parameters for Mo electrode in organic acids at immersion time of 60 seconds.

Acid media	I_{corr} mA/cm ²	E_{corr} mV(SCE)	B_a mV/decade	B_c	$C_R \times 10^{-3}$ mm/y	P_R $\Omega \text{ cm}^2$
Acetic	0.2	-7	-370	240	1.2	316.46
Formic	1.2	-10	-253	157	7.5	35.1
Oxalic	4.0	-16	-200	180	24.9	10.29

The data in Table (2) insure the same order of passivity that obtained by open circuit potential measurements.

I-3- Effect of applied current density on the behavior of Mo electrode:

Anodic oxide films are formed in 0.5 N solutions of acetic, formic and oxalic acids at different current densities of 1, 5, 10, 20, 50 and 80 mA/cm² at constant period of 180 second and tested potentiodynamically in the same test solution at a

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constant scanning rate of 1 mV/sec. The cathodic polarization tests are made separately from anodic ones to insure accurate results about the behavior of ionic oxide films (Figure 5).

In anodic polarization part, by scanning the potential in a negative direction, the corresponding current density is increased continually starting from zero current potential E° at which the rate of cathodic reaction is equal to the rate of the anodic one. For the potential far removed from E° , an active dissolution region is observed. In cathodic polarization, a passive potential region began after which hydrogen evolution took place.

The curves illustrated that oxalic acid is the most corrosive test solution and acetic acid is the little one. These results are in good agreement with those obtained previously.

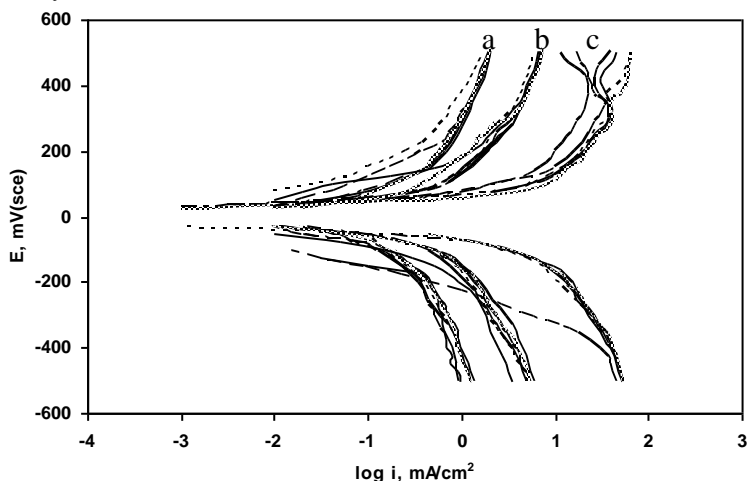


Figure (5) : E- log i curves of anodic oxides formed at 0.5 N solutions of a- acetic, b- formic, c- oxalic acids at different current densities in mA/cm²:

——— 1 - - - - 5 ····· 10 - · - · 20 - - - - 50 - - - - 80

The variations of reciprocal capacitance C_s^{-1} with time in the three studied acids are illustrated in Figure 6. Generally, C_s^{-1} decreases with increasing time in all applied current densities. At current density 1 mA/cm², a continuous decrease of C_s^{-1} is observed. Such a decrease is attributed to film dissolution whereas the decrease in C_s^{-1} for current densities > 1 mA/cm² may be due to a change in the film properties, this behavior is similar to that observed on Ta in NaOH solution ⁽¹⁵⁾.

On plotting C_s^{-1} vs. time at 1 mA/cm^2 for the three studied acids (Figure 7) it is observed that the rate of dissolution of anodic oxide film formed in oxalic acid is very rapid compared with that formed in acetic and formic acids.

On the other hand, studying the variation of reciprocal capacitance C_s^{-1} with applied current densities for the three studied acids illustrated that, Mo in oxalic acid is notably affected by applied current density in which C_s^{-1} decrease with increasing applied current density. On the contrary Mo in acetic and formic acids did not affect (Figure 8).

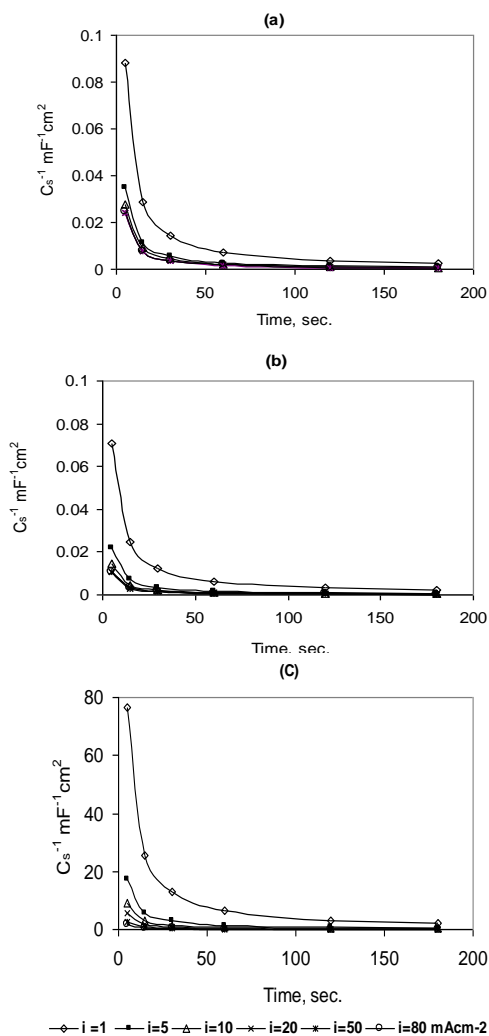


Figure (6): Variation of reciprocal capacitance, C_s^{-1} , with time for: a- acetic, b- formic, c- oxalic acids at different applied current densities

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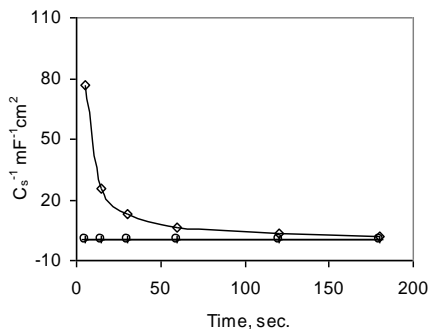


Figure (7) : Reciprocal capacitance vs. time at 1 mA/cm² for:

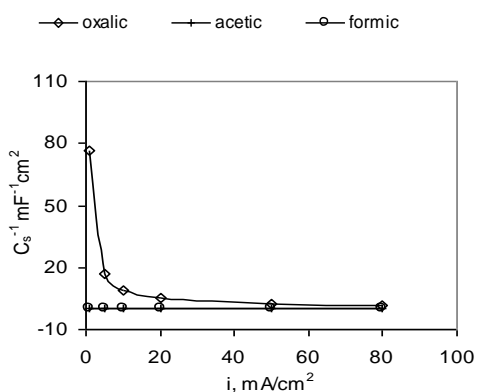


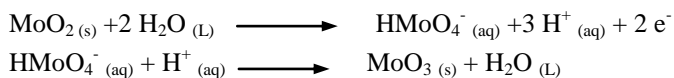
Figure (8) : initial reciprocal capacitance vs. applied c.d. for :

◆ oxalic + acetic ○ formic

II- Galvanostatic polarization measurements

The results of potential measurements give more details about the effect of applied current density, as shown in Figure 9. It is clear that at c.d. < 50 mA/cm² in case of acetic and formic acids and < 20 mA/cm² in oxalic acid, there is an independency of potential on time indicating the higher insulating properties of the film. On the other hand, for higher current densities, the potential becomes less positive with time indicating that the oxide films are subjected to a dissolution process.

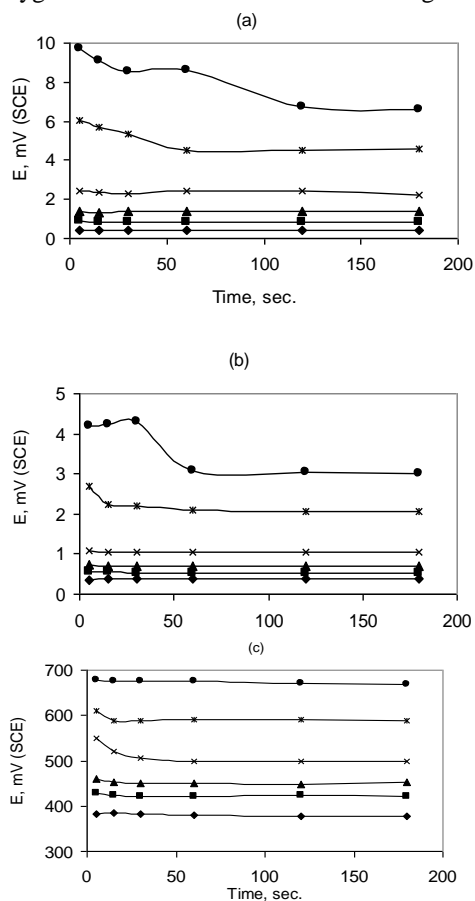
These oxides dissolve in aqueous solutions depending on the applied current density according to the following equilibria⁽¹⁶⁾:



In acidic solutions, any of these equilibria will be shifted towards the stabilization of the solid phase and hence a stable barrier film will occur.

It is observed that the behavior in oxalic acid is notably different. This may be facilitated as follows: oxalate acts as a bidentate ligand coordinating to the molybdenum atom through two deprotonated carboxylate groups⁽¹⁷⁾. While acetic and formic acids are monodentate ligands.

The reaction of molybdenum (VI) oxide with oxalic acid results in the formation of two series of molybdenum (VI) oxalate complexes: one of the general formula $[\text{Mo}_2\text{O}_5(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ and the other of the formula $[\text{MoO}_3(\text{C}_2\text{O}_4)_3]^{2-}$. In both types molybdenum ions are six-coordinated being surrounded by terminal oxo-oxygens, bridging oxygens and bidentate bonded oxalate ligands⁽¹⁸⁾.



Figur (9): E-t curves of Mo in 0.5 N solutions of studied acids :
(a) acetic, (b) formic, (c) oxalic at c.d. of.

◆ 1mA/cm2 ■ 5mA/cm2 ▲ 10mA/cm2
 × 20mA/cm2 * 50mA/cm2 ● 80mA/cm2

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III- Potentiostatic polarization measurements:

The anodic oxide films formed in 0.5 N acetic and formic acids at applied potential of -100 and +100 mV are stable and resist dissolution. In addition, the oxide film formed in 0.5N oxalic acid is stable at +100 mV while at -100 mV is more susceptible to dissolution and does not reach stability through the whole period of time (Figure 10). The high stability of the anodic oxide films formed in acetic and formic acids reflect the formation of a highly order and less defective oxide films at these two applied potentials⁽¹⁵⁾.

Comparing the behavior at the two applied voltages it is seen that at positive applied voltage, the curves of the three studied acids located above zero current density with the same passivity order mentioned previously. At negative applied potential, the curves located below zero current density with the opposite passivity order. Generally, positive applied voltage decreases the position of passivity of the three acids comparing with negative applied voltage. This means that the stability of the oxide film is affected by both the formation medium and the applied potential.

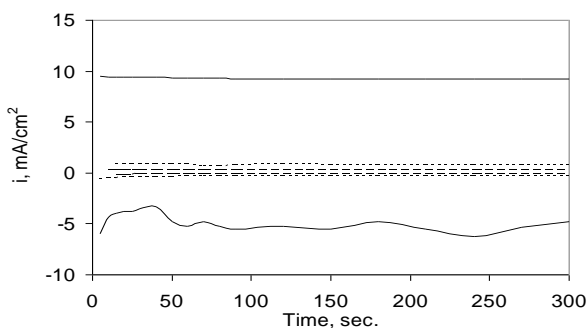


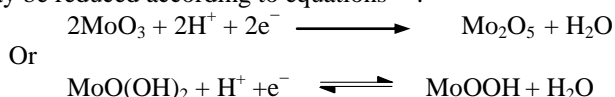
Figure (10): Effect of composition medium at constant applied voltage (+100 mV located above 0 mA/cm², - 100 mV located below 0 mA/cm²)

---- acetic formic — oxalic

The curve of oxalic acid in Figure 10 at applied potential of -100 mV showed the need to study the effect of applied voltage on oxalic acid in details; this is illustrated in Figure (11). Generally, the instantaneous current densities are increased with increasing applied potential. For positive potentials (+200 and +100 mV) the diagram showed no change in current density with time, and the current attaining constant values of 23.5 and 9.3mA/cm² respectively. At -100, -200 and -300 mV, the c.d. first increased to a little top then decrease in a repetition process with increasing time in a random way. On the contrary, at -400 and -500 mV, the current density first decreased to a minimum then increase to a top in a repetition process too. This

instability is smooth at applied voltage of -100 mV and becomes sharp with increasing the negativity of the applied voltage. The decrease of the anodic current coincides with the passivation of Mo metal. While increasing values coincide with the active dissolution of metal. The repetition of decreasing and increasing of current density values with time suggested that a new passive layer is formed in each case.

This behavior can be explained on the bases that the main constituent of the passive film is MoO₂ which contains a small ratio of MoO₃ and Mo(OH)₃ which may be reduced according to equations⁽¹⁹⁾:



Oxide film dissolution takes place according to the backward reaction. The current oscillation can be attributed to the competition between the anodic formation and chemical dissolution of the passive film on the electrode surface.

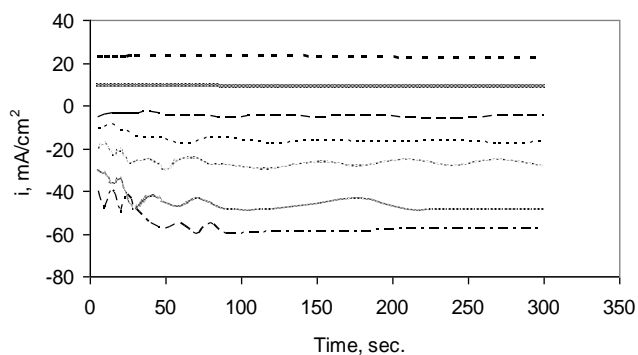


Figure (11): Effect of applied voltage on Mo in 0.5N oxalic acid

----- -500 mV -400 mV -300 mV -200 mV
 ----- -100 mV 100mV - - - -200mV

To determine the critical applied voltage below which the current start to oscillate the electrode is tested at +50, -50 and -80 mV which not included in the diagram. At applied potential of +50 and -50mV, the current density is constant with time. While applied potential of -80 mV show small oscillation and is considered as the critical applied voltage.

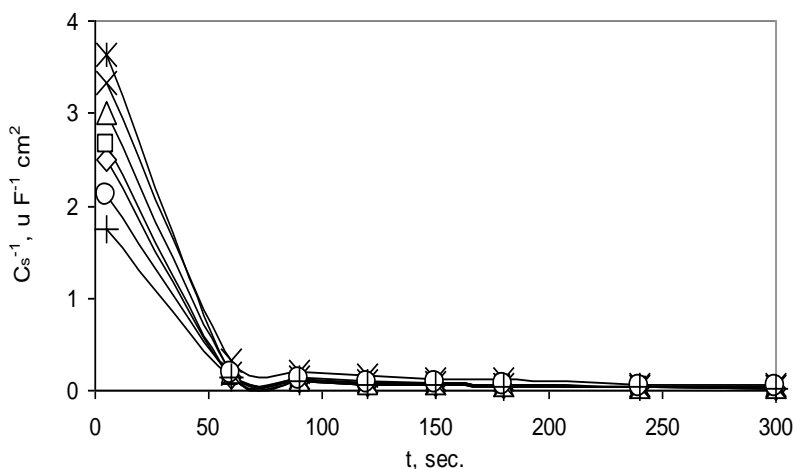
An increase in the applied potential corresponded to an increase in the electrical charge Q passed during potentiostatic polarization and the surface charging capacity C_s. Figure (12) shows the variation of reciprocal capacitance C_s⁻¹ with time for 0.5N oxalic acid. For negative applied voltage, the decrease in C_s⁻¹ becomes pronounced

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with the decrease in formation voltage. Also there is a break in the C_s^{-1} – time curves for all test solutions which splits the diagram into two segments. The data obey the equation ⁽¹⁵⁾:

$$C_s^{-1} = \alpha - \beta t$$

Where α is a constant equal to C_s^{-1} at zero time and corresponds to the initially formed anodic oxide film thickness and β is the slope which corresponds to the rate coefficient of dissolution. For negative applied potentials, the coefficients β_1 increase with increasing formation voltage. However, β_2 do not effect regularly with applied potentials (Table 3).



Figure(12): Variation of reciprocal capacitqnce C_s^{-1} of Mo electrode with time in 0.5 N oxalic acid solution at different formation voltages

—◇— -0.5V —□— -0.4V —△— -0.3V —×— -0.2V —*— -0.1V —○— 0.1V —+— 0.2V

The presence of two different rate coefficients for the dissolution led to the assumption that the barrier film on Mo is duplex in nature ⁽²⁰⁾. However, the values of β_1 and β_2 are the slopes of the first (outer) and second (inner) layer, respectively. If the outer oxyhydroxide film is stable the inner MoO_2 film is protected by the outer oxyhydroxide film and the MoO_2 film acts as the effective barrier against diffusion of matters through the film ⁽²¹⁾.

Table 3: The dissolution rate coefficients, β_1 and β_2 (in $\mu\text{f}^{-1} \text{cm}^2 \text{sec}^{-1}$) of anodic oxide films formed on molybdenum in 0.5 N oxalic acid.

V_f (mV)	$\beta_1 \times 10^{-2}$	$\beta_2 \times 10^{-4}$
-500	4.27	4.32
-400	4.59	4.12
-300	5.09	5.79
-200	5.48	5.77
-100	6.27	9.18
+100	3.50	5.25
+200	2.90	4.04

Conclusion

The stability of the oxide film on Mo electrode is affected by both the formation medium and the applied potential. Applied potential of -80 mV is considered the critical applied voltage. The rate of dissolution of Mo in oxalic acid is very rapid compared with that for acetic and formic acids. Oxalic acid is notably affected by applied current density in which C_s^{-1} decrease with increasing applied current density. On the contrary acetic and formic acids did not affect. In acetic acid solution, the time of anodization has no or little effect in the dissolution process.

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