JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 151-155

Effect of hydrogen on the impedance of passivating oxide films formed on aluminium in sodium nitrate solution

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Received 5 November 1990; revised 18 January 1991

A.c. impedance has been determined at room temperature on hydrogen-free and hydrogen-charged passivating oxide films on aluminium in 0.05 M Na_2SO_4 solution. Analysis of the impedance data enabled a clear distinction between the capacitance and inductance of the hydrogen-free oxide film and those of the hydrogen-charged oxide film to be made. The changes in capacitance and inductance by hydrogen-charging into the oxide films are discussed in relation to the compositional change from γ-Al_2O_3 to hydrated alumina.

1. Introduction

The role of hydrogen within the passivating films on metals has generated considerable research interest in the field of electrochemical corrosion processes. Pyun and Oriani [1] have proposed that hydrogen enters the passivating film on iron and nickel as a proton due to the ionic bonding character of the passive film and changes the average cationic valence in the passive film. This has been substantiated by Song *et al.* [2]. Pyun *et al.* [3] have also reported that the incorporation of protons into the passive film on iron yields the formation of hydrogen-containing species such as H_2O and/or OH^-, resulting in an accelerated breakdown of the passive film. It is interesting to investigate how hydrogen within the amphoteric aluminium oxide film behaves, since the oxidation state of aluminium ion is different in nature from that of the transition metal ions.

The aim of the present work is to understand how the hydrogen charged into the passivated aluminium modifies the passivating oxide film on aluminium. For this purpose, a.c. impedance has been determined at room temperature on the relatively thin passivating oxide films on aluminium during hydrogen-charging into the oxide films or without hydrogen-charging.

2. Experimental procedure

As-rolled pure aluminium (99.9%) of 100 μm thickness was annealed for 10 h at 400° C, followed by air cooling. Air-formed oxide on the foil specimen was eliminated by immersing the sheet specimen for 0.25 h in 0.5 N NaOH solution at room temperature as reported previously [4].

In an attempt to make a.c. impedance measurements with concurrent hydrogen-charging or without charging, an electrochemical double cell was employed as reported previously [1-3]. The aluminium foil specimen separated the cathodic compartment containing 0.05 M H_2SO_4 solution or air from the anodic compartment containing 0.05 M Na_2SO_4 solution.

The procedure for carrying out the impedance runs with and without the hydrogen-charging at 25° C was as follows. First the passivating oxide film was developed for 0.5 h on the anodic side of the foil specimen in the 0.05 M Na_2SO_4 solution potentiostatically with applied potentials ranging between -580 and 620 mV/SHE. Then the cathodic compartment was filled with the 0.1 N H_2SO_4 solution and at the same time hydrogen was charged into the cathodic side of the foil specimen galvanostatically with current densities of 1 to 10 mA cm^{-2}. After 1.5 h of hydrogen-charging, the impedance measurement was performed on the anodic (passive film) side of the foil specimen.

The impedance of the Al/passivating oxide film composite specimen was measured by superimposing an a.c. voltage of 5 mV amplitude on the film formation potentials of -580 to 620 mV/SHE from a potentiostat (EG & G Model 273) in conjunction with a frequency analyser (EG & G Model 5208) over the frequency range 10^{-2} to 10^4 Hz.

3. Results and discussion

Figure 1 illustrates the Nyquist plots obtained from the hydrogen-free Al/oxide film composites formed at various anodic film formation potentials. Perfect semicircles do not appear with the center on the abscissa. The diameter of the distorted capacitive semicircle decreases with increasing anodic formation potential. In Fig. 2, the Bode diagrams are plotted from some of the data of Fig. 1. It is seen that the shapes of the Nyquist and Bode diagrams remain unchanged with applied anodic potential. From Figs. 1 and 2, it is recognized that high-frequency capacitive and low-frequency inductive components exist.

Figure 3 presents the Nyquist plots obtained from the hydrogen-charged Al/oxide film composites formed

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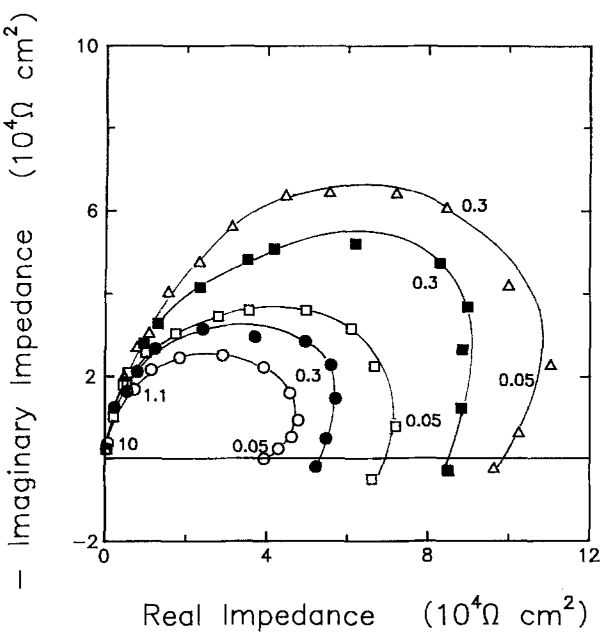

Fig. 1. Nyquist plots obtained from the hydrogen-uncharged Al/oxide film composites formed in 0.05 M Na_2SO_4 solution at various applied potentials: (○) −580; (●) −280; (□) 20; (■) 320; (△) 620 mV/SHE.

at the anodic film formation potential of 320 mV/SHE. The hydrogen-charged composite specimens clearly demonstrate the capacitive and inductive loops. The diameter of the capacitive semicircle decreases with increasing hydrogen-charging current density. It should be noted that the inductive components appear over the frequency range 10^{-2} to 1 Hz in contrast to the hydrogen-free composite specimen.

In order to analyse the measured impedance data as a function of applied anodic potential and hydrogen-charging current density, the equivalent circuit suggested by Bessone *et al.* [5] was employed. The equivalent circuit consists of a capacitance, C, in parallel to the series resistances, R_1 and R_2, and an inductance, L, in parallel to R_2. The electrolyte resistance, R_e, was measured to be of the order of 140 Ω. From the analyses of the measured impedance data, the circuit parameters such as capacitance and inductance were obtained by using a least-square fit method.

The capacitance, C, of the hydrogen-free Al/oxide film composite specimen is plotted against anodic film formation potential in Fig. 4. The capacitance, C, decreased with increasing applied formation potential. It is known that the thickness of a barrier-type oxide film, d, is linearly dependent on the applied anodic potential, as follows

$$d = \alpha (E_a - E_0) \tag{1}$$

where E_a and E_0 are the applied potential and the zero-thickness potential, respectively. The proportionality constant α is known to be about 0.75 nm V^{-1} for thin barrier films [5], which is different from the value of 1.4 nm V^{-1} for thick barrier films [6]. Regarding the oxide film on aluminium as dielectric material, the capacitance of the oxide film is given by the equation,

$$C = \frac{\varepsilon\varepsilon_0}{d}, \tag{2}$$

where ε is the dielectric constant which varies with the composition of the oxide film and $\varepsilon_0 = 8.85 \times 10^{-12}$ A s V^{-1}, is the permittivity of the vacuum. From Equations 1 and 2 it is expected that the capacitance is inversely proportional to the applied potential. Thus the occurrence of the high-frequency capacitive loop is based on the contribution of the thickness of the barrier oxide film to the capacitance.

Figure 5 illustrates the capacitance, C, of the hydrogen-charged composite specimen formed at a potential of 320 mV/SHE as a function of hydrogen-charging current density. The capacitance, C, was considerably reduced by the hydrogen-charging with 1 mA cm^{-2} and then slightly increased from 3.1 to 3.6 μF cm^{-2} as the hydrogen-charging current density increased from 1 to 10 mA cm^{-2}. The slight increase in the capacitance with hydrogen-charging current density is in agreement with the result of Bessone *et al.* [5]. The substantial decrease in the capacitance by the hydrogen-charging with 1 mA cm^{-2} is thought to be

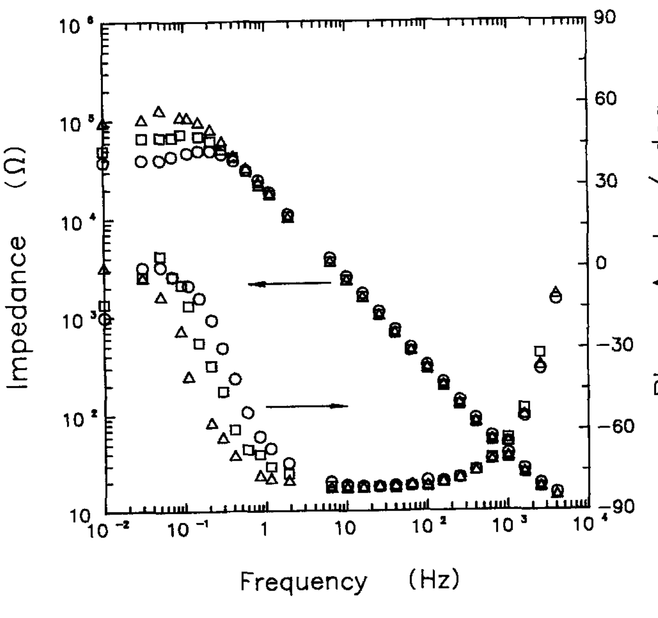

Fig. 2. Bode plots plotted from some data of Fig. 1: (○) −580; (□) 20 and (△) 620 mV/SHE.

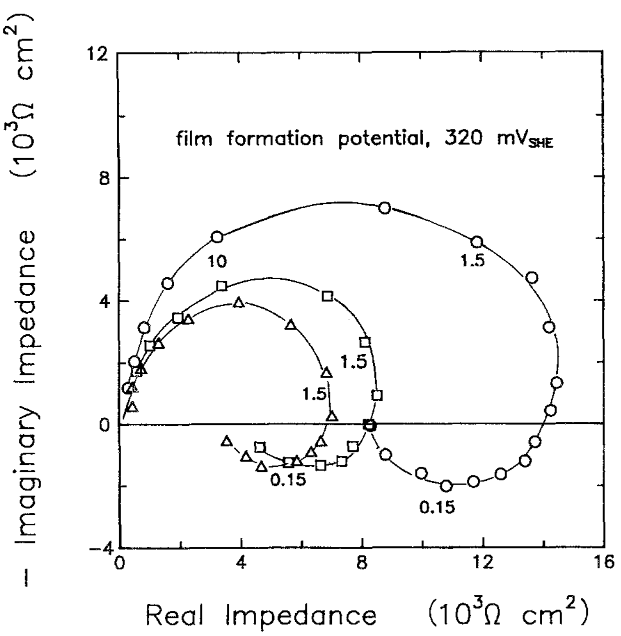

Fig. 3. Nyquist plots obtained from the hydrogen-charged Al/oxide film composites formed in 0.05 M Na_2SO_4 solution at the anodic potential of 320 mV/SHE, with hydrogen-charging current density of: (○) 1; (□) 5; and (△) 10 mA cm^{-2}.

mainly the decrease of the dielectric constant rather than the increase of the thickness of the oxide film. Thus the decrease in the capacitance by the hydrogen-charging is believed to be due to the compositional change of the oxide.

There is some evidence that certain of the migrating anions are OH^- ions [7], the remainder being O^{2-} ions. The OH^- ions are apparently enriched towards the film/electrolyte interface. It would be reasonable to expect a reverse gradient of the cations. Thus the oxide is considered to be composed of a series of layers: γ-Al_2O_3 close to the metal side and AlOOH or $Al(OH)_3$ close to the electrolyte side. This structure has also been proposed by Moshier *et al.* [8].

In the present work, hydrogen enters the oxide film from the metallic aluminium side. It is reasonable to assume that the hydrogen exists as a proton within the oxide film. The reaction occurring in the oxide close to the metal side is believed to be of the form,

$$Al_2O_3 + 2H^+ + O^{2-} \longrightarrow 2AlOOH \qquad (3)$$

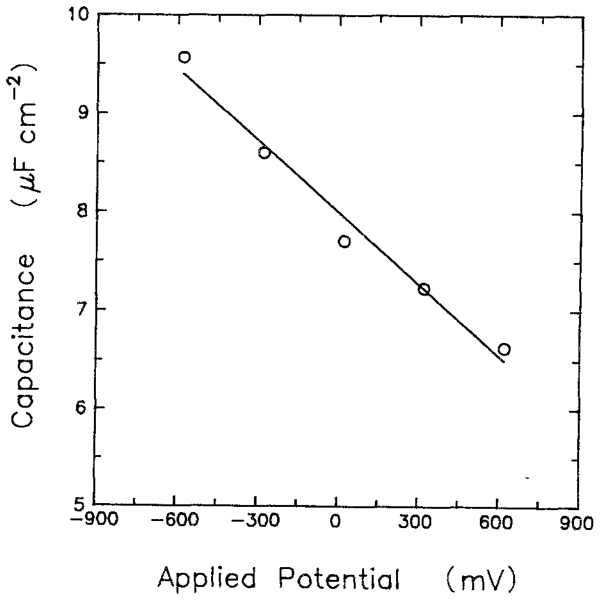

Fig. 4. The capacitance, *C*, of the hydrogen-free Al/oxide film composite as a function of anodic film formation potential.

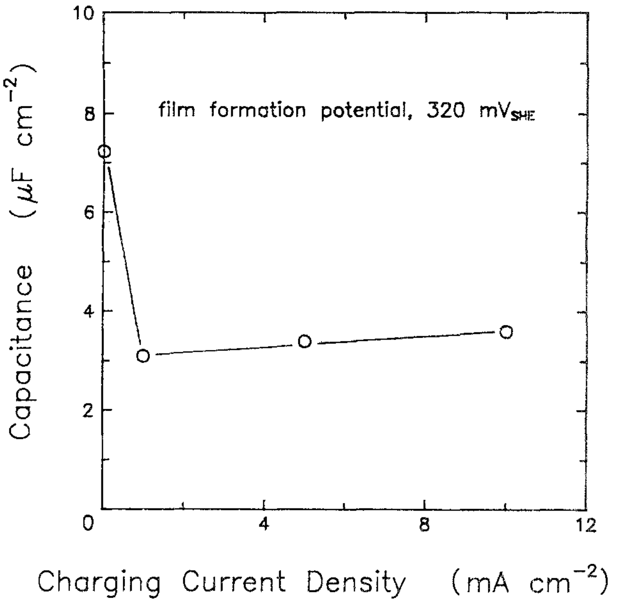

Fig. 5. The capacitance, *C*, of the hydrogen-charged Al/oxide film composite formed at the potential of 320 mV/SHE as a function of hydrogen-charging current density.

This consideration indicates that the incorporation of protons into the oxide film causes a compositional change from the γ-Al_2O_3 to hydrated alumina without a cationic valence change. Ikonopisov *et al.* [9] suggested that the decrease in dielectric constant was due to more extensive hydration of oxide films on aluminium. Hence, it may be inferred that the hydrated aluminium oxide film has a dielectric constant value lower than that for the γ-Al_2O_3 film. In the present work, a considerable decrease in the capacitance due to the hydrogen-charging is presumably attributed to the formation of hydrated alumina.

The hydrogen effects on the capacitance of the aluminium oxide in the present work differ from those found in the oxide of iron [2, 10]. It has been reported that the incorporation of protons into the passivating film on iron causes an increase in the capacitance. Song *et al.* [2] attributed this to an increase of the Fe^{2+} ion donor density resulting from the reduction in the cationic valence caused by incorporated protons. Sato and Kudo [10] have also suggested that the H_2O species formed due to the hydration reaction in the passive film may act as a donor site. These deductions are based on an *n*-type semiconducting mechanism. However, considering the dielectric nature of the aluminium oxide, the decrease in the capacitance by hydrogen-charging is related to the change in dielectric constant due to the compositional change of the oxide film.

The variations of inductance, *L*, of hydrogen-free and hydrogen-charged Al/oxide film composite specimens are shown in Figs 6 and 7, respectively. The inductance of the hydrogen-free oxide film increased

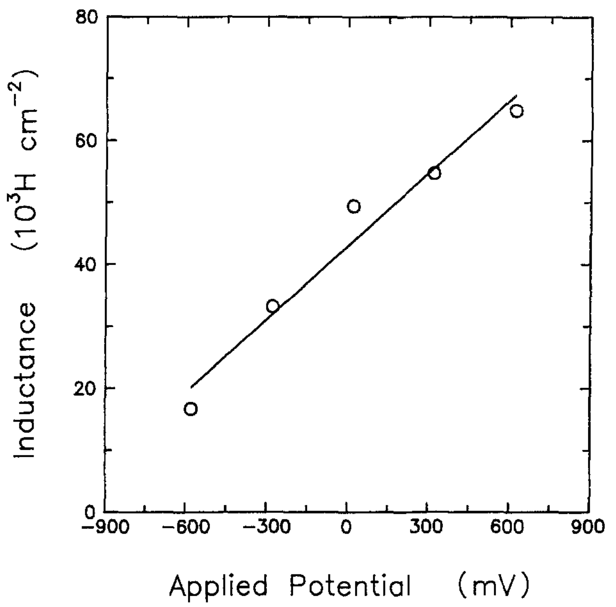

Fig. 6. The inductance, L, of the hydrogen-free Al/oxide film composite as a function of anodic film formation potential.

with increasing anodic potential (Fig. 6). The inductance was considerably reduced by the hydrogen-charging at 1 mA cm^{-2} and then decreased slightly with increasing charging current density (Fig. 7).

The low frequency inductive components indicate that there is an ionic relaxation effect on the faradaic process [11]. It has been proposed that the faradaic reaction is related to the metal dissolution process [5, 6]. In the dissolution reaction of the aluminium within the oxide film the fluxes of Al^{3+} and O^{2-} species across the oxide film should be considered. The model suggested by de Wit *et al.* [6] states that the relaxation phenomena are ascribed to time variations of O^{2-} ion built-up at the boundary layer close to the metal within the oxide film, which is determined by the rate of discharge of O^{2-} ion by positive charge carriers provided from the bulk metal.

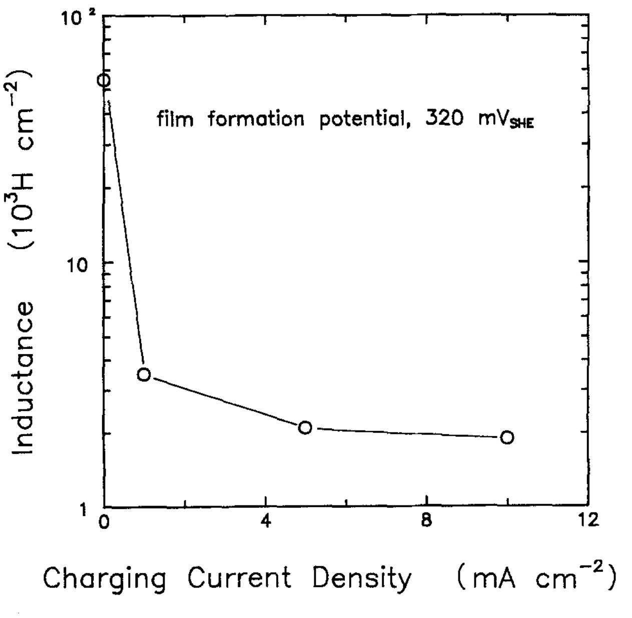

Fig. 7. The inductance, L, of the hydrogen-charged Al/oxide film composite formed at the potential of 320 mV/SHE as a function of hydrogen-charging current density.

The discharge rate of O^{2-} ion is inversely proportional to the relaxation time. Thus the high discharge rate of the O^{2-} ion means a low relaxation time constant, then resulting in a low inductance value because the time constant generally increases with inductance. In the present work, the discharge rate of O^{2-} ion is not actually determined. However, the results for the inductive behaviour can be qualitatively understood by considering the discharge rate of O^{2-} ion suggested by Armstrong and Henderson [12].

The observed applied potential dependence of the inductance (Fig. 6) indicates that the discharge rate of the O^{2-} ion at the boundary is decreased with increasing applied anodic potential. This may arise from the fact that the high anodic potential allows the more O^{2-} ions to enter the oxide from the electrolyte toward the boundary.

It is inferred from the above discussion on the capacitive behaviour that a compositional change of the oxide film is caused by the incorporated proton as *per* Reaction 3. According to this suggestion, the discharge rate of O^{2-} ion at the boundary is markedly accelerated by the protons provided by hydrogen-charging. This is in agreement with the decreased inductance by increasing the hydrogen-charging current density (Fig. 7).

4. Conclusions

In this investigation, a.c. impedance has been determined at room temperature on passivating oxide films on aluminium during hydrogen-charging into the oxide films or without the hydrogen-charging. The inverse proportional relationship between the capacitance and the applied anodic potential is certainly correlated to the thickness of the hydrogen-free oxide film. The inductive behaviour is understood by the model based upon the discharge rate of O^{2-} ion built-up at the boundary close to the metal within the oxide film. From the changes in capacitance and inductance with hydrogen-charging, it is concluded that the incorporation of protons into the oxide film causes a compositional change from γ-Al_2O_3 to hydrated alumina without reduction of the cationic valence.

Acknowledgements

The authors are indebted to the Korea Science and Engineering Foundation for its financial support.

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