THE KINETICS OF ELECTRODE REACTIONS ON METALLIC BISMUTH IN PURE MOLTEN BISMUTH CHLORIDE

Adolf KISZA and Jerzy KAŻMIERCZAK

Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland

Received December 29, 1990
Accepted September 30, 1991

The relaxation and impedance methods were applied to the study of electrode reaction on bismuth electrode immersed in pure molten bismuth chloride. The found kinetic and activation parameters are compared with the similar ones for other pure molten chlorides.

Electrode reactions in molten salts are very fast and the rate constants in most cases are too high to be measured by most electrochemical methods[1,2]. To overcome this problem we have proposed the application of the relaxation method to the study of the kinetics of electrode reactions in molten salts[3]. The relaxation method has been successfully applied to the study of the kinetics of electrode reactions on metallic tin and lead immersed in their pure molten chlorides[4,5] and on silver and zinc electrodes in pure molten silver and zinc chlorides[6,7]. The theory of the relaxation method has been extended to concentrated diffusional electrode systems without[8] and with the adsorption of the supporting electrolyte[9].

The purpose of this work is to study the kinetics of the electrode reaction:

$$\mathrm{Bi^{3+} + 3\,e = Bi} \qquad (1)$$

which occurs at the bismuth electrode surface in molten $BiCl_3$, by the relaxation and impedance methods.

THEORETICAL

In our relaxation method, the Bi indicator electrode, which is in equilibrium with its pure molten salt, is slightly displaced from equilibrium by a galvanostatic perturbation current impulse. During this perturbation, the electric double layer at the indicator electrode surface is charged and the equilibrium potential is changed to a nearby value:

$$E = E_e + \eta(t)\,. \qquad (2)$$

Only the decay of the resulting overpotential is recorded[6]:

$$\eta(t) = \eta_0 \exp\left(-k_c^* t\right). \qquad (3)$$

where the pseudo first order cathodic rate constant k_c^* is related to the faradaic relaxation time τ_f:

$$\tau_f = 1/k_c^* = R_{ct}C_d \,. \tag{4}$$

Here C_d is the double layer capacitance and R_{ct} is the charge transfer resistance[1].

The standard rate constant k_s of the studied electrode reaction may be calculated from the pseudo first order cathodic rate constant k_c^*, if the double layer capacitance C_d, is known from separate impedance measurements:

$$k_s = \frac{RT}{n^2F^2A\sqrt{c}}\,k_c^*C_d\,, \tag{5}$$

where A is the electrode area (cm^2), c is the concentration of the metal ions (mol . . cm^{-3}) and other symbols have their usual meaning. The relaxation method bears some analogy to the coulostatic method described by Delahay[10] and Reinmuth[11], in which the charge pulse is of much shorter duration and the treatment of the experimental data in the time domain – in the case of mass transport control – may be difficult.

EXPERIMENTAL

Materials. Bismuth chloride was prepared by dissolution of pure metallic Bi in a concentrated solution of HCl and HNO_3 with some amount of H_2O_2. The obtained solution was diluted with distilled water to cause precipitation of BiOCl. The latter was thoroughly washed with distilled water and dissolved in pure concentrated hydrochloric acid. From this solution a hydrate $BiCl_3.2\,H_2O$ was precipitated and dried in a vacuum exsiccator over P_2O_5. The final drying was performed by bubbling of dry nitrogen through the molten $BiCl_3$ in the measuring vessel at 350°C.

Apparatus and procedure. The hard glass vessel, similar to that described previously[5], contained liquid or solid bismuth indicator electrodes in glass spoons. A layer of liquid bismuth at the bottom of the glass vessel was used as the auxiliary electrode. All electrical connections were made by tungsten wires, which were sealed in the glass. The glass measuring vessel was placed in a steel block, heated in an electric furnace. The relaxation measuring circuit was identical to that described previously[6].

The double layer capacitance was performed by a computer controlled PAR Model 273 Impedance System, using the same three electrode measuring vessel as in relaxation measurements.

RESULTS AND DISCUSSION

Relaxation Results

A typical overpotential decay of a galvanostatically perturbed bismuth electrode in molten $BiCl_3$ together with the computer fit according to Eq. (*3*) is presented in Table I.

It is seen from data in Table I that Eq. (3) describes the experimental overpotential decay very well with the correlation coefficient $r^2 > 0{\cdot}99$ along the whole curve. Such measurements of the pseudo first-order cathodic rate constant k_c^*, have been performed at several temperatures and the results are presented in Table II. The temperature dependence of the cathodic pseudo first-order rate constant on the solid Bi electrode may be represented by the Arrhenius type equation:

$$k_c^* = 1{\cdot}48 \,.\, 10^7 \exp(-2\,855/T) \tag{6}$$

with the correlation coefficient $r^2 = 0{\cdot}9922$. A similar equation for the cathodic pseudo first-order rate constant on liquid Bi electrode is the following one:

$$k_c^* = 2{\cdot}2413 \,.\, 10^5 \exp(-708{\cdot}2/T)\,. \tag{7}$$

Pseudo first-order rate constants are not used in the discussions of the rates of electrode reactions. To compare the rates of the studied metal–pure molten metal chloride electrode reactions with those in other systems it is necessary to convert the k_c^* values into standard rate constants k_s given by Eq. (5). To do so, we had to

TABLE I

Relaxation curve of solid Bi electrode in pure molten $BiCl_3$. Current impulse 10 mA, time of perturbation 2 s, temperature 513 K

$\eta(t)$ mV	t μs	η_0 mV	$k_c^* \,.\, 10^{-4}$ s^{-1}	r^2
33·58	9·08			
31·03	10·5			
28·73	11·7			
26·17	13·2			
23·67	14·7	59·8	6·29	0·9991
21·25	16·5	59·4	6·23	0·9994
19·00	18·5	58·6	6·12	0·9992
16·67	20·7	58·3	6·08	0·9995
14·47	22·8	58·5	6·11	0·9996
12·58	25·3	58·3	6·07	0·9996
10·63	28·5	57·6	5·99	0·9994
9·00	30·7	58·0	6·03	0·9995
7·50	33·3	58·8	6·09	0·9993
6·33	36·2	59·0	6·12	0·9994
5·33	38·9	59·3	6·12	0·9995
4·30	42·2	59·3	6·18	0·9996
3·53	45·3	59·5	6·20	0·9996
2·83	48·3	60·0	6·24	0·9995

measure the double layer capacitance of our indicator electrode in a separate impedance experiment.

Impedance Results

In terms of equivalent circuits the metal–pure molten metal chloride electrode should be described by a simple three element equivalent circuit presented in Fig. 1*a*.

The complex impedance plot is usually used to present the experimental data[1]:

$$\hat{Z} = Z' - iZ'' \tag{8}$$

TABLE II

Cathodic pseudo first-order rate constants of the Bi(III)/Bi electrode reaction in pure molten $BiCl_3$ at various temperatures

T, K	$k_c^* \cdot 10^{-4}$, s^{-1}	Standard deviation	T, K	$k_c^* \cdot 10^{-4}$, s^{-1}	Standard deviation
503	5·03	0·38 . 10^4	570	6·46	0·54 . 10^4
513	5·61	0·07 . 10^4	593	6·84	0·08 . 10^4
523	6·38	0·09 . 10^4	613	7·03	0·19 . 10^4
533	6·87	0·21 . 10^4	633	7·22	0·10 . 10^4
544[a]	6·17	0·92 . 10^4	653	7·57	0·14 . 10^4
553	6·25	0·53 . 10^4	673	7·88	0·26 . 10^4
563	6·34	0·48 . 10^4			

[a] M.p. of Bi.

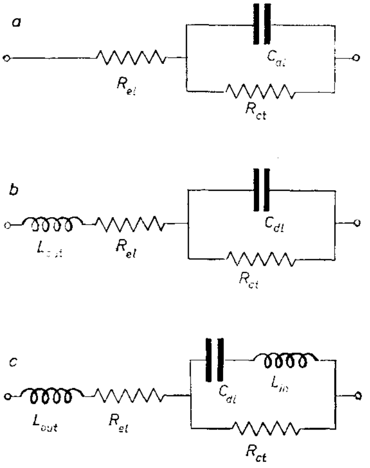

FIG. 1

Equivalent circuits of the metal–pure molten metal chloride electrode. R_{el} electrolyte resistance, C_d double layer capacitance, R_{ct} charge transfer resistance, L_{out} outer inductance, L_{in} inner inductance with: Z' – real and Z'' – imaginary parts of the complex cell impedance $\hat{Z}$. Due to the high rate of the electrode reaction the charge resistance is rather small in comparison to the electrolyte resistance and cannot be determined accurately from the results of impedance measurements. It has been observed experimentally that the registered impedance spectra are sensitive to small unavoidable lead inductances. To account for this behavior we have incorporated into the equivalent circuit (in series with the electrolyte resistance) a known outer inductance L_{out} (Fig. 1*b*). This made the recorded impedance spectra more characteristic especially when present them in the so called Bode plot[12] in which both parts of the complex cell impedance are plotted separately. Typical results of the impedance measurements of $BiCl_{3(l)}/Bi$ electrode at 733 K are presented in that manner in Fig. 2.

The experimental impedance spectrum presented in Fig. 2 shows (in the low frequency range) a characteristic hump in the imaginary part of the complex cell impedance. To account for this feature one has to introduce an inner inductance L_{in} into the equivalent circuit (Fig. 1*c*).

For the evaluation of the values of the parameters of the equivalent circuit presented in Fig. 1*c* from the experimental frequency dependence of the complex cell impedance a NLLSFit (NonLinear Least Squares Fit) performed by a computer program developed by Boucamp[12] has been used. Fig. 3 presents together with the experimental impedance spectrum also a simulated one. It is seen that the simulated spectrum has all the features of the experimental one.

Due to the fast electrode process and high concentration of the ions at the electrode surface, the measured double layer capacitances are very high. The values of double layer capacitances of the bismuth electrode immersed in pure molten $BiCl_3$

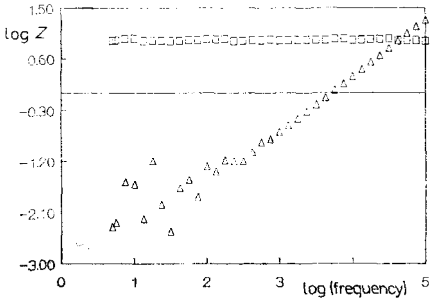

FIG. 2

Bode plot of the cell impedance at 733 K. □ real part (Z'), △ imaginary part (Z'') of the experimental cell impedance

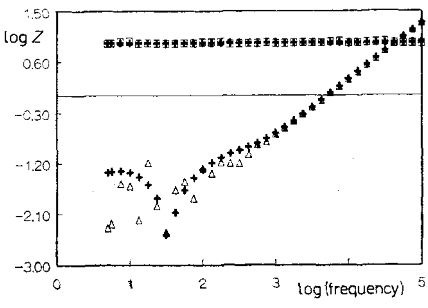

FIG. 3

Bode plot of the cell impedance at 733 K (as in Fig. 2). + simulated values according to the equivalent circuit presented in Fig. 1*c* together with the standard rate constant k_s at several temperatures are presented in Table III.

The temperature dependence of the standard rate constant on liquid bismuth electrodes immersed in pure molten $BiCl_3$ is presented by a similar Arrhenius type equations:

$$k_s = 30{\cdot}162 \exp(-4\,092/T) \tag{9}$$

with the activation parameters: $\Delta S^{\#} = -224$ J mol^{-1} K^{-1} and $\Delta H^{\#} = 34$ kJ . . mol^{-1}. The comparison of the up to now measured standard rate constants of metallic electrodes immersed in pure molten salts is presented in Table IV.

There are not many data on the double layer capacitance and rate of electrode reactions in pure molten salts. Most of the measurements of the double layer capaci-

TABLE III

Double layer capacitance and standard rate constants of the electrode reaction in pure molten $BiCl_3$ at several temperatures. Indicator electrode area 0·14 cm^2

T, K	k_c^*, s^{-1}	C_d, F	c, mol cm^{-3}	k_s, cm s^{-1}
733	85 200	0·26	0·0107	0·111
703	81 800	0·22	0·0109	0·0858
672	78 200	0·20	0·0111	0·0708
643	74 500	0·17	0·0114	0·0541
613	70 500	0·14	0·0116	0·0398
583	66 500	0·11	0·0118	0·0278
553	62 200	0·078	0·0120	0·0173
533	66 000	0·058	0·058	0·0131
513	53 400	0·013	0·0123	0·00227

TABLE IV

Standard rate constants of metallic electrodes in pure molten chlorides at 800 K

Electrode system	k_s cm s^{-1}	ΔH^{*} kJ mol^{-1}	ΔS^{*} J mol^{-1} K^{-1}
$SnCl_{2(l)}/Sn_{(l)}$	0·871	10·78	−240
$PbCl_{2(l)}/Pb_{(l)}$	0·593	13·28	−240
$ZnCl_{2(l)}/Zn_{(l)}$	0·311	92·8	−147
$BiCl_{3(l)}/Bi_{(l)}$	0·181	34·2	−224

tances has been performed in diluted solutions of molten salts, frequently on polarizable electrodes[13-16]. On the other hand the hitherto performed measurements of the rates of electrode processes in molten salts followed the routine procedure in aqueous solutions[17-19] – the indicator electrode was immersed in a diluted solution of the depolarizer in an inert fused solvent (e.g. molten LiCl–KCl eutectic mixture). Such methods could not be used for the determination of the kinetic parameters of the electrode reaction studied in this paper.

The values of the standard rate constants obtained are high indeed – but so are the rates of the electrode reactions in pure molten salts. It is seen in Table IV, that the value of k_s is slightly higher for the transfer of smaller Sn(I) ion in comparison to a heavier and larger Pb(II) cation. Similar trend is observed in the activation enthalpy presented in the Table IV.

It has to be pointed out, that the values of the standard rate constants in the case of Bi(III)/Bi and Zn(II)/Zn electrode reactions are influenced by the poor ionization of these melts, which is mostly pronounced in the pure molten $ZnCl_2$. This is also seen in the values of the activation enthalpies of these two latter molten chlorides. Their higher values, as compared to melts, like $SnCl_2$ and $PbCl_2$ is due to the fact that the increase of the temperature influences not only the rate of the electrode reaction, but also the ionization process. However, the question of ionization degree of pure molten chlorides like $ZnCl_2$ and $BiCl_3$ has not yet been solved.

As for most electrode reactions, the activation entropy is negative and very much the same for $SnCl_2/Sn$ and $PbCl_2/Pb$ electrodes but less negative for less ionized $BiCl_3/Bi$ and especially $ZnCl_2/Zn$ electrode reactions.

REFERENCES

1. Bard A. J., Faulkner R. L.: *Electrochemical Methods, Fundamentals andApplications.* Wiley, New York 1980.
2. Galus Z.: *Fundamentals of Electrochemical Analysis.* PWN, Warszawa 1976.
3. Kisza A.: Pol. J. Chem. *58*, 307 (1984).
4. Kaźmierczak J.: Pol. J. Chem. *63*, 597 (1989).
5. Kisza A., Kaźmierczak J.: Chem. Papers *45*, 187 (1991).
6. Kisza A., Kaźmierczak J.: Electrochim. Acta *30*, 57 (1985).
7. Kisza A., Kaźmierczak J.: J. Electroanal. Chem. in press.
8. Kisza A., Kaźmierczak J., Mició r E.: Collect. Czech. Chem. Commun. *55*, 1478 (1990).
9. Kisza A., Kaźmierczak J.: Pol. J. Chem., in press; Kisza A.: Wiadomości Chemiczne *44*, 11 (1990).
10. Delahay P.: J. Phys. Chem. *66*, 2204 (1962).
11. Reinmuth W. H.: Anal. Chem. *34*, 1272 (1962).
12. Boukamp B. A.: *Equivalent Circuit.* University of Twente, Twente 1989.
13. Laitinen H. A., Tischer R. P., Roe D. K.: J. Electrochem. Soc. *107*, 546 (1960).
14. Randles J. E. B., White W.: Z. Elektrochem. *59*, 666 (1955).
15. Kisza A., Grzeszczuk M.: J. Electroanal. Chem. *91*, 115 (1978).

16. Lievre D., De Guibert A., Plichon V.: Electrochim. Acta *24*, 1243 (1979).
17. Liu C. H., Johnson K. E., Laitinen H. A. in: *Molten Salt Chemistry* (M. Blander, Ed.). Interscience, New York 1964.
18. Laitinen H., Osteryoung R. A. in: *Fused Salts* (B. R. Sundheim, Ed.). McGraw-Hill, New York 1964.
19. Fung K. W., Mamantov G. in: *Advances in Molten Salt Chemistry* (J. Braunstein, G. Mamantov and G. P. Smith, Eds), Vol. 2. Plenum Press, New York 1973.

Translation revised by K. Micka.