BRIEF COMMUNICATIONS

IMPEDANCE OF THE SYSTEM: METAL IN THE SOLUTION OF ITS OWN IONS

E. A. Ukshe and B. M. Grafov

UDC 541.13

The system "metal in the solution of its own ions" occupies a special place in the theory of electrochemical impedance. On the one hand, this system lacks the processes of adsorption and diffusion of the reduced form of the electrochemically active substance, which substantially simplifies the calculations. On the other hand, the ionization and discharge of metals in aqueous solutions and molten salts usually occur at high rates, and the impedance method is of prime importance in kinetic studies of these processes.

We shall consider the reaction

$$M^{n+}+ne \rightleftharpoons M \quad (1)$$

under the following simplifying assumptions: 1) we shall assume that the probability of reaction (1) to occur is the same at any point of the electrode surface, while the incorporation of an atom of M into the crystal lattice and the escape from it occur without any hindrance; 2) we shall assume that as reaction (1) proceeds, the acquisition and loss of all n electrons occur simultaneously, i.e., that long-lived metal ions having an intermediate degree of oxidation do not exist; 3) we shall assume that the current in the electrolyte is carried by the ions of an indifferent base electrolyte.

The electrode impedance can be calculated by the method of multiterminal equivalent networks using the Onsager theorem as proposed in [1, 2]. In the following we shall use the graphical presentation of processes on the electrode which is shown in Fig. 1. Symbol v here denotes the state of the ion in the bulk of the electrolyte; symbol S denotes its state in the bulk of the electrolyte near the electrode surface; symbol *a* denotes the state of the adsorbed ion; symbol m denotes the state of the atom in the crystal lattice of the metal (or in a liquid metallic phase). Accordingly, line vS corresponds to the diffusion of M^{n+} ions; line Sm corresponds to the discharge of ions existing in the "bulk" state; *a*m corresponds to the discharge of adsorbed ions, and S*a* corresponds to the process of adsorption. Thus, it is assumed here that in the general case (Fig. 1a), reaction (1) can proceed via two pathways: through the adsorbed state, and through the "bulk" state near the electrode surface. In the following, processes Sm, *a*m, and S*a* will be denoted by the indices 1, 2, and 3, respectively.

The total discharge flow j must be composed of the discharge flow along pathway Sm (j_1) and of that along pathway *a*m (j_2), i.e.,

$$j=j_1+j_2. \quad (2)$$

The total amount of adsorbed metal ions can in this case be presented in the form

$$A=B_3+B_2, \quad (3)$$

where B_2 is the amount of ions having passed into the adsorbed state via the pathway *a*m, i.e., at the expense of ionization of metal atoms, while B_3 is the amount of ions having passed into the adsorbed state from the electrolyte (i.e., via the pathway S*a*). The flows of the corresponding processes are

$$j_2=dB_2/dt; \quad j_3=-dB_3/dt, \quad (4)$$

Institute of New Chemical Problems, Academy of Sciences of the USSR, Moscow. Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 9, No. 11, pp. 1624-1630, November, 1973. Original article submitted June 21, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

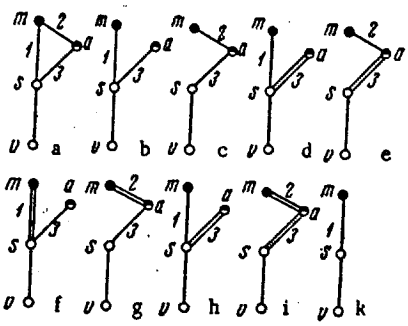


Fig. 1.

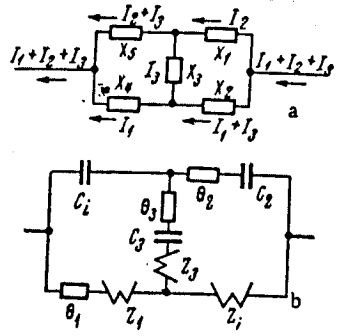


Fig. 2.

Fig. 1. Graphical presentation of the electrochemical reaction $M \rightleftarrows M^{n+}$. A double line signifies that there is equilibrium with respect to the process involved.

Fig. 2. Equivalent circuits for the short-circuited six-terminal network. $C_1=[(\xi-1)/\xi]C_0$; $C_2=[(\xi-1)^2/\xi]C_0$; $C_3=-(\xi-1)C_0$; $Z_1=(1/\xi)Z_W$; $Z_1=[(\xi-1)/\xi]Z_W$; $Z_3=-[(\xi-1)/\xi^2]Z_W$.

where t is the time, while the direction of flow from the metal to the electrolyte is taken as the positive one. It follows from (3) and (4) that

$$dA/dt=j_2-j_3. \tag{5}$$

The current flowing across the metal/electrolyte interface can be presented in the form

$$I=I_1+\frac{dQ}{dt} \tag{6}$$

where $I_1=nFj_1$ is the current corresponding to flow j_1, while Q is the total electrode charge [3]. Assuming that deviations from equilibrium are small and writing the total charge in the form of the function

$$Q=Q(\varphi, B_2, B_3), \tag{7}$$

we obtain

$$I=nFj_1+Q_\varphi\frac{d\varphi}{dt}+Q_{B_2}\frac{dB_2}{dt}+Q_{B_3}\frac{dB_3}{dt}, \tag{8}$$

where Q_φ, Q_{B_2}, and Q_{B_3} are partial derivatives of the form $(\partial Q/\partial\varphi)_{B_2,\ B_3}$, etc. Equation (8) corresponds to presenting the total current in the form of the sum

$$I=I_c+I_1+I_2+I_3, \tag{9}$$

where

$$\begin{aligned} I_c&=Q_\varphi(d\varphi/dt) \quad I_1=nFj_1\\ I_2&=Q_{B_2}(dB_2/dt)=j_2Q_{B_2}\\ I_3&=Q_{B_3}(dB_3/dt)=-j_3Q_{B_3}. \end{aligned} \tag{10}$$

Current I_C represents the charging current of the electric double layer and is independent of the other currents. Currents I_1, I_2, and I_3 are mutually connected. The electrical equivalent circuit of the electrode being studied must contain, therefore, the double-layer capacitance $C_d=C_\varphi$ and, in parallel with this, the impedance of the electrochemical process, the determination of which is the aim of the present work. In order to calculate this impedance we shall write down the flows corresponding to processes 1, 2, and 3 as functions of potential, bulk concentration of M^{n+} ions (c), and their adsorbed quantity (A). Evidently,

$$\begin{aligned} j_1&=j_1(\varphi, c)\\ j_2&=j_2(\varphi, A)\\ j_3&=j_3(\varphi, c, A). \end{aligned} \tag{11}$$

At small deviations from equilibrium we find for the complex amplitudes of the harmonic perturbations δj, $\delta\varphi$, δc, and δA [4]:

$$\begin{aligned} \delta j_1&=j_{1\varphi}\delta\varphi+j_{1c}\delta c\\ \delta j_2&=j_{2\varphi}\delta\varphi+j_{2A}\delta A\\ \delta j_3&=j_{3\varphi}\delta\varphi+j_{3c}\delta c+j_{3A}\delta A, \end{aligned} \tag{12}$$

where $j_{1\varphi}$, j_{1c}, etc. are the corresponding partial derivatives.

Since the total amount of charge being transferred across the electrode/electrolyte interface must equal nF, independently of the reaction pathway, one can write, with due regard to signs,

$$Q_{B_1}-Q_{B_3}=nF. \tag{13}$$

Thus, if we designate

$$Q_{B_1}/nF=-\xi, \tag{14}$$

we obtain

$$Q_{B_3}/nF=-(\xi-1). \tag{15}$$

Moreover, the following relations will hold for the harmonic perturbations [4]:

$$i\omega\cdot\delta A=\delta j_2-\delta j_3 \tag{16}$$

and

$$\sqrt{i\omega D}\cdot\delta_c=\delta j_1+\delta j_3, \tag{17}$$

where $i=\sqrt{-1}$. Putting (14) – (17) into (12) and using Eq. (10) we obtain

$$\begin{aligned}
\delta\varphi&=\left[\frac{1}{nFj_{1\varphi}}-\frac{j_{1c}}{nFj_{1\varphi}\sqrt{i\omega D}}\right]\delta I_1+\frac{-j_{1c}}{nF\xi j_{1\varphi}\sqrt{i\omega D}}\delta I_3\\
\delta\varphi&=\left[\frac{-1}{nFj_{2\varphi}(\xi-1)}+\frac{j_{2A}}{i\omega j_{2\varphi}nF(\xi-1)}\right]\delta I_2+\frac{j_{2A}}{i\omega j_{2\varphi}nF\xi}\delta I_3\\
\delta\varphi&=\frac{-j_{3c}}{nFj_{3\varphi}\sqrt{i\omega D}}\delta I_1+\frac{j_{3A}}{i\omega j_{3\varphi}nF(\xi-1)}\delta I_2+\left[\frac{1}{nFj_{3\varphi}\xi}+\frac{j_{3A}}{i\omega j_{3\varphi}nF\xi}-\frac{j_{3c}}{nFj_{3\varphi}\xi\sqrt{i\omega D}}\right]\delta I_3.
\end{aligned} \tag{18}$$

The corresponding ac circuit represents [1, 2] the short-circuited six-terminal network described by the transmission equations:

$$\begin{aligned}
\delta\varphi&=Z_{11}\delta I_1+Z_{12}\delta I_2+Z_{13}\delta I_3\\
\delta\varphi&=Z_{21}\delta I_1+Z_{22}\delta I_2+Z_{23}\delta I_3\\
\delta\varphi&=Z_{31}\delta I_1+Z_{32}\delta I_2+Z_{33}\delta I_3.
\end{aligned} \tag{19}$$

By comparing the systems of equations (18) and (19) one can readily obtain expressions for the diagonal (Z_{11}, Z_{22}, Z_{33}) and crossed (Z_{12}, Z_{13}, Z_{23}, etc.) impedance coefficients:

$$\begin{aligned}
Z_{11}&=\frac{1}{nFj_{1\varphi}}-\frac{j_{1c}}{nFj_{1\varphi}\sqrt{i\omega D}}\\
Z_{22}&=\frac{-1}{nFj_{2\varphi}(\xi-1)}+\frac{j_{2A}}{i\omega j_{2\varphi}nF(\xi-1)}\\
Z_{33}&=\frac{1}{nFj_{3\varphi}\xi}+\frac{j_{3A}}{i\omega j_{3\varphi}nF\xi}-\frac{j_{3c}}{nFj_{3\varphi}\xi\sqrt{i\omega D}}
\end{aligned} \tag{20}$$

$$\begin{aligned}
&Z_{12}=Z_{21}=0\\
&Z_{13}=\frac{-j_{1c}}{nFj_{1\varphi}\xi\sqrt{i\omega D}}=Z_{31}=\frac{-j_{3c}}{nFj_{3\varphi}\sqrt{i\omega D}}\\
&Z_{23}=\frac{j_{2A}}{i\omega j_{2\varphi}nF\xi}=Z_{32}=\frac{j_{3A}}{i\omega j_{3\varphi}nF(\xi-1)}.
\end{aligned} \tag{21}$$

The last three equations have been written while taking into account the Onsager theorem concerning equality of the crossed coefficients.

The equivalent circuit for the six-terminal network being discussed is shown in Fig. 2a. The elements of this circuit are expressed through the impedance coefficients in the following manner:

$$\begin{aligned}
X_1&=Z_{22}-Z_{23}=\theta_2+\xi Z_c/(\xi-1)^2\\
X_2&=Z_{13}=Z_w/\xi\\
X_3&=Z_{33}-Z_{13}-Z_{23}=\theta_3-(\xi-1)Z_w/\xi^2-Z_c/(\xi-1)\\
X_4&=Z_{11}-Z_{13}=\theta_1+(\xi-1)Z_w/\xi\\
X_5&=Z_{23}=\xi Z_c/(\xi-1).
\end{aligned} \tag{22}$$

In writing down Eqs. (22) the equalities

$$j_{2\varphi}/j_{2A}=(\xi-1)j_{3\varphi}/\xi j_{3A}$$

$$j_{3c}/j_{3\varphi}=j_{1c}/\xi j_{1\varphi} \tag{23}$$

following from the Onsager relations (21) were taken into account, and the notation

$$Z_c=j_{3A}/i\omega j_{3\varphi}nF\xi;\quad C_0=\xi nFj_{3\varphi}/j_{3A},$$
$$Z_w=-j_{1c}/nFj_{1\varphi}\sqrt{i\omega D},$$
$$\theta_1=(nFj_{1\varphi})^{-1};\quad \theta_2=[-nFj_{2\varphi}(\xi-1)]^{-1};\quad \theta_3=(nFj_{3\varphi}\xi)^{-1} \tag{24}$$

was introduced. The input impedance of the circuit shown in Fig. 2b can be calculated by using the triangle-star conversion known from the theory of linear circuits [5]. It is

$$Z_{in}=\frac{\theta_1\theta_2\theta_3+\theta_1Z_c\left[\theta_2+\frac{\xi^2\theta_3}{(\xi-1)^2}\right]+\theta_2Z_w\left[\frac{\theta_1}{\xi^2}+\theta_3\right]+Z_cZ_w\left[\frac{\theta_1}{(\xi-1)^2}+\theta_2+\frac{\xi^2\theta_3}{(\xi-1)^2}\right]}{\theta_1\theta_2+\theta_1\theta_3+\theta_2\theta_3+Z_c\left[\frac{\theta_1}{(\xi-1)^2}+\theta_2+\frac{\xi^2\theta_3}{(\xi-1)^2}\right]+Z_w\left[\frac{\theta_1}{\xi^2}+\frac{(\xi-1)^2}{\xi^2}\theta_2+\theta_3\right]}. \tag{25}$$

Equation (25) and the circuit of Fig. 2b provide the analytical and symbolic description, respectively, of the impedance of a metallic electrode in the most general case. A whole series of simpler circuits can be derived from these representations; some of these have already been described in the literature, and some have not been discussed so far. We shall consider these circuits

1. The case where discharge of an ion can only occur from the "bulk" state, i.e., $\theta_2=\infty$ (Fig. 1b). According to (25),

$$Z_{in}=\frac{\theta_1\theta_3+\theta_1Z_c+Z_cZ_w+Z_w(\theta_1\xi^{-2}+\theta_3)}{\theta_1+\theta_3+Z_c+(\xi-1)^2\xi^{-2}Z_w}. \tag{26}$$

The corresponding equivalent circuit is shown in Fig. 3a, where

$$C_A=(\xi-1)^2C_\varphi/\xi^2 \tag{27}$$

$$R_l=\frac{\xi(\theta_1+\xi\theta_3)}{(\xi-1)^2};\quad R_n=\frac{\xi\theta_1}{\xi-1};\quad R_m=-\frac{\theta_1}{\xi-1}. \tag{28}$$

2. The case where discharge can only occur from the adsorbed state, i.e., $\theta_1=\infty$ (Fig. 1c). Then, according to (25),

$$Z_{in}=\frac{\theta_2\theta_3+Z_cZ_w(\xi-1)^{-2}+\theta_2Z_w\xi^{-2}+Z_c[\theta_2+\theta_3\xi^2(\xi-1)^{-2}]}{\theta_2+\theta_3+(\xi-1)^{-2}Z_c+\xi^{-2}Z_w}. \tag{29}$$

The corresponding equivalent circuit is the same as in the preceding case (Fig. 3a), but with other values for the parameters:

$$R_l=\xi\theta_2;\quad R_n=\xi(\xi-1)\left(\theta_2+\frac{\xi}{\xi-1}\theta_3\right);\quad R_m=-(\xi-1)\theta_2. \tag{30}$$

We see here that different mechanisms of an electrode reaction lead to the same equivalent circuit, the difference being confined to the character of the link between the active resistances.

3. It is easy to verify that the schematic of Fig. 3a will be retained under the conditions $\theta_2=\infty$, $\theta_3=0$ (Fig. 1d) or $\theta_1=\infty$, $\theta_3=0$ (Fig. 1e), i.e., at an infinitely large rate of the elementary act of adsorption. This means, in fact, that adsorption equilibrium is retained (the adsorption isotherm holds) when alternating current is passed through the electrode. When $\theta_2=\infty$ and $\theta_3=0$,

$$Z_{in}=\frac{Z_cZ_w+\xi^{-2}\theta_1Z_w+\theta_1Z_c}{\theta_1+Z_c+(\xi-1)^2\xi^{-2}Z_w}, \tag{31}$$

$$R_m=-\frac{\theta_1}{\xi-1};\quad R_l=\frac{\xi\theta_1}{(\xi-1)^2};\quad R_n=\frac{\xi\theta_1}{\xi-1}. \tag{32}$$

When $\theta_1=\infty$ and $\theta_3=0$,

$$Z_{in}=\frac{Z_cZ_w+(\xi-1)^2\xi^{-2}\theta_2Z_w+(\xi-1)^2\theta_2Z_c}{(\xi-1)^2\theta_2+Z_c+(\xi-1)^2\xi^{-2}Z_w} \tag{33}$$

$$R_m=-(\xi-1)\theta_2;\ R_l=\xi\theta_2;\ R_n=\xi(\xi-1)\theta_2. \tag{34}$$

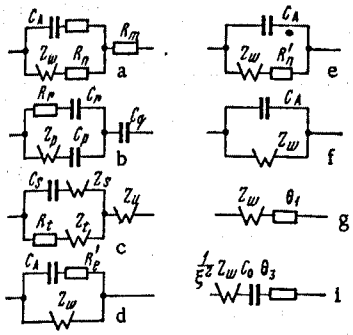


Fig. 3. Equivalent circuits of the processes pictured in Fig. 1.

It is easy to verify that Eqs. (31) and (33), apart from the circuit of Fig. 3a, can also describe the circuits of Fig. 3b and 3c. One then has, in the case $\theta_2=\infty$ and $\theta_3=0$,

$$R_r=\theta_1/(\xi-1)^2;\quad Z_p=Z_w/\xi^2;$$
$$C_p=-(\xi-1)C_0;\quad C_r=-(\xi-1)^2C_0/\xi;\quad C_q=(\xi-1)C_0/\xi \tag{35}$$

and

$$R_t=\theta_1;\quad C_s=C_0;$$
$$Z_s=-(\xi-1)Z_w/\xi^2;\quad Z_t=(\xi-1)Z_w/\xi;\quad Z_u=Z_w/\xi. \tag{36}$$

In the case $\theta_1=\infty$ and $\theta_3=0$ one has, similarly,

$$R_r=\theta_2;\quad Z_p=Z_w/\xi^2;$$
$$C_p=-(\xi-1)C_0;\quad C_r=-(\xi-1)^2C_0/\xi;\quad C_q=(\xi-1)C_0/\xi \tag{37}$$

and

$$R_t=(\xi-1)^2\theta_2;\quad C_s=C_0;$$
$$Z_s=-(\xi-1)Z_w/\xi^2;\quad Z_t=(\xi-1)Z_w/\xi;\quad Z_u=Z_w/\xi. \tag{38}$$

It is typical that the corresponding pairs of circuits for $\theta_1=\infty$ and $\theta_2=\infty$ only differ in the coefficients determining the active resistances. The situation that the same equation, (31) or (33), can be expressed by several equivalent circuits is typical for the theory of linear circuits [5], and should not lead to misunderstandings, inasmuch as from the links which are provided by Eqs. (32), (34), and (35)-(38), one can find from the circuit parameters the same kinetic and thermodynamic coefficients, which unambiguously belong to the given electrochemical system. The choice of one system or another is governed by considerations about the convenience of the calculations or about the construction of analog devices.

4. Further simplification of the equivalent circuit is attained under the condition $\theta_2=\infty$, $\theta_1=0$ (Fig. 1f), or $\theta_2=0$, $\theta_1=\infty$ (Fig. 1g), but at finite values of θ_3, i.e., with a finite adsorption rate. In the first case ($\theta_2=\infty$, $\theta_1=0$),

$$Z_{in}=\frac{Z_cZ_w+\theta_3Z_w}{\theta_3+Z_c+(\xi-1)^2\xi^{-2}Z_w}; \tag{39}$$

the corresponding equivalent circuit is given in Fig. 3d. Its elements are Z_W, C_A, and

$$R_t'=\xi^2\theta_3/(\xi-1)^2. \tag{40}$$

In the second case ($\theta_2=0$ and $\theta_1=\infty$)

$$Z_{in}=\frac{Z_cZ_w+\xi^2\theta_3Z_c}{(\xi-1)^2\theta_3+Z_c+(\xi-1)^2\xi^{-2}Z_w}. \tag{41}$$

The equivalent circuit is shown in Fig. 3e, and includes the elements Z_W, C_A, and

$$R_n'=\xi^2\theta_3. \tag{42}$$

In contrast to the earlier cases, one now can distinguish the discharge mechanisms via the "bulk" and adsorbed state. We note that for the circuit of Fig. 3e, the adsorption effect only becomes manifest in the appearance of the capacitance C_A, which in the measurements appears added to the double-layer capacitance. In this case the resistance R_n' characterizes the adsorption kinetics rather than the discharge kinetics.

5. If both the discharge rate and the adsorption rate are infinitely large, i.e., if $\theta_2=\infty$ and $\theta_1=\theta_3=0$ (Fig. 1h) or $\theta_1=\infty$ and $\theta_2=\theta_3=0$ (Fig. 1i), then one has in both cases

$$Z_{in}=\frac{Z_cZ_w}{Z_c+(\xi-1)^2\xi^{-2}Z_w}, \tag{43}$$

while the equivalent circuit has the form shown in Fig. 3f. The two discharge mechanisms become again indistinguishable here. The role of adsorption reduces to that of raising the total measured capacitance C_A+C_d relative to the capacitance that can be measured in the pure base electrolyte.

6. We shall, at last, consider two cases leading to generally known results. With $\theta_2=\theta_3=\infty$ and finite θ_1, i.e., in the absence of adsorption (Fig. 1k),

$$Z_{in}=\theta_1+Z_w, \tag{44}$$

which corresponds to Érshler's circuit [6] (Fig. 3g). With $\theta_1=\theta_2=\infty$ and finite θ_3, i.e., for the ideally polarizable electrode in the presence of adsorption,

$$Z_{in}=\theta_3+Z_c+\frac{1}{\xi^2}Z_w, \tag{45}$$

which corresponds to the circuit of Fig. 3i, and coincides with the impedance found by Frumkin and Melik-Gaikazyan [7] for the adsorption of substances not involved in the electrochemical reaction.

The authors thank Academician A. N. Frumkin and D. I. Leikis for discussing the results of the present work.

LITERATURE CITED

1. B. M. Grafov and É. V. Pekar, Élektrokhimiya, 6, 547 (1970); 8, 8 (1972).
2. B. M. Grafov and É. V. Pekar, J. Electroanal. Chem., 31, 137 (1971).
3. A. N. Frumkin, O. A. Petrii, and B. B. Damaskin, Élektrokhimiya, 5, 614 (1970).
4. E. A. Ukshe, Synthesis of Electrochemical ac Circuits, Article deposited at VINITI, No. 1410-70
5. G. I. Atabekov, Fundamentals of Circuit Theory [in Russian], Énergiya, Moscow (1969).
6. B. V. Érshler, Zh. Fiz. Khim., 22, 683 (1948).
7. A. N. Frumkin and V. I. Melik-Gaikazyan, Dokl. Akad. Nauk SSSR, 77, 855 (1951).