EFFECT OF HYDROGEN ON THE SEMICONDUCTIVE PROPERTIES OF THE PASSIVE FILM ON IRON

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The effects of hydrogen on the corrosion behavior of metals have attracted more and more attention recently, because hydrogen can be generated in many industrial processes, such as cathodic protection, electroplating, acid pickling and welding in the wet condition. One of the most obvious effects of hydrogen on the corrosion behavior of metals is that hydrogen increases their pitting susceptibility [1]. However the mechanism for the hydrogen promoted pitting is still not clear. Investigations showed that the semiconductive properties of passive films on metals are related to their pitting resistance [2]. Therefore the objective of this work is to investigate the effect of hydrogen on the semiconductive properties of the passive film on iron by photoelectrochemical method and advance the mechanism of hydrogen promoted pitting.

Fig.1 shows the photocurrent spectra of passive films on uncharged and charged iron formed at 0.4V for 2.5 hours in a 0.3M H_3BO_3+0.075M $Na_2B_4O_7\cdot 10H_2O$ solution. It was observed that hydrogen increases photocurrent of the passive film. Fig.1 also shows attenuated but measurable photocurrents down to relatively low photon energies for both passive films. This type of behavior is known as the Urbach tail and characterized by a logarithmic dependence of the photocurrent on photon energy, obeying the empirical relationship of $\alpha = \alpha_0 \exp[\gamma(h\nu - E_g)]$, where α is the optical absorption coefficient, $h\nu$ the photon energy, E_g the bandgap energy, α_0 and γ are constants [3]. The higher the value of γ, the lower the number of localized sates in the mobility gap. Fig.2 shows Urbach tail plots of the passive film in Fig.1 based on the assumption that i_{ph} is proportional to α, giving straight lines for both passive films with almost the same slope or γ value, which indicates that the density of states in the vicinity of the conduction band is similar in both passive films [4]. This result suggests that hydrogen might influence photoelectrochemical behavior of the passive film partly by increasing deep localized states in the passive film. Fig.3 shows the determination of bandgap energies of the passive films in Fig.1 according to $(\alpha * h\nu) = A(h\nu - E_g)^n$ with n=2 for a highly disordered passive films [3]. A is a constant. It can be seen that hydrogen decreases the bandgap energy of the passive film. Fig.4 shows the variation of the values of E_g with film formation potentials. It can be seen that hydrogen decreases the bandgap energies of the passive films formed at potentials lower than 0.6V and almost does not influence E_g at potentials higher than 0.6V.

In summary, hydrogen increases the photocurrent of the passive film and decreases the bandgap energies of passive films formed at potentials lower than 0.6V.

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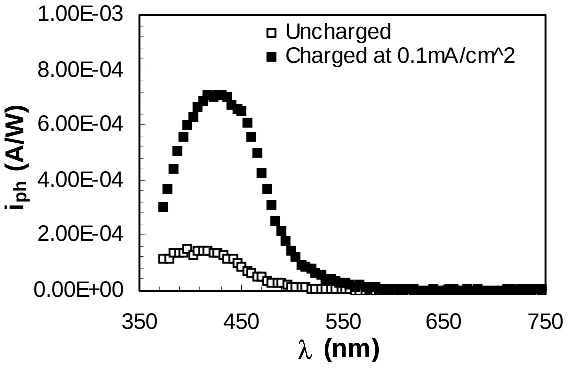

[4] N. E. Hakiki, M. Da Cunha Belo, A.M. P. Simoes and M. G. S. Ferreira, J. Electrochem. Soc., **145**, 3821(1998).

Fig.1 Photocurrent spectra of the passive films on uncharged and charged iron formed at 0.4V for 2.5hrs.

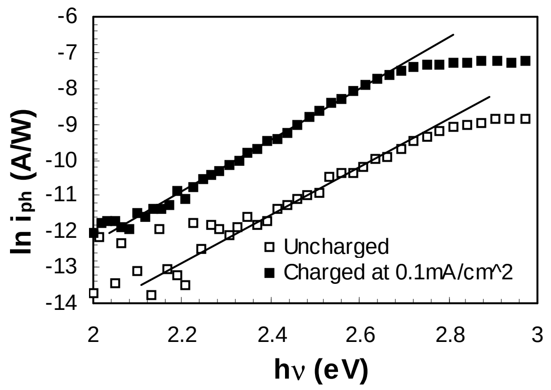

Fig.2 Urbach tail plots of the passive films on uncharged and charged iron formed at 0.4V for 2.5hrs.

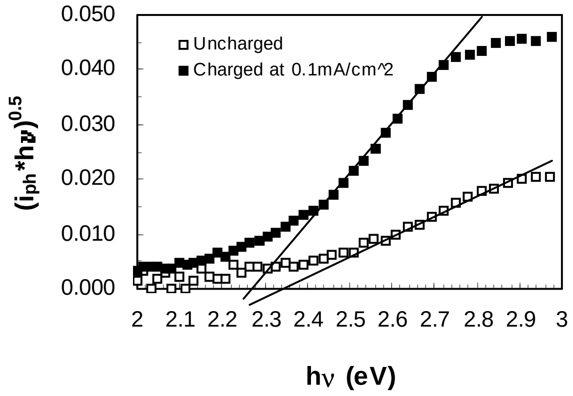

Fig.3 Determination of bandgap energies of the passive films on uncharged and charged iron formed at 0.4V for 2.5hrs.

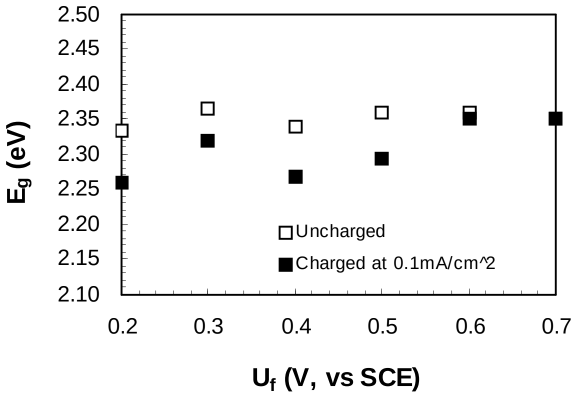

Fig.4 The variation of bandgap energies of passive films with film formation potentials.