Study of Ion Adsorption at Passive Iron by Using the Impedance and Photoadmittance Methods

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Abstract—Intensity-modulated photocurrent (photoadmittance) and electrochemical impedance of anodic-oxidized iron electrode in neutral nitrate solutions and in the presence of \( \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Cl}^{-}, \text{C}_6\text{H}_5\text{COO}^- \) (benzoate) are studied. It is shown that the ion adsorption at passive iron affects but slightly the system’s impedance; by contrast, it affects the photocurrent value significantly: when adsorbing, the anions increase the photoeffect, while the cations decrease it. These effects are associated with the potential drop redistribution in the Helmholtz layer and the film. The dissimilar changes of the generation current in the presence of similarly charged ions at their equal concentration evidence their different adsorption activity. The correlation between the generation current and surface-active ion concentration in solution is found. The photoelectrochemical spectroscopy allows evaluating qualitatively the surface-active ion adsorption at the passive iron and judging on the ion adsorption by the dependence of the generation current on the ion concentration.

Key words: adsorption, passive iron electrode, surface-active ions, impedance technique, photoadmittance, generation current

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INTRODUCTION

The passive iron in the electrolyte aqueous solutions is a complicated system whose electrochemical and photoelectrochemical properties were studied rather thoroughly [1–6]. However, the surfactant adsorption at passive iron electrodes practically was not investigated. Our earlier studies demonstrated considerable promise of the using of the electrochemical impedance and photoadmittance methods [7, 8]. In particular, we succeeded in the separating of the impedance of the passive film and the interfacial boundary.

In this work we used the spectroscopy of electrochemical impedance combined with the intensity-modulated photocurrent spectroscopy (the IMPS method) in the studies of the effects of surface-active ions on the processes occurring in the film and at the oxidized iron/solution interface.

The photocurrent at the passive iron was thoroughly studied by Peter [1] and Bockris [2], in order to reveal the passive film composition, structure, and properties, as well as to identify the processes occurring therein. It was found [2] that the photoeffect is determined by the electric field in the film; in particular, the higher the field strength, the higher is the photocurrent. Because the field in a passive film can be varied not only by the applying of the external potential difference, but also by adding surface-active ions to solution, we intended to measure their adsorption by the observing of changes in the photocurrent.

We chose the passive iron in neutral medium as a model system; the solution was buffer-free because buffer additives produce salt films at electrode surfaces [6]. Therefore, we used nitrate solution in which iron has the only passivity region [6]. \( \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Cl}^{-}, \text{C}_6\text{H}_5\text{COO}^- \) (benzoate) were the surfactant ions.

EXPERIMENTAL

The measurements were performed at an Armco-iron disk (4 mm in diameter) in 0.5 M NaNO\(_3\) pH 6.8 deaerated solution at 20°C in the presence of \( \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Cl}^{-}, \text{C}_6\text{H}_5\text{COO}^- \) at a concentration of 0.1 M. Saturated silver chloride electrode was the reference electrode; the electrode potential values are given against this electrode.

The salts used were reagent grade, ultra-high purity grade, or analytical grade; they were further purified by double recrystallization. All solutions were prepared using twice-distilled water.

Prior to experiments, the working electrode was ground by emery paper (the State Standard GOST-10054-75), then polished using AM5/3 and AM1/0 diamond paste, degreased with ethanol, and rinsed with twice-distilled water. The electrode was put into a three-electrode cell filled with the working solution and subjected to electrochemical pretreatment. To this purpose, it was kept at a potential of 1.2 V for 2 min; at –0.9 V, for
The passive iron electrode impedance was measured using a setup [9, 10] comprised a sine signal generator, a PI-50 potentiostat equipped with a programming unit, and a computerized PAR-5204 synchronous analyzer. A sine signal with the 5 mV-amplitude was superimposed on the fixed potential. The real (Re) and imaginary (Im) components of the impedance were recorded by using the PAR-5204 instrument.

During the photoelectrochemical measurements, the electrode was illuminated with monochromatic light from an LMP-11 Helium-Cadmium laser (the quantum energy 2.8 eV). The light intensity was modulated in a periodical mode; to this purpose, the light beam was passed through an ML-102A optical modulator. The photocurrent was measured after achieving its steady-state value at a chosen potential. The light intensity was controlled by measuring a photodiode current. Any phase-frequency distortion introduced by the instrumentation (in particular, the potentiostat) manifested itself at the frequencies below 10 Hz or above 2 kHz; it was removed by the photocurrent complex dividing at the electrode and the photodiode at different frequencies. The photodiode current was preliminarily normalized with respect to its value in the frequency range where no distortion is observed.

All measured signals were set into PC and processed using a specially developed program.1

**EXPERIMENTAL RESULTS**

In Fig. 1 we show frequency spectra of impedance of passive iron electrode in 0.5 M NaNO₃ solutions with and without Ba²⁺ and Cl⁻ surfactant-ions. We see that the introducing of Ba²⁺ and Cl⁻ ions to the solution affects but weakly the electrode impedance. In the presence of Ba²⁺ and Cl⁻ the impedance amplitude |Z| somewhat decreases only at lower frequencies. The chloride mainly affects the phase shift angle θ between the potential and current over the entire frequency range. The negligible effect of the adsorbed ions on the passive electrode impedance can be explained by the film low capacitance as compared with that of the electrical double layer at the passive film/solution interface. Here we assumed that the film capacitance is adsorption-independent.

And yet, these ions (as well as benzoate-ion and Ca²⁺) affect strongly the photocurrent value. In Figs. 2 and 3 we give the complex-plane plots of the impedance frequency spectra (the Nyquist diagrams). They are represented by arcs that differ from semicircles in their shape. The photocurrent low-frequency limit approaches zero (the curves start at the origin), which evidences the absence of a steady-state photocurrent.

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1 The program for the processing of the impedance and photoelectrochemical data was developed by A.L. Klyuev whose contribution is acknowledged.