SHORT COMMUNICATIONS

Admittance Behavior of Electrode Reaction of Water at a Dropping Mercury Electrode

Kiyoshi MATSUDA, Katsuo TAKAHASHI, and Reita TAMAMUSHI
The Institute of Physical and Chemical Research, Wako-shi, Saitama
(Received June 4, 1971)

The DC and AC polarographic behavior of dropping mercury electrode (DME)/dilute aqueous electrolyte solution systems was studied in the potential region from zero to ± 5V. In AC polarography, conductance and susceptance components of the cell admittance were measured by a phase-sensitive AC polarograph constructed in our laboratory.[1]

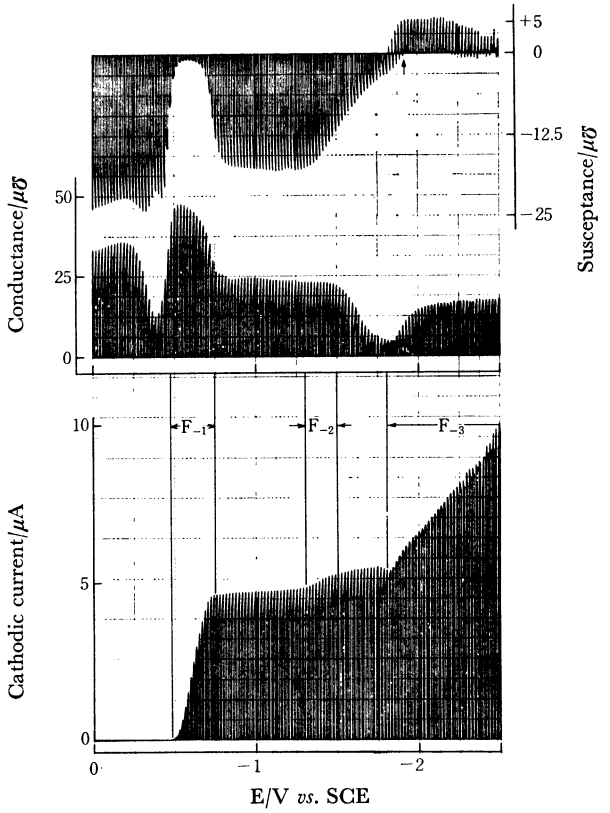

Fig. 1. DC polarogram, conductance-potential and susceptance-potential curves of a DME/0.5 mM $Cd(NO_3)_2$ system in negative potential region at 25°C, the conductance and susceptance being measured at 31 Hz.

Figure 1 shows typical DC and AC polarograms of a DME/0.5 mM $Cd(NO_3)_2$ system (pH=4—5) in the negative potential region. The reduction waves of cadmium and hydrogen ions were observed on the DC polarogram in potential regions F_{-1} and F_{-2}, respectively. The cathodic current increased almost linearly with potential in the more negative potential region F_{-3}. This increase in cathodic current is attributed to the reduction of water.[2]

In the potential region F_{-3}, a remarkable change in the direction of the susceptance vector was observed as indicated by an arrow in Fig. 1, when the admittance was measured at relatively low frequencies. This type of anomaly in the susceptance component was also observed in solutions of various cations such as H^+, Na^+, K^+, Ag^+, Hg_2^{2+}, Tl^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. Exceptions were solutions containing Mg^{2+}, NH_4^+, $(CH_3)_4N^+$ and $HgCl_2$; in case of Mg^{2+} the DC reduction wave of Mg^{2+} and that of water overlapped, and in NH_4^+-, $(CH_3)_4N^+$- and $HgCl_2$-systems the DC and AC polarograms were strongly disturbed in the potential region F_{-3}, which prevented us from making further analysis of susceptance components.

The analysis of the frequency dispersion suggested the contribution of some inductive components to the electrical equivalent circuit of the cell system in the potential region F_{-3}. The admittance behavior of this nature has been reported by Epelboin and his coworkers[3] in the electrochemical dissolution of iron and nickel electrodes. In case of cathodic processes, the possibility of the contribution of inductive components to the faradaic admittance has been suggested theoretically for hydrogen evolution.[4] It seems, however, that this paper provides the first experimental evidence for the contribution of an inductive susceptance to the equivalent circuit of the cathodic reduction of water at a DME.

In solutions containing hydroxide and thiocyanate ions, inductive susceptances were also detected in the positive potential region where anodic currents are observed. Details of the experimental results and the theoretical consideration will be reported elsewhere.

1) K. Matsuda, K. Takahashi, and R. Tamamushi, *Sci. Papers Inst. Phys. Chem. Res.*, **64**, 62 (1970).

2) D. Ilkovič, *Coll. Czech. Chem. Commun.*, **4**, 480 (1932); T. Okada and S. Yoshizawa, *Kogyo Kagaku Zasshi*, **49**, 183 (1964).

3) For example: I. Epelboin, M. Keddam and J.-C. Lestrade, *Revue Générale de l'Electricité*, **76**, 777 (1967); R. Wiart, *Oberfläch-Surface*, **9**, 213, 241, 275 (1968); I. Epelboin and M. Keddam, *J. Electrochem. Soc.*, **117**, 1052 (1970).

4) H. Gerischer and W. Mehl, *Z. Elektrochem.*, **59**, 1049 (1955); I. M. Novosel'skii and N. N. Gudina, *Elektrokhim.*, **5**, 820 (1969).