



The effects of hydrogen on anodic dissolution and passivation of iron in alkaline solutions



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ABSTRACT

Effects of hydrogen on anodic dissolution and passivation of iron in alkaline solutions are investigated by electrochemical measurements on iron, hydrogen-charged iron and cathodically pre-cleaned iron using a Devanathan dual cell. Shifting of open circuit state of iron in bicarbonate solutions from passivity to active dissolution and the appearance of active dissolution range for hydrogen-charged iron are primarily caused by the surface cleaning effect. Hydrogen hinders the transition from active dissolution to passivation. Inductive coupled plasma analyses of solutions confirm the enhancing effect of hydrogen on anodic dissolution. The effects of hydrogen and solution compositions on anodic reactions are analyzed.

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1. Introduction

Hydrogen can enter into iron and its alloys through many sources during manufacturing, fabrication and service processes [1–4]. There have been reports on the effect of hydrogen in metals or alloys on mechanical properties [1,5–7], phase transformation [1,8], and corrosion and environmentally assisted cracking properties in aqueous environments [1,9–34]. Hydrogen in iron or ferritic steels can affect the corrosion and localized corrosion behavior, electrochemical kinetics and properties of interfacial films [14–29], and dissolution or oxidation at stress corrosion tips [30–34]. Hydrogen affects the electrochemical processes and the surface film properties and therefore contribute significantly to the corrosion and localized corrosion behavior of iron and ferritic steels.

Pyun et al. [14] reported the pitting initiation behavior of hydrogen-charged passive films on pure iron in a boric acid with borate solution of pH 8.4. The pitting induction time decreased with increasing input hydrogen-charging pressure. Hydrogen reduced

resistance to pit initiation by chloride ions by increasing the hydroxyl and water contents of the film. Hu et al. [15] reported that, for carbon steel in an ammonium nitrate solution, hydrogen decreased the dissolution rate in the active region, but increased the anodic reaction rates in the passive and transpassivation regions. Zeng et al. [16] reported that the charged hydrogen delayed the film formation processes and increases the dissolution rate of iron at passive state in a borate solution. Hydrogen increased the capacitance and adulated concentration of the surface film, but decreases the flat band potential.

Yu et al. [17–22] have conducted a series of research works on the electrochemical processes, the surface stability and pitting behavior of iron in a slightly alkaline solution with pH 8.4. Yu et al. [17] observed a change of open circuit state from passivity state for non-charged iron to active dissolution for hydrogen-charged iron was observed. Hydrogen produced an increases of donor density of the passive film and decreases the pitting resistance. Yu et al. [18] showed that the passive film on iron became unstable after hydrogen permeation in the passive film. Hydrogen decreased the open circuit potential, the cathodic charge for reduction and the electron-transfer resistance of the passive film, and the pitting resistance in solutions with chlorides. By using electrochemical noise technique and the scanning reference electrode technique, Yu et al. [19]

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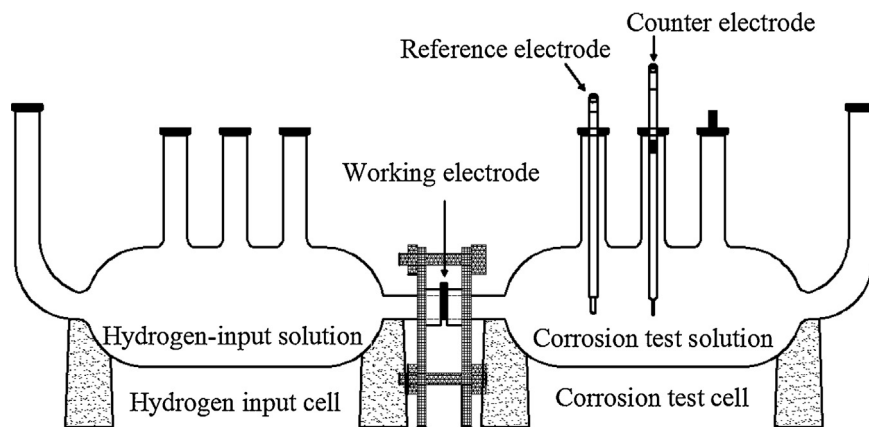


Fig. 1. The schematic of the electrochemical setup for investigating the effects of hydrogen on electrochemical behavior of iron.

found that hydrogen promoted metastable pitting of iron and its evolution into stable pitting. Yu et al. [20] reported that hydrogen increased the number of active sites for formation of metastable pits as precursors for stable pits as the results of the hydrogen effects on the properties of passive film and the anodic dissolution rate of iron. Based on the results of Auger electron spectroscopy, secondary ion mass spectroscopy and nuclear reaction analysis, Yu et al. [21] found that hydrogen decreased the open circuit potential, decreased the film thickness and oxygen content in the film, reduces the valence state of iron, and increases the iron content in the film and the degree of non-stoichiometry of the film. The hydrogen in proton form could react with oxygen ions to form OH^- in the passive film. Results of photoelectrochemical measurements by Yu et al. [22] showed that hydrogen increased the magnitude of the photocurrents from the passive films formed on iron at all investigated potentials, and decreased the bandgap energies of the passive films formed at potentials lower than 0.6 V, indicating the effect of hydrogen on the bond strength of the oxides comprising the passive films.

Zeng et al. [23–25] reported that hydrogen retarded the passive film formation and decreased its stability in the range of passive potentials for pipeline steels in bicarbonate solutions with or without chlorides. Hydrogen decreased the resistance towards charge transfer and ion diffusion, increased the capacitance and donor density of the passive film, and decreased the flatband potential and the space-charge layer thickness of the passive film. It was proposed that hydrogen created an additional electric repulsion on Fe^{2+} or Fe^{3+} and oxygen vacancies, and enhanced the diffusion rate of cations and anion vacancies, resulting in changes in the structure and a decrease in the thickness of the passive films. Zeng et al. [26] showed that the photocurrent of the film was enhanced by hydrogen, but the photocurrent did not return to the initial value before hydrogen charging. Zhang et al. [27] showed that charged hydrogen could react with the original film of duplex structure to form more continuous film containing hydroxyl groups. Li et al. [28] reported that oxidation of hydrogen in X70 steel changes the environment near the surface of iron in a phosphoric acid solution and therefore retards the formation of a passive film and enhance the anodic dissolution. Li and Cheng [29] reported that hydrogen enhanced the anodic dissolution of X-70 pipeline steel in NS4 solution of pH 6.5. Hydrogen changed the corrosion potential, the interfacial double-charge layer capacitance and the charge-transfer resistance.

Gu et al. [30,31] have reported that hydrogen could diffuse into the pipeline steels around the crack tip during stress corrosion cracking in bicarbonate solutions and therefore increases the anodic dissolution of steels and stress corrosion cracking intensity. Mao et al. [32] proposed the mechano-electrochemical mechanism

for stress corrosion cracking of metals under the effects hydrogen, stress and dislocation effect. The synergistic effect between hydrogen and stress on anodic dissolution reaction is modeled based on the thermodynamic analyses. Lu et al. [33] pointed out that the synergistic effect of hydrogen and stress on active dissolution of X60 pipeline steel in NS4 solution deaerated by 5% CO_2 + 95% N_2 was negligible. Thermodynamic calculations show that the elastic-deformation was insufficient to produce a significant effect on active dissolution.

Das and Shoji [35] investigated the effect of hydrogen on the oxidation of nickel and chromium by using the density function theory and tight-binding quantum chemical molecular dynamics. It was found that hydrogen changes to a negatively charged condition in the interstitial sites. Interstitial hydrogen initiated the charge transfer and extended the metal atomic bonds and makes the metal surface more chemically active.

The effects of hydrogen on corrosion and related electrochemical reactions are dependent on the types of metal-environment systems, the involved element processes and their rate-determining steps. It is important to identify and quantify the fundamental aspects of the effects of hydrogen on the element electrochemical processes. The effects of hydrogen on electrochemical corrosion processes can arise from several sources such as the change of the surface condition, the direct oxidation of hydrogen atoms, the change of active dissolution kinetics of the metals, the change of formation and dissolution kinetics of the film on the metal, and the properties and stability of the film. In the present study, alkaline solutions of pH values from 8.4 to 13 are used to investigate the effect of hydrogen on anodic dissolution and passivation of iron in environments with different pH values and passivating species. Bicarbonate solutions of various concentrations were used as slightly alkaline solutions in the tests of the present work. The corrosion and electrochemical behavior of iron and steel in aqueous solutions containing bicarbonate and carbonate ions has been investigated due to the implication to corrosion and cracking of pipeline steels, corrosion of steels in oil and gas fields, and the importance in understanding the fundamentals of dissolution and passivation of iron and steels [36–54]. The effects of bicarbonate ions on the electrochemical behavior and pitting corrosion have been investigated. Pouorbaix provided the thermodynamic data for bicarbonate solutions [36]. Jelinek and Neufeld measured the anodic polarization curves of pre-cathodic polarized mild steel in bicarbonate solutions with chlorides and discussed the pitting behavior [40]. The pitting corrosion of X80 pipeline steel in dilute bicarbonate solutions with chloride ions was investigated by Mao et al. [45], showing the effects of bicarbonate concentration on open circuit potential and corrosion current density. Simard et al. [46,47]

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