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硫酸根离子对铁在弱碱性溶液中阳极溶解和钝化行为的影响

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摘要: 采用浸泡实验, 电化学测试和表面分析技术研究了硫酸根离子浓度对铁在稀碳酸氢钠溶液中开路状态和阳极极化行为的影响. 在无硫酸根离子及含有少量硫酸根离子的碳酸氢钠溶液中, 铁的开路电位约为 (-0.225 ± 0.005) V, 并呈现钝化状态, 其电化学阻抗很大, 腐蚀速率较低. 在含有较高浓度硫酸根离子的碳酸氢钠溶液中, 铁的开路电位为 (-0.790 ± 0.010) V 并呈现活性溶解状态, 其电化学阻抗较小, 腐蚀速率较高, 同时阳极极化曲线上能观察到活化-钝化转变现象. 由于铁在含有较高浓度硫酸根离子的碳酸氢钠溶液中处于活化状态, 阳极极化曲线上存在数个电流峰. 足够高的硫酸根离子浓度会导致铁表面预先形成或转变而成的氧化膜失效. 相比于自然曝氧状态, 在除氧条件下较低的硫酸根离子浓度即可引起铁在碳酸氢钠溶液中由钝态向活性溶解态的转变.

关键词: 铁; 电化学行为; 腐蚀失重; 钝态; 阳极溶解; X射线光电子能谱; 电位-pH图
中图分类号: O646; TG171

Effects of Sulfate Ions on Anodic Dissolution and Passivity of Iron in Slightly Alkaline Solutions

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Abstract: The effects of sulfate concentration on the open circuit state and anodic polarization behavior of iron in dilute bicarbonate solutions were investigated using immersion tests, electrochemical measurements, and surface analysis techniques. In the absence of sulfate or in the presence of a low concentration of sulfate in dilute bicarbonate solutions, iron was in a passive state, with a corrosion potential of (-0.225 ± 0.005) V. A high electrochemical impedance and low corrosion rate were obtained. No obvious active-passive transition was observed in the anodic polarization curves. In the presence of a high concentration of sulfate in dilute bicarbonate solutions, iron was in an active dissolution state, with a corrosion potential of (-0.790 ± 0.010) V. A low electrochemical impedance, high corrosion rate, and typical active-passive transition in anodic polarization curves were observed and related to the sulfate concentration. In the presence of a high concentration of sulfate, the anodic polarization curves showed current peaks as a result of iron activation by sulfate ions. Sulfate ions of sufficiently high concentration in solutions degraded previously formed oxide layers on iron or transformed oxide layers in bicarbonate solutions. The transition of the open circuit state from passivity to active dissolution occurs at a lower sulfate concentration in a deaerated solution than in an aerated solution.

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Key Words: Iron; Electrochemical behavior; Corrosion weightloss; Passivity; Anodic dissolution; X-ray photoelectron spectroscopy; Potential–pH diagram

1 Introduction

Bicarbonate and sulfate ions are often present in natural and industrial environments.^{1–21} The electrochemical behavior of iron, carbon steels and low alloy steels in bicarbonate-bearing solutions has been studied due to its theoretical importance in understanding of anodic reaction mechanisms,^{1–15} and due to the practical applications such as corrosion in oil and gas fields, corrosion and stress corrosion cracking of gas transmission pipeline steels, corrosion in concrete pore environments, and corrosion in simulating groundwater environments of candidate waste disposal sites.^{22–36} Bicarbonate ions have multiple effects on anodic reactions, such as participating anodic dissolution through active adsorption, inhibiting further anodic dissolution by forming protective film, and enhancing anodic dissolution through dissolving the protective film. Depending on the initial condition, iron in bicarbonate solutions could exhibit two kinds of open circuit states, passive state or active state.^{5,15} Open circuit state has a critical effect on corrosion kinetics. Open circuit state could be affected by both passivating species and aggressive species. The effects of sulfate on corrosion and electrochemical behaviors of iron and steels have been reported.^{16–21}

This work is designed to investigate if sulfate as an aggressive type anion can affect the type of open circuit states and the resultant anodic dissolution/passivation kinetics. The result could provide a direct judgment on the corrosivity of environments, which is also expected to provide relevant information on the anodic behavior at the stress corrosion crack tip where aggressive ions could accumulate. The changes of open circuit states and anodic processes of iron with sulfate concentration in dilute bicarbonate solutions were investigated by measurements of open circuit potential (OCP), immersion corrosion tests, surface observations and surface film analysis technology, potentiodynamic polarization measurements and electrochemical impedance spectroscopy measurements. The effects of anions on electrode kinetics and thermodynamics are discussed in terms of potential (*E*)–pH diagrams and electrochemical measurements. Both aerated and deaerated solutions were used for various filed applications and theoretical analyses.

2 Experimental

Specimens were fabricated from iron rods with purity of 99.9%. The electrode size was 10 mm×10 mm×8 mm. Copper wire was welded to the back of the iron specimen. The iron electrode was embedded with epoxy resin with an exposed area of 1.0 cm². The surface of the iron electrode was grinded to 1200-grit SiC paper then rinsed in ethanol and acetone prior to the electrochemical measurements. All tests were carried out in naturally aerated and deaerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions at 25 °C, with *x* of 0.02 and 0.05 and *y* of 0, 0.003, 0.5, 1. All test solutions

were prepared by deionized water and analytical reagents. Deaeration was achieved by bubbling N₂ gas into the test solution for 1 h before the measurements and N₂ gas was kept continuous bubbling during the process of experiment. The conductivity and pH values of test solutions were measured.

A three-electrode cell was used for electrochemical measurements. Open circuit potential, anodic polarization curve, and electrochemical impedance spectroscopy (EIS) were measured by using a German Zahner-Zennium electrochemical workstation. The working electrode was the pure iron specimen, the counter electrode was a platinum plate, and the reference electrode was a saturated calomel electrode (SCE). All potentials were measured and quoted against SCE if not specially mentioned.

Prior to anodic polarization tests, the working electrode was immersed in the test solution for 600 s and OCP values were recorded. Anodic polarization curves were measured at a sweep rate of 0.333 mV·s^{−1}. Prior to EIS tests, the working electrode was immersed in the test solution for 2 h. EIS measurements were performed at open circuit potentials. The frequency range was from 100 kHz to 10 mHz. The amplitude of sinusoidal excitation voltage was 5 mV. The data collected was interpreted with software Zsimpwin. Each test was repeated three times and showed good reproducibility. No prior cathodical polarization was applied before OCP test.

Immersion tests were performed using 15 mm×15 mm×3 mm coupons. The coupons were polished to 1200-grit SiC paper, and then rinsed with ethanol and acetone in sequence before immersion tests. The surface areas were calculated and, the difference between the initial weights and the final weight (ΔW), was measured. Average corrosion rates (v_{cor}) in mm·year^{−1} were calculated. The surface morphologies of specimens with corrosion products removed after immersion tests were observed with CamScan Apollo 300 thermal field emission scanning electron microscope (SEM).

The samples for X-ray photoelectron spectroscopy (XPS) tests were 5 mm×5 mm×3 mm iron coupons immersed in test solutions for 2 h. XPS analysis was performed by using a Japan Physical Electronics Quantum 2000 Scanning ESCA Microprobe. Spectra were generated using a focused monochromatic Al K_α X-ray source operated at 25.1 W (1486.6 eV) and pass energy of 58.7 eV. The ion gun was operated with an Ar⁺ at energy of 2 kV and the sputtering beam current was 29 nA with an incident angle of 45°. The sputter rates of 0.25 nm per cycle for first 20 cycles and then 2.5 nm per cycle were used. Sputter rates were determined by sputtering a known thickness of SiO₂ on Si using the same sputter conditions. The sputter rates were for SiO₂. The samples measured in an “as received” condition with no other surface cleaning treatment. Binding energy calibration was done by linking the reference to C 1s line, the binding energy of C—C or C—H located at 284.8 eV.

3 Results

3.1 Open circuit potentials

3.1.1 Open circuit potentials in aerated solutions

Open circuit potential vs immersion time curves for iron in aerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05$; $y=0, 0.003, 0.5, 1$) solutions are shown in Fig.1 and Fig.2. Open circuit potentials for iron in aerated NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ exhibited a trend of moving in the positive direction with increasing immersion time. Open circuit potential for iron in aerated NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ moved in the negative direction with increasing immersion time. The initial OCP values, $\text{OCP}_{t=0 \text{ h}}$, for iron in 0.02 and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solutions decreased gradually with increasing sulfate concentration from 0 to $1 \text{ mol} \cdot \text{L}^{-1}$. For iron in NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, OCP values at an immersion time of 2 h , $\text{OCP}_{t=2 \text{ h}}$, were between -0.23 and -0.22 V . The differences between $\text{OCP}_{t=0 \text{ h}}$ and $\text{OCP}_{t=2 \text{ h}}$ were less than 0.06 V , and the electrode surfaces were bright after the immersion test. For iron in NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions, values of $\text{OCP}_{t=2 \text{ h}}$ were in the range of -0.80 to -0.78 V . The differences between $\text{OCP}_{t=0 \text{ h}}$ and $\text{OCP}_{t=2 \text{ h}}$

were more than 0.30 V , and the electrode surfaces after immersion were dark. These results show that adding sulfate in bicarbonate solutions caused a negative shift of OCP. OCP values for iron in $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ with adding 0.02 or $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ were significantly lower than that for iron in $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution.

3.1.2 Open circuit potentials in deaerated solutions

Open circuit potential vs immersion time curves for iron in deaerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05$; $y=0, 0.003, 1$) solutions are shown in Fig.3 and Fig.4. Open circuit potentials for iron in deaerated $0.02, 0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions firstly decreased and then increased with increasing immersion time. Open circuit potential for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4, 0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions moved in the negative direction with increasing immersion time. For iron in deaerated $0.02, 0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions, values of $\text{OCP}_{t=2 \text{ h}}$ were between -0.44 and -0.41 V . The differences between $\text{OCP}_{t=0 \text{ h}}$ and $\text{OCP}_{t=2 \text{ h}}$ were less than 0.04 V . For iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4, 0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1}$

Fig.1 Open circuit potential vs immersion time curves for iron in aerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions

The OCP data for iron in aerated $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ are also listed.

Fig.2 Open circuit potential vs immersion time curves for iron in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions

The OCP data for iron in aerated $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ are also listed.

Fig.3 Open circuit potential vs immersion time curves for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions

Fig.4 Open circuit potential vs immersion time curves for iron in deaerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions

$\text{L}^{-1} \text{Na}_2\text{SO}_4$, and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions, values of $\text{OCP}_{t=2\text{h}}$ were around -0.82 V . The differences between $\text{OCP}_{t=0\text{h}}$ and $\text{OCP}_{t=2\text{h}}$ were more than 0.25 V . These results are different from those in aerated solutions. Open circuit potentials for passivity state and active dissolution state in deaerated solutions are lower than their corresponding values in aerated solutions. In deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution, adding $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ could cause the transition from passivity state to active dissolution state.

3.2 Electrochemical impedance spectroscopy

3.2.1 In aerated solutions

EIS diagrams for iron in aerated $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ and $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05$; $y=0, 0.003, 0.5, 1$) solutions are shown in Fig.5 and Fig.6. Based on the reported analyses of similar test systems,^{14,33} the obtained EIS results were fitted and analyzed. For iron in aerated NaHCO_3 solution without

sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, EIS results were fitted with an equivalent circuit for passivity, as shown in Fig.7a. In this equivalent circuit, R_s , R_f , C_f , and R_{ct} represent solution resistance, resistance across the passive film, passive film capacitance, interfacial capacitance, and charge transfer resistance. The results are summarized in Table 1. For iron in aerated NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, EIS results were fitted with an equivalent circuit for active dissolution, as shown in Fig.7b. In this equivalent circuit, R_s , C_{dl} , R_{ct} represent solution resistance, interfacial capacitance, charge transfer resistance. The results are summarized in Table 2.

Solution resistance R_s decreased with the increase of Na_2SO_4 concentration, showing the increase of the electrical conductivity of solutions, as shown in Tables 1 and 2. The values of R_{ct} for iron in aerated NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ were more than $100 \text{ k}\Omega \cdot \text{cm}^2$, showing that the surface layer formed on the electrode surface had a good protective effect on the matrix. In aerated NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, the values of R_{ct} were far less than those in aerated NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, showing that corrosion of iron would take place under active dissolution.

3.2.2 In deaerated solutions

EIS diagrams for iron in deaerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1}$

Fig.5 Nyquist impedance representation plots for iron in aerated (a) $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions and (b) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions

The data for iron in aerated $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ are also listed.

Fig.6 Impedance module representation plots for iron in aerated (a) $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions and (b) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions

The data for iron in aerated $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ are also listed.

Fig.7 Equivalent circuits proposed for analyzing the electrochemical impedance response for iron in $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions for (a) passive state and (b) active dissolution state

$\text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0, 0.003, 1$) solutions at 25°C are shown in Figs.8 and 9. For iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003$) solution, EIS results were fitted with an equivalent circuit for passivity, as shown in Fig.7a. The results are summarized in Table 3. For iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0.003, 1$) and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions, EIS results were fitted with an equivalent circuit for active dissolution, as shown in Fig.7b. The results are summarized in Table 4.

Similarly, solution resistance R_s decreased with the increase of Na_2SO_4 concentration, as shown in Tables 3 and 4. The values of R_{ct} for iron in deaerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ were about $100 \text{ k}\Omega \cdot \text{cm}^2$, showing the presence of a good protective surface layer. In deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0.003, 1$) and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions, the significantly low values of R_{ct} indicated the active dissolution of iron.

The values of R_{ct} for iron in deaerated solutions under passivity state were lower than those in aerated solutions. The values of R_{ct}

for iron in deaerated solutions under active dissolution state were higher than those in aerated solutions.

3.3 Anodic polarization curves

3.3.1 In aerated solutions

Anodic polarization curves for iron in aerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0, 0.003, 0.5, 1$) solutions at 25°C are shown in Fig.10 and Fig.11. The maximum current $i_{\max}$ occurred at the potential $E_{\max}$. $E_{\text{passive}, i}$, $E_{\text{passive}, f}$, and E_{passive} represent the initial potential, final potential, and the width of the passive region, respectively. i_{passive} is the current in the passive region. Increasing the sulfate concentration had negligible effects on the $E_{\text{passive}, f}$. In NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, no current peak existed on the anodic polarization curves and no active-passivation transition phenomenon could be found. Adding $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ slightly increased i_{passive} . In NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, active-passivation transition appeared on curves and single or multiple current peaks were observed. $i_{\max}$ increased with increasing the sulfate concentration. $E_{\max}$, $E_{\text{passive}, i}$, and E_{passive} for $y=0.5$ were close to those for $y=1$.

3.3.2 In deaerated solutions

Anodic polarization curves for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions at 25°C are shown in Fig.12. $E_{\text{passive}, f}$ was not sensitive to sulfate concentration, while E_{passive} decreased with increasing sulfate concentration. No current peak or active-passivation transition phenomenon could be found on the anodic polarization curves for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution. For $y=0.003, 1$, active-passivation transition was observed on polarization curves and multiple current peaks appeared due to transition of open circuit state from passivity to active dissolution state in deaerated solution. i_{passive} for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution was a little higher than that in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution. $i_{\max}$ for iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution was lower than that in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution.

Table 1 EIS component values for iron in aerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0, 0.003$) solutions*

Component	$R_s/(\Omega \cdot \text{cm}^2)$	$10^4 C_d/(\text{F} \cdot \text{cm}^{-2})$	n_c	$R_f/(\Omega \cdot \text{cm}^2)$	$10^4 C_{df}/(\text{F} \cdot \text{cm}^{-2})$	n_d	$10^{-5} R_{ct}/(\Omega \cdot \text{cm}^2)$
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$	176.2	1.21	0.78	14.63	7.34	0.83	1.75
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	123.3	5.04	0.80	30.13	8.83	0.82	1.92
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$	72.16	5.07	0.80	11.48	9.70	0.82	1.42
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	64.05	4.99	0.66	17.61	10.8	0.85	1.79

*fitted with equivalent circuit in Fig.7a; n represents dispersion coefficient of capacitance components.

Table 2 EIS component values for iron in aerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0.5, 1$) solutions*

Component	$R_s/(\Omega \cdot \text{cm}^2)$	$10^4 C_d/(\text{F} \cdot \text{cm}^{-2})$	n_d	$R_{ct}/(\Omega \cdot \text{cm}^2)$
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	5.29	3.71	0.76	1247
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	3.07	4.24	0.79	1036
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	5.10	3.65	0.77	1282
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	3.06	3.88	0.78	1006

*fitted with equivalent circuit in Fig.7b

Fig.8 Nyquist impedance representation plots for iron in deaerated (a) $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions and (b) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions

Anodic polarization curves for iron in deaerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions at 25°C are shown in Fig.13. Neither current peak nor dissolution/passivation transition could be observed on the anodic polarization curves for $y=0$ and $y=0.003$, which was similar to that for iron in aerated solutions. For $y=1$, several current peaks appeared on the anodic

Fig.9 Impedance module representation plots for iron in deaerated (a) $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions and (b) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 1$) solutions

polarization curve.

Characteristic parameters of anodic polarization curves in aerated and deaerated solutions are different. In deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$, i_{passive} was close to that in aerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution. In deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, i_{passive} was higher than that in aerated solution. E_{max} and i_{max} in deaerated solutions were lower than those in aerated solutions.

In deaerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003$) solutions, i_{passive} values of anodic polarization curves were also close to those in aerated solutions. In deaerated $0.05 \text{ mol} \cdot \text{L}^{-1}$

Table 3 EIS component values for iron in deaerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0, 0.003$) solutions^a

Component	$R_s/(\Omega \cdot \text{cm}^2)$	$10^4 C_d/(\text{F} \cdot \text{cm}^2)$	n_c	$R_d/(\Omega \cdot \text{cm}^2)$	$C_d/(\text{F} \cdot \text{cm}^2)$	n_d	$10^{-4} R_{ct}/(\Omega \cdot \text{cm}^2)$
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$	161.4	1.38	0.85	47.24	3.74×10^{-4}	0.89	9.44
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$	58.24	1.73	0.86	18.04	2.67×10^{-6}	0.92	10.1
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	55.44	1.67	0.82	16.73	1.18×10^{-6}	0.86	11.7

^afitted with equivalent circuit in Fig.14a; n represents dispersion coefficient of capacitance components.

Table 4 EIS component values for iron in deaerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05; y=0.003, 1$) solutions^a

Component	$R_s/(\Omega \cdot \text{cm}^2)$	$10^4 C_d/(\text{F} \cdot \text{cm}^2)$	n_d	$R_{ct}/(\Omega \cdot \text{cm}^2)$
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	112.3	3.87	0.80	9415
$0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	39.81	4.01	0.80	2647
$0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$	3.45	3.04	0.82	2306

^afitted with equivalent circuit in Fig.14b; n represents dispersion coefficient of capacitance components.

Fig.10 Anodic polarization curves for iron in aerated 0.02 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0, 0.003, 0.5, 1) solutions

Fig.11 Anodic polarization curves for iron in aerated 0.05 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0, 0.003, 0.5, 1) solutions

Fig.12 Anodic polarization curves for iron in deaerated 0.02 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0, 0.003, 1) solutions at 25 °C

NaHCO₃+1 mol·L⁻¹ Na₂SO₄ solution, i_{passive} , i_{max} , and E_{max} were higher than those in aerated solutions.

3.4 Immersion test results

Results from the immersion tests are shown in Fig.14. Weightloss vs immersion time curve for iron in aerated 0.05 mol·L⁻¹ NaHCO₃+1 mol·L⁻¹ Na₂SO₄ solution exhibited an approximately linear relationship within the test period of 72 h test, leading to a corrosion rate of about 0.103 mm·year⁻¹ at OCP of about -0.80 V. Iron showed a rather small amount of weightloss for a 72 h immersion test in aerated 0.05 mol·L⁻¹ NaHCO₃+0.003

Fig.13 Anodic polarization curves for iron in deaerated 0.05 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0–1) solutions at 25 °C

Fig.14 Weightloss vs test time for iron in aerated 0.05 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0.003, 1) solutions

mol·L⁻¹ Na₂SO₄ solution, leading to a corrosion rate of about 5.46×10^{-4} mm·year⁻¹ at OCP of about -0.30 V. Corrosion rate is strongly affected by sulfate concentration.

After immersion tests in aerated 0.05 mol·L⁻¹ NaHCO₃+y mol·L⁻¹ Na₂SO₄ (y=0.003, 1) solutions, the corrosion products on the specimen surfaces were cleaned with a soft rubber and then observed with SEM. The surface morphologies are shown in Fig.15. The specimen surfaces of iron after immersion in aerated 0.05 mol·L⁻¹ NaHCO₃+1 mol·L⁻¹ Na₂SO₄ solution were dark and rough, showing that active corrosion occurred during the immersion test. With increasing of immersion time, pits became more and larger, and grinding marks became less clear, as shown in Fig.15(a–c). The specimens surface of iron was bright after immersion in aerated 0.05 mol·L⁻¹ NaHCO₃+0.003 mol·L⁻¹ Na₂SO₄ solution and grinding marks during specimen preparation were still visible, showing that the surfaces were not significantly affected by the immersion procedure, as shown in Fig.15d.

3.5 XPS analysis

The variation in chemical composition with XPS depth profiles of iron, oxygen, and carbon obtained from the XPS survey scans for iron specimens immersed in aerated 0.02 mol·L⁻¹ NaHCO₃, 0.05 mol·L⁻¹ NaHCO₃, and 0.05 mol·L⁻¹ NaHCO₃+0.003 mol·L⁻¹ Na₂SO₄ solutions are shown in Fig.16. As observed in Fig.16, iron concentration increased with depth and oxygen concentration decreased with depth as expected. The high carbon concentration

Fig.15 Surface morphologies of specimens after immersion tests in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions

(a) $y=1$, $t=24 \text{ h}$; (b) $y=1$, $t=48 \text{ h}$; (c) $y=1$, $t=72 \text{ h}$; (d) $y=0.003$, $t=72 \text{ h}$

at the surface of each specimen may be due to organic carbon contamination during the specimen preparation and post-immersion storage or the formation of FeCO_3 . The carbon con-

centration decreased markedly after first sputtering the surface and remained nearly constant afterwards for all specimens. According to Fig.16, oxygen concentrations decreased to half of their initial values at the depth of about 3 nm. The place where oxygen concentration decreases to half of its initial value is the interface of oxide and transition layer. If the distance between the surface and the interface is defined as the thickness of oxide layer, the thickness of oxide layer on test specimens is about 3 nm.

Fig.17 and Fig.18 present the high resolution of XPS spectra of iron in $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution for the $\text{Fe } 2p_{3/2}$, $\text{O } 1s$, and $\text{C } 1s$ region with different sputter depths. The binding energies for the peaks have been referenced to C—C bond at 284.8 eV. As shown in Fig.17, at the sputter depth of 0 nm, FeCO_3 , Fe_2O_3 , and FeO existed in the surface film. As showed in Fig.18, at the sputter depth of 0.9 nm, FeCO_3 disappeared and Fe_2O_3 and FeO were still present. Metallic iron was found at both depths because the film was very thin. The binding energy values for fitting are identical with those reported in literature.^{38,46–50} The emergence of FeO may be due to the sputtering process.^{46,47,50}

4 Discussion

Previous research showed that the value of pH was approximately 8.4 for the concentrations of bicarbonate solutions from 0.01 to $1.0 \text{ mol} \cdot \text{L}^{-1}$.³ The measured conductivity and pH values of $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions ($x=0.02, 0.05$; $y=0, 0.003, 0.5, 1$) are shown in Fig.19. With the increase of sulfate concentration, the conductivity of $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions ($x=0.02, 0.05$; $y=0, 0.003, 0.5, 1$) increased. The values of conductivity of $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions were higher than those of $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) solutions for the same sulfate concentration. The solution pH values of 0.02 or $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solutions slightly increased with adding $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$. The pH value decreased with sulfate concentration for $y \geq 0.003$. The pH values of $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) were higher than those of $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($y=0, 0.003, 0.5, 1$) except for $y=1$.

According to the thermodynamic equilibrium calculations, the main ionic species in $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions in this study are Na^+ , OH^- , HCO_3^- , and SO_4^{2-} . The anodic behaviors of iron are mainly the results of the combined actions

Fig.16 XPS depth profiles for iron, oxygen, and carbon recorded for the iron specimens immersed in aerated (a) $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$, (b) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$, and (c) $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions

Fig.17 High resolution of XPS spectra for iron immersed in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution at the sputter depth of 0 nm
(a) C 1s region, (b) O 1s region, (c) Fe $2p_{3/2}$ region

of anions OH^- , HCO_3^- , and SO_4^{2-} . In the dilute solutions used here, the activity coefficient of HCO_3^- is 0.863 in a $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution and 0.804 in a $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution.⁵¹ Thus the activity of HCO_3^- is 0.017 in a $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution and 0.04 in a $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solution. Potential-pH diagram of Fe-H₂O system is used to analyze the thermodynamic information of iron in dilute NaHCO_3 solutions with or without sulfate addition^{3,52} assuming $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. Candidate anodic reactions are:^{15,37,40,41}

Fig.18 High resolution of XPS spectra for iron immersed in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution at the sputter depth of 0.9 nm
(a) O 1s region, (b) Fe $2p_{3/2}$ region

The dominant anodic reactions are dependent on the concentrations of active species and the electrode potential.

In aerated NaHCO_3 solution without sulfate or with $0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, the stable OCP values are (-0.225 ± 0.005) or $(0.015 \pm 0.005) \text{ V}$ (vs SHE), as shown in Fig.1 and Fig.2. These OCP values are located in the region of Fe_2O_3 in E -pH diagram of Fe-H₂O system, as shown in Fig.20. From the immersion test results,

Fig.19 Conductivity and pH values of $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions ($x=0.02, 0.05$; $y=0, 0.003, 0.5, 1$)

the surfaces of specimens were still bright and grinding marks were visible, and there was very low corrosion weight loss after immersing in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ for 72 h, as shown in Fig.14 and Fig.15d. High values of R_{ct} from the fitting results of EIS data of electrode in above-mentioned solutions are shown in Table 1. All these results indicate the high protective property of the surface layer formed on electrode surface. This kind passivity of iron was mainly caused by the pre-formed oxide film in air. After a short period of prior cathodic polarization, iron could not maintain the passivity in bicarbonate solutions of $0.01\text{--}1.0 \text{ mol} \cdot \text{L}^{-1}$.^{5,15,53} Mao *et al.*³¹ pre-treated the X80 pipeline steel in deaerated bicarbonate solutions at -0.95 V for 30 min to reduce air-formed oxide films before the potentiostatic test. Passive film could not form on bare surface iron in bicarbonate solutions. XPS data also showed that the inner surface film formed on iron in bicarbonate solutions were ferric oxide, Fig.18. FeCO_3 observed only on the outmost layer was thought to the product of the prior formed oxide with bicarbonate ions after immersion in bicarbonate solutions, Fig.17.

For iron in aerated NaHCO_3 solution with 0.5 and $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$, the stable OCP values are (-0.790 ± 0.010) and $(-0.550 \pm 0.010) \text{ V (vs SHE)}$, as shown in Fig.3 and Fig.4. According to Eqs. (2) and (3),⁴⁰ the equilibrium potentials for Fe/FeCO_3 and $\text{FeCO}_3/\text{Fe}_2\text{O}_3$ are calculated with the measured solution pH values and values of HCO_3^- activity by following equations:

$$E_h = -0.488 - 0.0296 \lg[\text{HCO}_3^-] - 0.0296 \text{ pH} \quad (\text{for Eq.(2)}) \quad (10)$$

$$E_h = 0.747 + 0.059 \lg[\text{HCO}_3^-] - 0.118 \text{ pH} \quad (\text{for Eq.(3)}) \quad (11)$$

The results are shown in Fig.20. The OCP values for iron in aerated $x \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + y \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ ($x=0.02, 0.05$; $y=0.5, 1$) solutions are both in the thermodynamics stability region of FeCO_3 and Fe^{2+} in $E\text{--pH}$ diagram of $\text{Fe}\text{--H}_2\text{O}$ system. However, a low reaction resistance and a high corrosion rate were observed for iron in aerated $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution, as shown in Fig.14, Fig.15b, and Table 2. It is proposed that sulfate ions of sufficiently high concentrations in solutions could degrade the prior formed oxide layer on iron or the transformed oxide layer in bicarbonate solutions. As the result, high concentrations of sulfate anions cause a significantly negative

shift of open circuit potential. In the absence of protective film, anodic dissolution reactions of iron or formation reactions of non-protective oxide films are favored.

The open circuit potential for iron in $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ was more positive than those in $1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ with a low concentration of bicarbonate, showing that bicarbonate would have a strong effect on the electrified lay at the metal-solution interface.

The open circuit states of iron in deaerated solutions are somewhat different from those in aerated solutions. The open circuit states of iron in aerated and deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3$ solutions are in passivity state. The open circuit states of iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ and $0.05 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 1 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solutions are in active dissolution state. The open circuit state of iron in deaerated $0.02 \text{ mol} \cdot \text{L}^{-1} \text{NaHCO}_3 + 0.003 \text{ mol} \cdot \text{L}^{-1} \text{Na}_2\text{SO}_4$ solution is in active dissolution state, which is in passive state in the aerated solution. In deaerated solutions, oxygen reduction reaction becomes negligible. Open circuit potentials in deaerated solutions are lower than those in aerated solutions. In aerated solutions, oxygen would facilitate the formation of oxide film or the film transition to form a more protective layer that could not be attacked by a low concentration sulfate.

Fig.10–Fig.13 show that relatively high concentration sulfate ions have a significant effect on anodic polarization behavior. In aerated bicarbonate solutions without sulfate, there was no active-passivation phenomenon on anodic polarization curves. Adding $0.003 \text{ mol} \cdot \text{L}^{-1}$ sulfate in aerated NaHCO_3 solutions does not have significant effect on the configuration of anodic polarization curves. Adding 0.5 or $1 \text{ mol} \cdot \text{L}^{-1}$ sulfate could cause a transition of open circuit state from passivity to active dissolution and active-passive transition in the anodic polarization curves. Similar effects of sulfate on anodic polarization behavior in deaerated bicarbonate solutions are observed, but a lower concentration of sulfate is necessary to attack the passive film.

A high concentration of sulfate would result in a high conductivity and facilitate the dissolution of surface film, which thus would hinder the formation of protective film on iron in bicar-

Fig.20 Potential-pH ($E\text{--pH}$) diagram of $\text{Fe}\text{--H}_2\text{O}$ system considering bicarbonate species at 25°C

- (1) equilibrium potential line of $\text{Fe}_2\text{O}_3/\text{FeCO}_3$ for $0.02 \text{ mol} \cdot \text{L}^{-1} \text{HCO}_3^-$; (2) equilibrium potential line of Fe/FeCO_3 for $0.02 \text{ mol} \cdot \text{L}^{-1} \text{HCO}_3^-$; (3) equilibrium potential line of $\text{Fe}_2\text{O}_3/\text{FeCO}_3$ for $0.05 \text{ mol} \cdot \text{L}^{-1} \text{HCO}_3^-$; (4) equilibrium potential line of Fe/FeCO_3 for $0.05 \text{ mol} \cdot \text{L}^{-1} \text{HCO}_3^-$

bonate solutions, leading to a higher $i_{\max}$ at a higher $E_{\max}$, a more positive of E_{passive} , and a narrower passive region. Appearance of one or more anodic current peaks in bicarbonate solutions with high concentration of sulfate comes from the reactivation of several dissolution or oxidation reactions. According to Fig.20, reactions (1) to (11) may happen at different electrode potentials. The results show that corrosion rate of iron in bicarbonate solutions can be significantly high if a high concentration of sulfate is present.

5 Conclusions

In the absence of sulfate or in the presence of a low concentration of sulfate in dilute bicarbonate solutions, iron is in passive state with corrosion potential of (-0.225 ± 0.005) V. High electrochemical impedance and low corrosion rate were obtained. No obvious active-passive transition was shown on anodic polarization curves.

In the presence of a high concentration of sulfate in dilute bicarbonate solutions, iron is in active dissolution state with corrosion potential of (-0.790 ± 0.010) V. Low values of electrochemical impedance, high corrosion rate, and typical active-passive transition on anodic polarization curves were observed and related to the sulfate concentrations. Transition of open circuit state from passivity to active dissolution occurs at a lower sulfate concentration in a deaerated solution than in an aerated solutions.

Anodic polarization curves of iron in dilute bicarbonate solutions change with sulfate concentration. In the presence of a high concentration of sulfate, anodic polarization curves exhibit current peaks as the results of the activation of iron by sulfate ions.

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