

## SHORT COMMUNICATION

**Effect of hydrogen on impedance of the passivating film on iron**

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**1. Introduction**

The role of hydrogen in the passivating films that form on metals has been the subject of much speculation as relating to the structure, composition and other properties of the film [1–4]. In previous work we reported that hydrogen present in the passive film increases the susceptibility to pitting [5, 6]. The resistance to corrosion depends on the electrical properties of the film because the breakdown involves the electronic and ionic transport in the film [4]. However, the relationship between hydrogen in the passive film and the electrical properties has not yet been clarified.

In this work hydrogen injection into the passive film on iron has been carried out by using a permeation technique [7, 8]. Before and after hydrogen injection the electrical impedance of the passive film has been measured and the result is discussed in relation to the valence change of the metal ions by the protons inserted into the film.

**2. Experimental details**

The iron specimens (0.003% C, 0.06% Si, 0.003% P, 0.004% S by weight) were prepared by melting electrolytic iron in an induction furnace under vacuum and by cold-rolling to the thickness of 400  $\mu\text{m}$ . The sheet specimens were annealed in vacuum at 950°C for 1 h, followed by furnace-cooling in vacuum, and were ground with successively finer emery paper, ending with 600 grit.

The hydrogen was injected into the passivated iron specimen at 30°C with a double cell of the type developed by Devanathan and Stachurski [8]. The input side of the specimen was coated with a thin palladium layer to minimize surface contamination and to eliminate surface impediments for hydrogen entry. Hydrogen was produced in the input cell with a constant cathodic potential of  $-900\text{ mV}_{\text{SHE}}$  in a 0.1 N NaOH solution. The exit side was subjected to a constant anodic potential between 400 and 800  $\text{mV}_{\text{SHE}}$  in an equivolume mixture of 0.15 N  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and 0.15 N  $\text{H}_3\text{BO}_3$  solutions. Before passivation, the exit side of the membrane specimen was cathodically reduced at  $-556\text{ mV}_{\text{SHE}}$  for 20 min to remove the air-formed film [3] and then the potential was raised in steps to a desired value to form the passivating oxide film.

Prior to impedance measurements, the passive film on the exit side was aged for 24 h in the anodic cell, then hydrogen was charged into the Pd-coated entry surface of the membrane specimen. After 8 h of hydrogen charging, which is sufficient to attain the steady-state hydrogen permeation current [9], the measurement of the electrical impedance of the passive film on the iron specimen was conducted by superimposing an AC voltage of 5 mV amplitude with a frequency of  $10^{-1}$  to  $10^3$  Hz on a DC bias from a potentiostat (EG & G, Model 273) in conjunction with a lock-in analyzer (EG & G, Model 5208). The impedance of the uncharged specimen was also obtained after the same time of passivation as that of the hydrogen-charged specimen. We suggest an equivalent circuit for the passive film in the frequency range of  $10^{-3}$  to  $10^3$  Hz.

**3. Results**

The applied anodic potentials used in this study are located fully in the passive region characterized by the very low passive currents [9]. Figure 1 shows the Bode plot of the passive film at 600  $\text{mV}_{\text{SHE}}$ . From the impedance diagram we infer that an equivalent circuit for the passive iron consists of a series connection of the parallel RC circuit of the passive film with the resistance of the solution, in agreement with the result of Tsuru and Haruyama [10], but different from that of Azumi *et al.* [11], which is composed of a series of two parallel RC components and the solution resistance. The necessity for the different equivalent circuit may be attributed to the different experimental parameters such as passivation potential and passivation time, etc. The capacitance  $C_{\text{SC}}$  of the space-charge layer in the passive film was estimated from the diagram and is presented in Fig. 2.  $C_{\text{SC}}$  decreases with increasing applied anodic potential, whereas  $C_{\text{SC}}$  is increased by hydrogen charging.

The dielectric constant  $\varepsilon$  of the passive film was calculated from the capacitance data according to the following equation:

$$\varepsilon = \frac{d_{\text{SC}} C_{\text{SC}}}{\varepsilon_0} \quad (1)$$

where  $\varepsilon_0$  and  $d_{\text{SC}}$  are the permittivity of the free space and the thickness of the space-charge layer in the passive film on iron, respectively. The  $d_{\text{SC}}$  is assumed to be approximately equal to the thickness of the

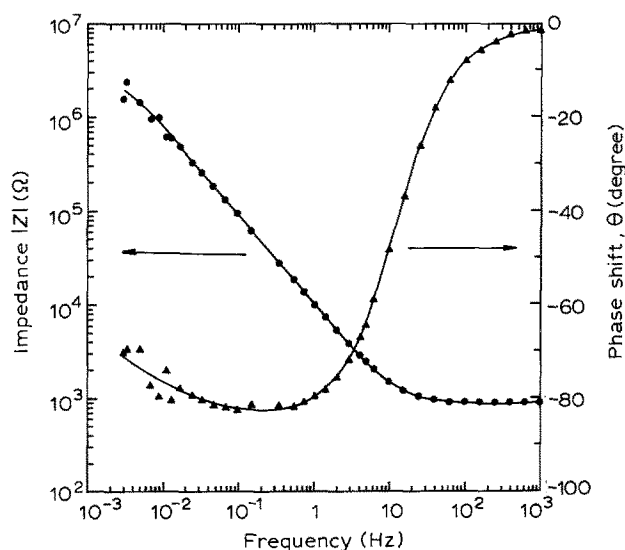


Fig. 1. Frequency dependence of the magnitude of the electrical impedance,  $|Z|$ , and of the phase shift,  $\theta$ , for the uncharged passive film formed on iron at the applied anodic potential of  $600 \text{ mV}_{\text{SHE}}$ .

passive film, which was measured by the ellipsometric method in the previous work [9]. Values of the dielectric constant determined from Equation 1 are summarized in Table 1. Increasing the applied anodic potential decreases the dielectric constant of the passive film, while hydrogen charging increases it.

The simplified Mott-Schottky relation is given by

$$C_{\text{SC}}^{-2} = \frac{2kT}{e\epsilon\epsilon_0 N_{\text{D}}} (V_{\text{m}} - V_{\text{fb}} - kT/e) \quad (2)$$

where  $k$  and  $T$  are the Boltzmann constant and absolute temperature, respectively,  $e$  is the charge of the electron,  $N_{\text{D}}$  is the donor density, and  $V_{\text{m}}$  and  $V_{\text{fb}}$  are the potentials at which the impedance measurements are carried out and the flatband potential, respectively. In the Mott-Schottky plots for the uncharged and hydrogen-charged specimens shown in Fig. 3, linearity is observed in the range 400 to

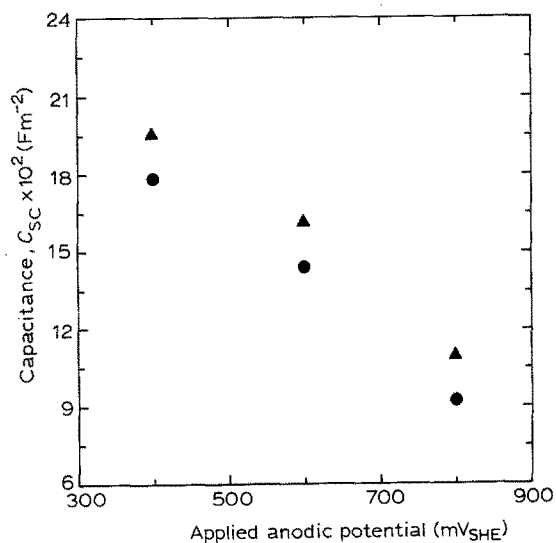


Fig. 2. Effect of applied potential on the capacitance  $C_{\text{SC}}$  of the space-charge layer of the uncharged and hydrogen-charged passive films on iron: (●) uncharged specimen; (▲) hydrogen-charged specimen.

Table 1. Effect of applied anodic potential on the dielectric constant  $\epsilon$  of the uncharged and hydrogen-charged passive films on iron

Applied anodic potential ( $\text{mV}_{\text{SHE}}$ )	Dielectric constant, $\epsilon$	
	Uncharged specimen	Hydrogen-charged specimen
400	45.1	49.1
600	42.3	47.6
800	30.6	39.6

$800 \text{ mV}_{\text{SHE}}$ . By using Equation 2 the donor density is calculated from the slope of the linear region and the flatband potential is obtained from the intercept of the linear portion by subtracting  $kT/e$ . The values of  $N_{\text{D}}$  for one uncharged and hydrogen-charged passive film are estimated to be  $2.5 \times 10^{20}$  and  $2.8 \times 10^{20} \text{ cm}^{-3}$ , respectively, thus, the donor density of the passive film is slightly increased by the hydrogen charging. The flatband potentials for the uncharged and hydrogen-charged specimens are found to be  $151$  and  $146 \text{ mV}_{\text{SHE}}$ , respectively. The flatband potential has been reported to be decreased by increasing the pH of electrolyte [12] and also by increasing the donor density of the space charge layer [13]. During the hydrogen permeation through the passivated iron the permeated hydrogen conceivably decreases the pH of the electrolyte near the interface (passive film/electrolyte), but on the other hand the injected hydrogen increases the donor density of the passive film. Hence we infer that the slight decrease of the flatband potential with the hydrogen charging is mainly caused by an increase in the donor density.

#### 4. Discussion

It has been reported that the passive film on iron is composed of  $\text{Fe}_3\text{O}_4$  in the inner layer and of  $\gamma\text{-Fe}_2\text{O}_3$  in the outer layer [14]. The dielectric constants of the

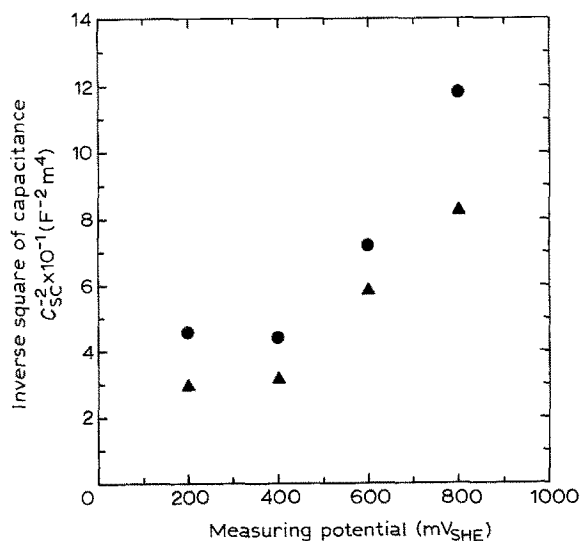


Fig. 3. Mott-Schottky plots for the uncharged and hydrogen-charged passive film formed on iron at the applied anodic potential of  $800 \text{ mV}_{\text{SHE}}$ : (●) uncharged specimen; (▲) hydrogen-charged specimen.

iron oxides are also known to be 250 for  $\text{Fe}_3\text{O}_4$  and 10 for  $\gamma\text{-Fe}_2\text{O}_3$  [15]. This means that the presence of the  $\text{Fe}^{2+}$  ion in the oxide leads to an increase in the dielectric constant. From the value of the dielectric constant of about 40 obtained in this work we infer that the passive film contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

In previous work [6] it was found that with increasing time of passivation the capacitance of the passive film decreases and the mean cationic valence increases. The present results are consistent with those, and show that the decrease of the capacitance with ageing time is owing not only to the increase of film thickness [2] but also to the loss of protons from the film and the accompanying decrease of  $\text{Fe}^{2+}$  ion concentration. The passage of protons from the oxide film into the electrolyte must be associated with proton transport within the film. The diffusive transport is driven by the electric field across the oxide and by a gradient in proton concentration, and proceeds by jumping of the protons from and to  $\text{O}^{2-}$  and  $\text{OH}^-$  ions.

Increasing the applied anodic potential causes an increase in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio [6] and a smaller proton concentration, both of which lead to a decrease of the dielectric constant of the passive film. Charging hydrogen into the passive film increases the dielectric constant of the film by a small amount. The hydrogen injection into the passive film causes a transition of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions because equivalent numbers of protons and electrons are inserted into the passive film by the hydrogen. Consequently the hydrogen charging increases the  $\text{Fe}^{2+}$  ion concentration, producing a high dielectric constant, similar to the case of hydrogen-injected titanium oxide [16].

The passive film on iron has a semiconducting character because the  $\text{Fe}_2\text{O}_3$  tends to be oxygen deficient and  $\text{Fe}^{2+}$  donors in the oxide give rise to an *n*-type conductivity [17]. Assuming that the density of  $\text{Fe}_2\text{O}_3$  consisting of the passive film is  $3\text{ g cm}^{-3}$  the maximum concentration of  $\text{Fe}^{3+}$  ions is estimated to be *ca.*  $1.1 \times 10^{22}\text{ cm}^{-3}$ . Since the donor density  $\approx 10^{20}\text{ cm}^{-3}$  is much less than the concentration of  $\text{Fe}^{3+}$  ions, the concentration of  $\text{Fe}^{2+}$  ions in the passive film is considered to be very small. Under the hydrogen charging conditions used in this work the proton concentration in the passive film has been reported to be *ca.*  $10^{21}\text{ cm}^{-3}$  [9]. If all the inserted protons were associated with the reduction of the cations, the increment of the donor density caused by the hydrogen charging would be equal to the number of the injected protons. However, the increment has been found to be  $3 \times 10^{19}\text{ cm}^{-3}$ , which is much less than the concentration of the inserted protons.

Thus it is thought that a part of the protons within the passive film is associated with the reduction of the cations. It has been reported that protons are located at cation vacancies or at interstitial sites of the oxide

[18]. The protons residing at interstitial sites decrease the valence of the cation but the protons residing at cation vacancies will only compensate the charge of the missing iron ions without a change of metal ion valence, followed by diffusion of oxygen ions. Sato and Kudo [19] insisted that  $\text{H}_2\text{O}$  present in the passive film acts as a donor site but the present work gives no evidence of it. Our results are properly explained in terms of the change of cation valence.

In summary, both the dielectric constant and donor density of the passive film on iron are increased by the hydrogen charging. This is due probably to the increase of a proton concentration and thus to the increase of an  $\text{Fe}^{2+}$  ion concentration in the passive film. This means that the hydrogen present in the passive film may play a role of a medium for changing the valence of metal ion. The results suggest that hydrogen provides electronic defects within the passivating film, which help the semiconducting mechanism of the film.

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