A. N. BARABOSHKIN, L. T. KOSIKHIN, N. A. SALTYKOVA

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. N. BARABOSHKIN, L. T. KOSIKHIN, N. A. SALTYKOVA

EXCHANGE CURRENTS IN PURE MOLTEN SILVER NITRATE

(Presented by Academician A. N. Frumkin, July 2, 1964)

Only a small number of works have been devoted to the study of the electrochemical kinetics proper of electrode processes in molten salts. Ion discharge and the deposition—dissolution of metals in these media at high temperatures are very rapid processes, which creates considerable difficulties in detecting and measuring the activation overvoltage. In dilute solutions it is always masked by concentration polarization. This can be partially avoided by using the so-called relaxation methods, in which measurements are carried out under nonstationary conditions, for example the methods of faradaic impedance ([1–4]), double pulse ([5]), and voltage step ([5]).

Numerical data on exchange currents in pure molten salts are practically entirely lacking. In them there is no concentration polarization, and the measured polarization includes only the activation overvoltage and the voltage drop in the electrolyte. Nevertheless, despite the high electrical conductivity of molten salts, it has still not been possible to create a cell in which the ohmic resistance of the electrolyte between the reference electrode and the electrode under investigation would not be many times greater than the resistance of the electrochemical reaction ([6–8]).

In one of such cells we used a cylindrical electrode. More favorable ratios between the ohmic resistance and the resistance of the electrochemical reaction are obtained for spherical or hemispherical microelectrodes. It is easy to show that for a hemispherical electrode the ohmic resistance is

$$R_{\text{om}} = {}^{1}/_{2\pi r\chi}, \tag{1}$$

where r is the radius of the sphere, and χ is the specific electrical conductivity of the melt.

The resistance of the electrochemical reaction at sufficiently small overvoltages ($\eta \ll RT/zF$) can be given by the expression ([9])

$$R_{\text{reak}} = RT/2\pi r^2 zFi_0. \tag{2}$$

Fig. 1. Typical overvoltage-time curve $\dot{\eta} = \operatorname{tg}\varphi;\ \dot{\eta}_1 = \operatorname{tg}\varphi_1$

Figure 1: Fig. 1. Typical overvoltage-time curve $\dot{\eta} = \operatorname{tg}\varphi;\ \dot{\eta}_1 = \operatorname{tg}\varphi_1$

It is evident that the activation overvoltage can be detected and measured only when

$$R_{\text{reak}} \gg R_{\text{om}}, \tag{3}$$

i.e., when

$$ri_0 \ll 8.62 \cdot 10^{-5} T\chi/z. \tag{4}$$

Usually $T\chi/z = 500\text{–}3000$ deg · mol/ohm · cm · g-eq. Consequently, conditions favorable for measurements will be obtained when

$$ri_0 \ll 0.05 - 0.3 \text{ A/cm}. \tag{4a}$$

If the exchange currents are high, then the dimensions of the electrode must be very small. For $i_0 = 1000$ A/cm^2 the radius of the sphere must be on the order of 10^{-4} cm. It is apparently difficult to fabricate such microelectrodes artificially. However, crystallites of precisely such dimensions can be deposited on the cathode in the initial period of electrolysis. In one of our in studies (10), the formation of silver crystal nuclei on a platinum cathode during electrolysis at constant current was investigated for solutions of $AgNO_3$ in a molten eutectic mixture of sodium and potassium nitrates. Similar work was also carried out with pure $AgNO_3$ (11). Overvoltage-time curves were obtained with characteristic maxima (see Fig. 1), and the number of crystallites forming on the cathode was counted. These data enabled us to calculate the exchange current of silver in a pure $AgNO_3$ melt. It was assumed that the shape of the growing crystallites is close to hemispherical and that all of them (if more than one forms) have identical sizes, and also that the electrode capacitance is a single-valued function of the potential (i.e., that the capacitance on the ascending and descending branches of the η-t curve in the given experiment is the same at the same overvoltage).

Fig. 1. Typical overvoltage-time curve $\dot{\eta} = \operatorname{tg}\varphi;\ \dot{\eta}_1 = \operatorname{tg}\varphi_1$

The equivalent circuit of a microelectrode with a crystallite growing on it is shown in Fig. 2. At the initial moment, when the current is switched on, while there is not yet a crystallite ($R_{\text{reak}} \to \infty,\ R_{\text{om}} \to \infty$), only charging of the double layer of the platinum electrode occurs and the overvoltage increases. This continues until a silver crystallite nucleus appears on the cathode ($\eta \approx \eta_{\max}$), the subsequent growth of which proceeds both at the expense of the external

Fig. 2. Equivalent circuit of a platinum cathode with a silver crystallite growing on it

Figure 2: Fig. 2. Equivalent circuit of a platinum cathode with a silver crystallite growing on it

current and at the expense of discharge of the double layer of the platinum microelectrode:

$$I_{\text{growth}} = I - C\dot{\eta}, \tag{5}$$

where I is the external polarizing current, C is the capacitance of the electrode, $\dot{\eta} = (d\eta/dt)_{t=t}$, i.e., the rate of decrease of the potential at the given point on the descending segment of the η-t curve.

Fig. 2. Equivalent circuit of a platinum cathode with a silver crystallite growing on it

The value of the capacitance C is found from the slope of the ascending branch of the η-t curve at the same value of the potential (to which the time t_1 corresponds)

$$C = I/\dot{\eta}_1, \tag{6}$$

where $\dot{\eta}_1 = (d\eta/dt)_{t=t_1}$. Then

$$I_{\text{growth}} = I\left(1 - \dot{\eta}/\dot{\eta}_1\right). \tag{7}$$

On the other hand, the growth rate of a hemispherical crystallite is

$$I_{\text{growth}} = \eta_{\text{eff}}/(R_{\text{reak}} + R_{\text{om}}). \tag{8}$$

Here

$$\eta_{\text{eff}} = \eta - 2\sigma V/r, \tag{9}$$

where η is the measured overvoltage, σ is the surface tension of the deposited metal (silver) at the boundary with the melt, and V is the molar volume of the deposited metal.

From equations (1), (2), (7), (8), and (9) we obtain:

$$\frac{1}{i_0} = \left(\frac{2\pi zFr^2}{RTI\left(1 - \eta/\eta_1\right)}\right)\left(\eta - \frac{2\sigma V}{r}\right) - \frac{zFr}{RT\varkappa}. \tag{10}$$

We determine the radius of a crystallite from the balance of the quantity of electricity at the electrode. It is obvious that, for the growth of a crystallite by the time t, when the overvoltage is equal to η, there is expended a quantity of electricity equal to the difference between the total quantity of electricity (It) and the quantity of electricity required to charge the electrode to the same overvoltage (It_1) (see Fig. 1). Then, for a hemispherical form of the crystallite:

Table 1

I, μA	z	Δt, msec	$r \cdot 10^5$, cm	η/η_1	η_{meas}, mV	$\frac{1}{i_0} \cdot 10^3$	I, μA	z	Δt, msec	$r \cdot 10^5$, cm	η/η_1	η_{meas}, V	$\frac{1}{i_0} \cdot 10^3$
353	126	0.65	4.54	0.024	45.9	1.37	58.2	30	2.25	6.07	0.078	13.9	1.82
353	135	0.62	4.37	0.026	24.0	2.44	58.2	31	1.15	4.81	0.457	24.0	1.56
58.2	18	1.00	5.50	0.573	34.4	1.35	2.3	1	2.28	6.46	0.204	18.1	2.10
58.2	37	2.75	6.05	0.013	10.8	1.79	2.3	1	0.8	4.55	0.113	21.1	1.18
58.2	3	2.90	6.40	0.015	10.4	1.61							

$$I(t - t_1) = zF2\pi r^3/3V. \tag{11}$$

Using equations (10) and (11),* and the experimental data on the study of the formation of silver crystal nuclei during electrolysis of pure molten silver nitrate, the exchange currents for the deposition–dissolution reaction of silver were calculated.

The experiments were carried out at temperatures of 220-350° with platinum microcathodes of area $3.14 \cdot 10^{-4}$ and $7.85 \cdot 10^{-3}$ cm^2. Their procedure was analogous to that described previously (^{10}).

Table 2

t, °C	220	250	300	350
i_0, A/cm^2	$\overset{90}{440\pm60}$	$\overset{210}{600\pm120}$	$\overset{350}{830\pm180}$	$\overset{600}{1200\pm300}$

The measurement results for 250° are given in Table 1. In calculating the exchange currents it was assumed** that $\sigma = 10^{-4}$ J/cm^2 (^{12}). The values of the specific electrical conductivity were taken by us from the work of Sakai (^{13}). Table 2 gives the exchange currents found from the arithmetic mean values of $1/i_0$ for each temperature. Let us compare these exchange-current values with data of other authors.

Inman, Bockris, and Blomgren (^{1}) found an exchange current for silver in nitrate melt at 250° and $C_{\text{Ag}} = 9.8 \cdot 10^{-6}$ mol/cm^3 equal to 1.6 A/cm^2. Then, at the

Fig. 3. Temperature dependence of the exchange current in pure molten silver nitrate

Figure 3: Fig. 3. Temperature dependence of the exchange current in pure molten silver nitrate

concentration of silver ions corresponding to pure molten silver nitrate ($C_{\mathrm{Ag}} = 2.3 \cdot 10^{-2}$ mol/cm^3 (15)) and $\alpha = 0.5$, the exchange current calculated from the relation

$$i_0 = K C_{\mathrm{Ag}}^{1-\alpha}, \tag{12}$$

should be equal to 77 A/cm^2. If, however, $\alpha = 0.16$ (16) is taken, the exchange current should be 1600 A/cm^2. As can be seen, the value of i_0 determined by us lies between these values.

---

* If N crystallites grow on the cathode, then in equations (10) and (11) I must be replaced by I/N.

** Our lack of knowledge of the exact value of σ did not lead to appreciable errors in the calculations, since under the conditions of our measurements the quantity $2\sigma V/r$ did not exceed fractions of a millivolt, which was even below the limits of accuracy of the overvoltage measurements (±1 mV).

Leitinen, Tischer, and Roe (⌢5) studied the concentration dependence of the exchange current for a silver electrode in a KCl—LiCl—AgCl melt at 450°. They found that $\alpha = 0.16 \pm 0.05$. Extrapolating their data to pure molten silver chloride ($C_{\mathrm{Ag}} = 3.4 \cdot 10^{-2}$ mol/cm^3 (⌢15)), we obtain $i_0 = 3600$ A/cm^2.

It should be noted that the values obtained by us correspond to the exchange currents of the surface of a growing crystallite with the melt and, consequently, may be assigned to the so-called "true" exchange currents (⌢17). As is known, high values are characteristic of them even in aqueous solutions (⌢18).

Fig. 3. Temperature dependence of the exchange current in pure molten silver nitrate

From the temperature dependence of the exchange current (Fig. 3), according to the equation

$$\partial \ln i_0 / \partial (1/T) = -E/R \tag{13}$$

we found the activation energy of the silver discharge—ionization reaction at the equilibrium potential (⌢14). It is equal to 5.0 ± 1.5 kcal/mol.

The only work in which the temperature dependence of exchange currents in molten salts was investigated is the work of Leitinen et al. (ˆ5). For cadmium in a chloride melt they determined $E = 3 \pm 1$ kcal/mol.

Analysis of the systematic errors associated with the uncertainty both of the measurements and of the model led us to the conclusion that our data on exchange currents are more likely to be underestimated than overestimated.

Institute of Electrochemistry
Ural Branch of the Academy of Sciences of the USSR

Received
2 VII 1964

REFERENCES

1. D. Inman, J. O' M. Bockris, E. Blomgren, *J. Electroanal. Chem.*, **2**, 506 (1961).
2. G. J. Hills, K. E. Johnson, *J. Electrochem. Soc.*, **108**, 1013 (1961).
3. H. A. Laitinen, H. C. Gaur, *J. Electrochem. Soc.*, **104**, 730 (1957).
4. E. Ukshe, N. Bukun, *ZhFKh*, **35**, 2684 (1961).
5. H. A. Laitinen, R. P. Tischer, D. H. Roe, *J. Electrochem. Soc.*, **107**, 506 (1960).
6. R. Piontelli, G. Sternheim, *J. Chem. Phys.*, **23**, 1971 (1955).
7. R. Piontelli, *Ann. New York Sci.*, 1025 (1960).
8. N. A. Saltykova, A. N. Baraboshkin, *Proceedings of the Institute of Electrochemistry, Ural Branch, Academy of Sciences of the USSR*, issue 2, p. 35, Sverdlovsk, 1963.
9. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow, 1952.
10. A. N. Baraboshkin, L. T. Kosikhin, N. A. Saltykova, *Proceedings of the Institute of Electrochemistry, Ural Branch, Academy of Sciences of the USSR*, issue 5, Sverdlovsk, 1964.
11. A. N. Baraboshkin, L. T. Kosikhin, N. A. Saltykova, *DAN*, **155**, No. 4 (1964).
12. L. M. Shcherbakov, V. S. Baibakov, *Collected Papers of the Interuniver-*

sity Conference. Surface Phenomena in Metallurgical Processes, Moscow, 1963.

13. K. Sakai, *J. Chem. Soc. Japan*, **75**, 1821 (1954).
14. J. Bokris, *Some Problems of Modern Electrochemistry*, Moscow, 1958, p. 227.
15. N. K. Boardman, F. H. Dorman, E. Heymann, *J. Phys. Chem.*, **53**, 375 (1949).
16. J. L. Barton, J. O' M. Bockris, *Proc. Roy. Soc.*, **268A**, No. 1335, 485 (1962).
17. H. Fischer, *Elektrolitische Abscheidung u. Elektrokristallisation von Metallen*, Berlin, 1954.
18. P. B. Price, D. A. Vermilyea, *J. Chem. Phys.*, **28**, 720 (1958).

Note: Figure translations are in progress. See original paper for figures.