# IMPEDANCE STUDIES OF THE Pb – $PbSO_4$ SYSTEM IN SULFURIC ACID SOLUTIONS UNDER NONEQUILIBRIUM CONDITIONS

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It had been shown in [1] that during anodic polarization of lead in sulfuric acid, the modulus of impedance of this system decreases at low frequencies with increasing size of the polarizing current, which is in good qualitative agreement with a mechanism where $PbSO_4$ is dissolved and subsequently deposited during the anodic dissolution of lead under these conditions [2]. In the present work, by using the IKS-5 fast-rise instrument to measure complex impedance [3],* we were able to investigate lead passivation at different ac frequencies. Overpotential and the impedance components were recorded as functions of time with three PDP 4-002 recording potentiometers. All measurements were made with a smooth, cylindrical lead electrode in 5.2 M sulfuric acid solution. The procedure of surface preparation was the same as described in [1].

The mutual dependence of the impedance components plotted in Sluyters' coordinates [4] is reported in Fig. 1 for sulfuric acid solution. Higher anodic current densities lead to lower values both of the resistive and the reactive component of impedance.

Under equilibrium conditions, the character of these impedance plots can in certain cases be explained both by slow electrochemical reaction and by slow diffusion of the lead compounds in solution or a slow crystallization step [5]. The corresponding equivalent circuit is presented in Fig. 2. The elements of this circuit are described by the following expressions:

$$R_r=\frac{RT}{nF}\frac{1}{i_0};\quad R_k=\frac{RT}{n^2F^2kc^p p};\quad Z_w=\frac{RT}{n^2F^2c\sqrt{j\omega D}}, \tag{1}$$

where k and p are constants characterizing the crystallization of lead sulfate at the electrode, and c is the concentration of potential-determining species near the electrode.

At the equilibrium potential, c is determined by the solubility of lead sulfate in sulfuric acid solution, and equals the total concentration of lead compounds in the bulk of the solution. In the present work, measurements of the impedance components were made also under nonequilibrium conditions, when an anodic current of known size was flowing through the system. It had been shown in [6], and in a more general form, without adsorption of the species undergoing discharge at the electrode, in [7], that under conditions were the electrochemical system departs from equilibrium, the analytical expression for the impedance, and thus the electrical equivalent circuit, remain the same as under equilibrium conditions, but instead of the concentration of potential-determining species in the bulk of the solution, they now contain the concentration in the layer next to the electrode. Under our conditions, the amount of charge imparted to the electrode during anodic polarization was not higher than 0.02 C, i.e., the average thickness of the lead sulfate deposit (cf. [2]) was not over $10^{-5}$ cm. Thus, the average thickness of the lead sulfate deposit formed on the electrode is negligibly small as compared to the distances from the electrode to which the change in the concentration of reacting species extends into the solution when, under galvanostatic discharge conditions, there is concentration polarization which is governed only by diffusion in the bulk of the solution [8]. Hence one assumes, to a first approximation, that lead sulfate crystallization during the anodic dissolution of the lead electrode can be included into the boundary condition. In this case the concentration of anodic dissolution products near the electrode is obtained from the solution of Fick's equation

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2} \tag{2}$$

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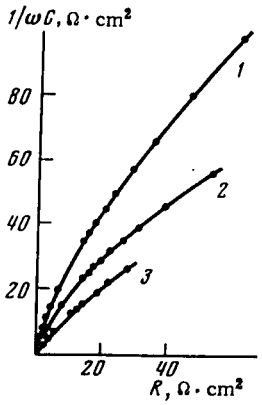


Fig. 1

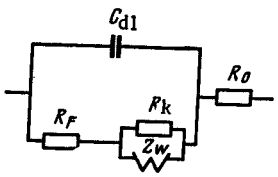


Fig. 2

Fig. 1. The reactive component of impedance as a function of the resistive component in 5.2 M sulfuric acid at anodic current densities of 0 (1), 25 (2), and 50 μA/cm² (3). The frequency range: 0.02 to 10 kHz.

Fig. 2. The probable electric equivalent circuit of the lead/sulfuric acid interface.

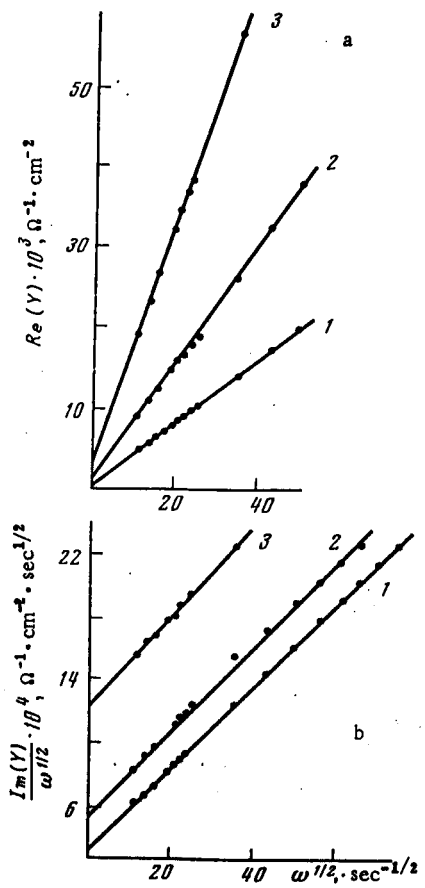


Fig. 3. The frequency dependences of Re(Y) (a) and $Im(Y)/\omega^{1/2}$ (b) for 5.2 M sulfuric acid at anodic current densities of 0 (1), 25 (2), and 50 μA/cm² (3).

with the following starting and boundary conditions:

$$c(x, 0)=c^0 \quad c(\infty, t)=c^0, \tag{3}$$

$$i-k(c-c^0)nF=-nFD\left(\frac{\partial c}{\partial x}\right)_{x=0}, \tag{4}$$

where c is the concentration of lead sulfate in the solution, $c^0$ is the equilibrium concentration of lead sulfate, $i$ is the anodic polarizing current density, and k is the rate constant of lead sulfate crystallization. This problem is readily solved with the use of Laplace transformation. The time dependence of the lead sulfate concentration near the electrode is described by the following expression:

$$c(0, t)=c^0+\frac{i}{nFk}\left[1-\exp\left(\frac{k^2t}{D}\right)\operatorname{erfc}\left(\frac{k\sqrt{t}}{\sqrt{D}}\right)\right]. \tag{5}$$

One can readily show that for $k \to 0$, i.e., when the lead sulfate produced in anodic dissolution is removed into the bulk of the solution only by diffusion, (5) changes into the well-known equation of Sand [8]:

$$c(0, t)=c^0+\frac{2i}{nF\sqrt{D}}\sqrt{t}. \tag{6}$$

To the contrary, when $k^2t/D \gg 1$ and the rate of diffusion of lead sulfate into the bulk of the solution can be neglected as compared to the rate of crystallization,

$$c(0, t)=c^0+\frac{i}{nFk}. \tag{7}$$

In the last expression, the concentration of anodic dissolution products near the electrode does not change with time. The potential of the $Pb-PbSO_4$ system is known to remain practically unchanged at constant anodic current densities which are not very high; it is logical to suggest, therefore, that in this case, Eq. (7) can be used to determine the concentration of anodic lead dissolution products in the layer next to the electrode. Then the impedance of the system under nonequilibrium conditions is obtained (see above) from the expressions for the impedance which were derived under equilibrium conditions when replacing the bulk concentration of potential-determining species by their concentration in the layer next to the electrode.

It had been shown in [5] that in cases where the rate of the charge transfer step is so large that the corresponding resistance, $R_F$, in the equivalent circuit can be neglected, the expressions for the resistive and reactive component, Re(Y) and Im(Y), of admittance $Y=1/(z-R_p)$ (where z is the impedance of the interface and $R_p$ is the solution resistance) are of the form

$$Re(Y)=\frac{1}{R_k}+\frac{n^2F^2c(0, t)\sqrt{D}}{\sqrt{2}RT}\omega^{1/2}, \tag{8}$$

$$\frac{Im(Y)}{\omega^{1/2}}=\frac{n^2F^2c(0, t)\sqrt{D}}{\sqrt{2}RT}+C\ \omega^{1/2} \tag{9}$$

The plots of Re(Y) and $Im(Y)/\omega^{1/2}$ against $\omega^{1/2}$ reported in Fig. 3 show that relations (8) and (9) yield a satisfactory description of the frequency dependence of the admittance components of lead in sulfuric acid. The electric double-layer capacity, $C_{dl}$, determined from the slope of the plots of $Im(Y)/\omega^{1/2}$ against $\omega^{1/2}$ was found to be 21.4, 26.1, and 28.6 $\mu F/cm^2$ for anodic polarizing current densities of 0, 25, and 50 $\mu A/cm^2$, respectively. The slight increase in double-layer capacity with polarizing current apparently can be attributed to the displacement of electrode potential in the positive direction (the electrode potential shifts 20 mV away from the equilibrium value when the anodic current density is 50 $\mu A/cm^2$).

Using Eqs. (8) and (9) one can determine $c(0, t)\sqrt{D}$ from the slope of the plot of Re(Y) against $\omega^{1/2}$ and from the intercepts produced by the plot of $Im(Y)/\omega^{1/2}$ against $\omega^{1/2}$ on the ordinate axis. Assuming a value of $10^{-5}$ $cm^2/sec$ for the diffusion coefficient one finds values of $1\times10^{-8}$, $2\times10^{-8}$, and $4\times10^{-8}$ mole/$cm^3$ for the concentration of potential-determining species near the electrode surface for anodic polarizing current densities of 0, 25, and 50 $\mu A/cm^2$, respectively. The concentration of lead compounds in the layer next to the electrode ($1\times10^{-8}$ mole/$cm^3$) which was determined from the impedance data for equilibrium conditions ($i=0$) in order of magnitude agrees with the data for the solubility of lead sulfate in sulfuric acid of the same concentration ($0.47\times10^{-8}$ mole/$cm^3$ [9]).

The data reported in Fig. 3a were used to determine $1/R_k$ for different polarizing current densities. At current densities of 0, 25, and 50 $\mu A/cm^2$, these values are $0.7\times10^{-3}$, $1.4\times10^{-3}$, and $3.0\times10^{-3}$ $\Omega\cdot cm^2$. With

these data and with relation (1) for $R_k$, the quantities characterizing the reaction order of the dissolution and crystallization of lead sulfate were found: $p = 1$, and its rate $k = 4 \times 10^{-3}$ cm/sec. It follows from relation (7) that quantity k can also be determined from the relation found by us for the concentration of potential-determining ions near the electrode surface as function of polarizing current density. Constant k calculated in this way was found to be $6 \times 10^{-3}$ cm/sec, i.e., in order of magnitude it agrees with the above k value that was determined from circuit element $R_k$.

The data reported in the present work also show that up to current densities corresponding to ignition discharge, the anodic oxidation of lead to $PbSO_4$ in sulfuric acid solution takes place via the solution.

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# MECHANISM OF THE ACCELERATING ACTION OF DICARBOXYLIC ACIDS IN CADMIUM ELECTRODEPOSITION


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The addition of halide and thiocyanate ions and of thiourea is known to lead to an acceleration of electrode reactions involving metal cations. It follows from [1] that any conclusions concerning the nature of the accelerating action of additives will appear sounder when data on the kinetics and mechanism are compared for homogeneous and electrochemical redox reactions. Thus, the mechanism of a number of inner-sphere redox reactions in solution involving electron transfer via bridging ligands has been studied rather well [2]. It is desirable in this connection to extend the range of systems studied previously, and examine the kinetics of metal ion electroreduction in the presence of other known bridging ligands, in particular the dicarboxylate anions. This choice is related to the fact that it becomes possible for us to examine their influence in a homologous series.

The chronopotentiometric and potentiodynamic measurements were performed with the aid of a P-5848 potentiostat, the i vs $\Delta\varphi$ curves were recorded with a KSP-4 recorder, the ordinary ($\varphi$ vs t) and differential ($d\varphi/dt$) chronopotentiograms were recorded with an S1-19B oscillograph. The measurements were made in a thermostatted three-electrode cell (25°C) with separate cathode and anode compartment. Working electrode was the end of a cadmium cylinder, of 0.418 $cm^2$, pressed into teflon. Prior to the measurements it underwent polishing with fine abrasive paper followed by electrochemical reduction of the oxide layers in 0.5 M $H_2SO_4$.

The initial sections of the i vs $\Delta\varphi$ curves (up to 10 mV) were measured with a PO-5122 oscillograph, where the x-scan had been expanded.

The solutions were prepared with twice-distilled water from chemically pure, recrystallized salts. The test solutions were deaerated by passing electrolytic hydrogen.

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