

ADSORPTION OF NITRATES AND NITRITES ON CADMIUM

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The nature of a metal has a much greater influence on the electroreduction of nitrates [1-3] than certain unadsorbed anions, i.e., persulfate, tetrathionate, and ferrocyanide, the reduction kinetics of which are quite thoroughly described by the theory of slow discharge [4-7]. In particular, the electroreduction of NO_3^- on mercury occurs at high negative surface charges [8] where the anion is not adsorbed, since it is known that the latter displays only a weak specific adsorption on mercury near the potential of zero charge [9, 10]. On the other hand, studies on the (100) plane of a silver single crystal and on polycrystalline silver [2, 3] show that nitrates begin to reduce at low surface charges where marked anion adsorption is observed. The nitrates are easily reduced on cadmium to give a single irreversible wave having a half-wave potential of $E_{1/2} = -0.89$ to -0.97 V (SCE) close to the electrode's potential of zero charge. Under these conditions, at -0.85 to -1.6 V (SCE) and a pH of > 3 , the only nitrate reduction product on cadmium was nitrite [1].

In this connection, we thought it of interest to elucidate the electroreductive adsorption capability of cadmium with regard to nitrates and nitrites. This was done by measuring the impedance of a cadmium electrode in 0.01 N KF containing 0.001, 0.002, and 0.005 N KNO_3 at pH 4. The measurements were made with a R-5021 ac bridge connected in series. Constant-current polarization was accomplished with the aid of a P-5827 potentiostat. The electrodes were cadmium with a purity of 99.9997% (KD-000). Preparation of the metal surface included chemical polishing by a method described in [11] and a 1.5-h cathodic polarization at -1.03 V (SCE) in a KF solution free of atmospheric oxygen. All the reagents used were recrystallized and cp, and the solutions were prepared with doubly-distilled water. The electrode potentials were measured vs a saturated calomel electrode.

Figure 1 presents polarization curves for cadmium taken between -0.85 and -1.6 V in the presence of NO_3^- . The nitrate electroreduction was characterized by a limiting current at potentials more negative than

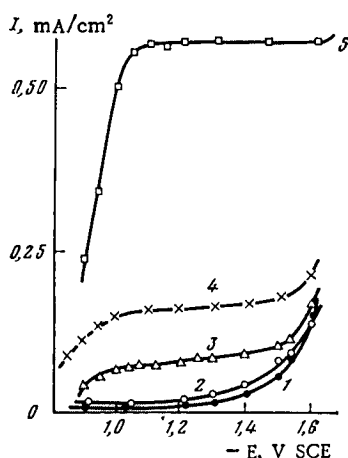


Fig. 1. Polarization curves for cadmium in the following solutions (concentrations given in normality): 1) 0.01 KF (pH 6); 2) 0.01 KF + HNO_3 (pH 4); 3) 0.01 KF + 0.001 KNO_3 (pH 4); 4) 0.01 KF + 0.002 KNO_3 (pH 4); 5) 0.01 KF + 0.005 KNO_3 (pH 4).

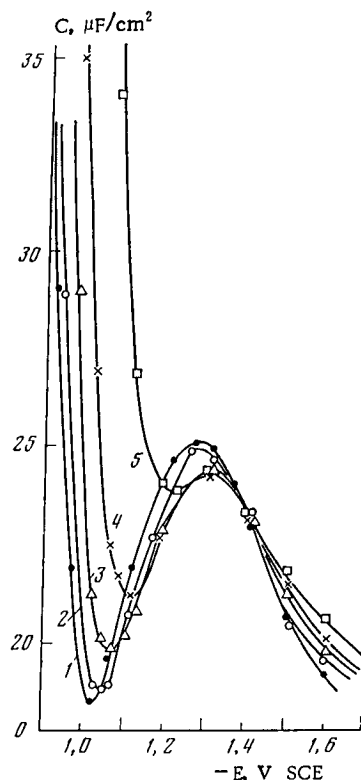


Fig. 2

Fig. 2. The C vs E curves obtained for a cadmium electrode in the same solutions as those given in Fig. 1.

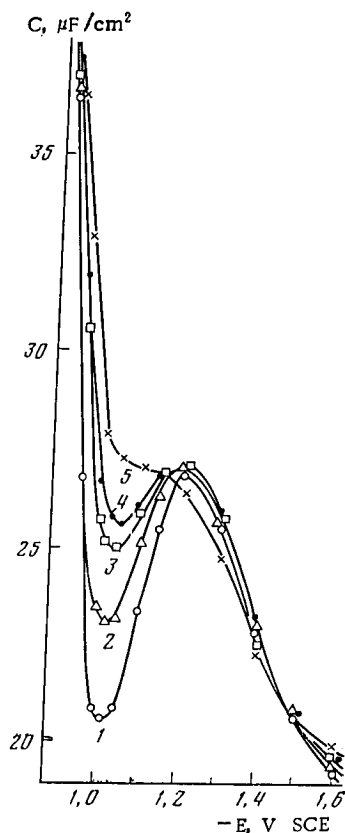


Fig. 3

Fig. 3. The C vs E curves obtained for a cadmium electrode at various NaNO_2 concentrations: 1) 0.01; 2) 0.02; 3) 0.03; 4) 0.04; 5) 0.07 N.

-1.0 V. This was confirmed by a linear relationship between the limiting currents and the appropriate potassium nitrate concentrations.

Measurements of the capacitance constituent (C) of the impedance as a function of the cadmium electrode potential (E) were carried out at the potential ranges corresponding to the limiting currents. At a frequency range of 80 to 510 Hz the relation of the capacitance to frequency for 0.01 N KF at -0.95 to -1.4 V was practically indistinguishable from that for the same solution with potassium nitrate additions. It should be noted that at these frequencies no dependence of the active impedance components on electrode potential was observed at the above KNO_3 concentrations. Rather, these components were virtually equal to the solution resistance. Consequently, under our nitrate reduction conditions, the capacitance found for the impedance component is thought to be identical with the double-layer capacitance at a selected frequency of 210 Hz.

The C vs E curves obtained for the polished cadmium electrode are given in Fig. 2. Differential capacitance curves for various concentrations of background KF solutions were no different from those given in the literature [12]. As is evident from Fig. 2, the addition of potassium nitrate shifts the minimum capacitance potential in the negative direction, with the amount of shift increasing with a rise in KNO_3 concentration from 0.001 to 0.005 N. The potential reaches 180 mV at 0.005 N. At this concentration the capacitance minimum almost disappears, whereas a minimum is sharply defined even in the more concentrated KF solutions.

The fact that increasing the potassium nitrate concentration not only shifts the potentials at the minima and the more positive parts of the differential capacitance curves in the negative direction but also increases the capacitance at such minima indicates nitrates or their reduction products to be surface-active. Since the only nitrate reduction product is nitrite at pH 4 and potentials more positive than -1.6 V [1], we thought it of interest to elucidate the question of nitrite-ion adsorption. Figure 3 shows C vs E curves at various NaNO_2

concentrations. At potentials more positive than -1.6 V the cadmium polarized well and the current did not exceed around 1 microampere per cm^2 of apparent electrode surface. As is evident from Fig. 3, increasing the sodium nitrite concentration produces slight shifts of the minima in the negative direction and causes that for the 0.07 N solution to disappear. The capacitance at the minimum, which corresponds to the maximum double-layer diffusivity, is somewhat higher in NaNO_2 than in KF solutions of similar concentrations [12].

These C vs E curves thus indicate a small specific adsorption of nitrite on cadmium. This was confirmed by analyzing the dependence of the double-layer capacitance at the potential of the (C) minima and the diffusion-layer capacitance (C_d) by a method proposed in [13] for a surface-inactive electrolyte. Averages of slope cotangents in coordinates of $1/C$ vs $1/C_d$ showed that for sodium nitrite to be 1.7 to 2 and for KF to be 1.2 to 1.3 [12]. If we assume, as was done earlier for a silver electrode [14], that the increase in the slope of the $1/C$ vs $1/C_d$ curve is due to weak, specific anion adsorption, then the above data are also indicative of a small, specific adsorption of nitrite on cadmium.

Thus, adsorption of both NO_3^- and NO_2^- takes place upon reduction of KNO_3 on a cadmium electrode, but the NO_3^- adsorption is much greater. This is probably why the electroreduction of nitrates on cadmium proceeds at a lower surface charge than on mercury.

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