

Kinetics of electrode reactions on metallic electrodes in pure molten chlorides

A. KISZA and J. KAŹMIERCZAK

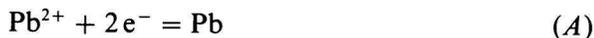
*Institute of Chemistry, University of Wrocław,
PL-50-383 Wrocław*

Received 19 March 1990

*Dedicated to Associate Professor K. Matiašovský, DrSc.,
in honour of his 60th birthday*

Using the relaxation method developed previously for the determination of the cathodic pseudo-first-order rate constant k_c^* and the faradaic impedance method for the determination of the double-layer capacitance C_d , the standard rate constant and the activation parameters of the electrode reaction in the electrode systems $\text{SnCl}_2(\text{l})/\text{Sn}(\text{l})$ and $\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$ have been determined.

Electrode reactions in molten salts are very fast and the rate constants in most cases are too high to be measured by the use of most electrochemical methods [1, 2]. To overcome this problem we proposed in 1984 the application of the relaxation method to the study of the kinetics of electrode reactions in molten salts [3]. The purpose of this work is to study the kinetics of the electrode reaction



which occurs at the lead electrode surface in molten PbCl_2 , by the application of the relaxation and impedance methods.

The impedance measurements of the tin electrode reaction in pure molten SnCl_2 will be also presented. These measurements will allow for the calculation of the standard rate constant of the $\text{Sn}(\text{II})/\text{Sn}$ electrode reaction from previous relaxation measurements [4].

In our relaxation method, the indicator electrode, which is in equilibrium with its pure molten salts, is slightly displaced from equilibrium by the application of a galvanostatic perturbing 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

$$E = E_c + \eta(t) \quad (1)$$

Only the decay of the resulting overpotential is recorded

$$\eta(t) = \eta_0 \exp(-k_c^* t) \quad (2)$$

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

$$\tau_f = 1/k_c^* = R_{ct} C_d \quad (3)$$

Here C_d is the double-layer capacitance and R_{ct} is the charge-transfer resistance [5].

The standard rate constant k_s of the studied electrode reaction may be thus calculated from the pseudo-first-order cathodic rate constant k_c^* , providing that the double-layer capacitance is known from separate impedance measurements [1]

$$k_s = \frac{RT}{n^2 F^2 A \sqrt{c}} k_c^* C_d \quad (4)$$

where A is the electrode area (in cm^2) and c concentration of the M^{n+} ions (in mol cm^{-3}).

So far the theory of the relaxation method has been worked out for an electrode reaction in pure molten salt [3, 5], for a charge-transfer reaction without [6] and with the effect of mass transportation [7–9, 10]. In a recent paper [11], the influence of the supporting electrolyte on the interpretation of the relaxation curves has been considered theoretically and tested experimentally.

The developed relaxation method bears some analogy to the coulostatic method described by *Delahay* [12] and *Reinmuth* [13], 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 controll — may turn the over-potential—time relationship to a complex quantity.

Experimental

Materials

Stannous chloride (m.p. = 519.6 K, POCH, Gliwice) was dried in a stream of dry nitrogen for 20 h. Metallic tin (99.99 %) was further purified by equilibration with pure molten SnCl_2 .

Lead(II) chloride (m.p. = 774 K, POCH, Gliwice) was also melted in a stream of dry, free from oxygen, nitrogen for 20 h. Metallic lead (anal. grade, POCH, Gliwice) was purified by further equilibration with pure molten PbCl_2 .

Apparatus and procedure

The hard glass vessel, similar to that described previously [4] contained liquid lead (or tin) indicator and reference electrodes in glass spoons. A layer of liquid lead (or tin)

placed at the bottom of the glass vessel was used as the auxiliary electrode. All electrical connections were made using tungsten wires, which were sealed into the glass. The glass measuring vessel was placed into a steel block, heated in an electric furnace. The temperature of the electric furnace was kept constant to 0.2 K. The relaxation measuring circuit was identical to that described previously [4, 5].

The measurements of the double-layer capacitance have been performed by a computer-controlled impedance measuring system ATLAS (A. Solich, Gdańsk, Poland), using the same three-electrode measuring vessel as in relaxation measurements.

Results

Relaxation results

A typical overpotential decay of a galvanostatically perturbed electrode in molten PbCl_2 together with the computer fit according to eqn (2) is presented in Table 1.

Table 1

Numerical analysis of the experimental $\eta(t)$ curve of the $\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$ electrode
Temperature 798 K, perturbing galvanostatic impulse 0.09 A, time of perturbation 2 s

$\eta(t)$	t	η_0	$k_c^* \cdot 10^{-4}$	r^2
mV	μs	mV	s^{-1}	
11.80	3.53			
11.07	4.33			
10.33	5.17			
9.61	6.17			
8.92	7.33	15.22	7.38	0.9973
8.20	8.43	15.19	7.32	0.9985
7.47	9.58	15.25	7.41	0.9988
6.79	10.8	15.29	7.46	0.9993
6.11	12.1	15.37	7.54	0.9994
5.45	13.6	15.42	7.60	0.9996
4.83	15.2	15.44	7.62	0.9996
4.21	17.3	15.38	7.56	0.9996
3.67	19.2	15.32	7.52	0.9996
3.19	21.5	15.18	7.40	0.9991
2.70	24.0	15.05	7.30	0.9988
2.29	26.5	14.92	7.21	0.9986
1.99	29.2	14.73	7.08	0.9979
1.73	31.5	14.56	6.96	0.9974
1.49	34.3	14.37	6.84	0.9968
1.39	37.0	14.06	6.66	0.9941

It is seen from Table 1 that eqn (2) describes the experimental overpotential decay very well, with the correlation coefficient $r^2 > 0.99$ 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 2.

Table 2

Cathodic pseudo-first-order rate constants of the $\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$ electrode reaction at several temperatures

T K	$k_c^* \cdot 10^{-4}$ s^{-1}	Standard deviation $s \cdot 10^{-4}$
783	6.42	0.19
798	6.52	0.24
813	6.62	0.12
828	6.71	0.12
843	6.83	0.18
858	6.90	0.18

The temperature dependence of the cathodic pseudo-first-order rate constant may be represented by an Arrhenius type equation

$$k_c^* = 1.4875 \times 10^5 \exp(-659.0/T) \quad (5)$$

with the correlation coefficient $r^2 = 0.969$. The values of the activation enthalpy and activation entropy [1], as calculated from the equation

$$k_c^* = \frac{kT}{h} \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (6)$$

are: $\Delta H^\ddagger = 5479 \text{ J mol}^{-1}$ and $\Delta S^\ddagger = -154.3 \text{ J mol}^{-1} \text{ K}^{-1}$ at 800 K.

A comparison of the hitherto measured kinetic parameters of electrode reactions in pure molten chlorides is presented in Table 3.

Table 3

Activation parameters of the metal—pure molten metal chloride electrode reaction

Electrode system	k_c^*/s^{-1} at 800 K	ΔH^\ddagger	ΔS^\ddagger	Ref.
		kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	
$\text{AgCl}(\text{l})/\text{Ag}(\text{s})$	5.84×10^5	10.37	-129.8	[5]
$\text{SnCl}_2(\text{l})/\text{Sn}(\text{l})$	7.41×10^4	4.83	-153.8	[4]
$\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$	6.53×10^4	5.48	-154.1	This paper

Pseudo-first-order rate constants k_c^* 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 the rates of electrode reactions in other systems, it is necessary to convert the k_c^* values into the standard rate constants k_s given by eqn (4). To do so we had to measure the double-layer capacitance of our indicator electrode in a separate impedance experiment.

Impedance results

In terms of equivalent circuit the metal—pure molten metal chloride electrode may be described by a simple three-element equivalent $R(RC)$ circuit presented in Fig. 1.

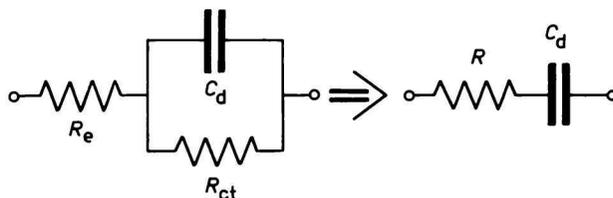


Fig. 1. Equivalent circuit of the metal—pure molten metal chloride. R_e — electrolyte resistance, C_d — double-layer capacitance, R_{ct} — charge-transfer resistance.

Due to the high rate of the electrode reaction, the charge-transfer resistance is negligible in comparison to the electrolyte resistance and cannot be determined from the results of impedance measurements.

Typical results of the impedance measurements of $\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$ and $\text{SnCl}_2(\text{l})/\text{Sn}(\text{l})$ electrode reactions are presented in the complex plane in Fig. 2.

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

$$\hat{Z} = Z' - iZ'' \quad (7)$$

with Z' — real and Z'' — imaginary parts of the complex cell impedance. In the numerical evaluation of the double-layer capacitance from the experimental impedance spectrum, the simple RC element (Fig. 1) has been used. In such case the values of the real and imaginary parts of the electrode impedance are

$$Z' = R_e \quad (8)$$

$$Z'' = 1/(\omega C_d) \quad (9)$$

For the evaluation of the electrolyte resistance R_e and double-layer capacitance C_d values from the experimental frequency dependence of the complex electrode impedance a NLLSFIT (Nonlinear Least Squares FIT) performed by a computer program developed by *Boukamp* [14] has been used.

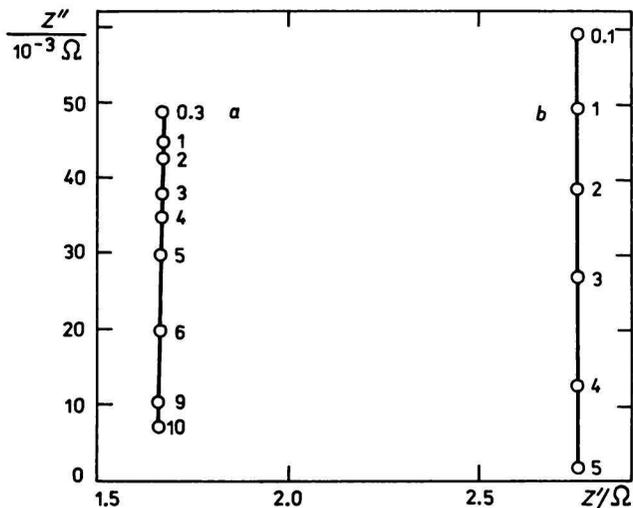


Fig. 2. Complex impedance plot of the electrode reactions: a) $\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$, b) $\text{SnCl}_2(\text{l})/\text{Sn}(\text{l})$. Numbers indicate the frequency in kHz.

Due to the fast electrode process and high concentration of ions at the electrode surface, the measured double-layer capacitances are very high. The reproducibility of the impedance measurements was not good enough to find its temperature dependence. The results thus obtained are presented in Table 4.

Table 4

Double-layer capacitance and standard rate constants of the electrode reactions in pure molten chlorides at 800 K
Indicator electrode area 0.12 cm^2

Electrode system	k_c^*	C_d	k_s
	s^{-1}	F	cm s^{-1}
$\text{SnCl}_2(\text{l})/\text{Sn}(\text{l})$	7.41×10^4	1.02 ± 0.2	0.889
$\text{PbCl}_2(\text{l})/\text{Pb}(\text{l})$	6.53×10^4	0.81 ± 0.2	0.545

Discussion

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 capacitances have been performed in diluted molten salts solutions, frequently on polarizable electrodes [15—18]. On the other hand, the hitherto performed measurements of the rates of electrode processes in molten salts followed the routine procedure from aqueous solutions [19—21]; the indicator electrode was immersed in a diluted solution of the depolarizer ion in an inert fused solvent (*e.g.* molten LiCl—KCl mixture). Such method could not be used for the determination of the kinetic parameters of the electrode reactions studied in this paper.

It is seen from the presented results that we were able to obtain — to our knowledge for the first time — by our relaxation method, with the separate measurements of the double-layer capacitance by impedance method, the standard rate constants of the electrode reactions in pure molten salts.

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 4 that the value of k_s is slightly higher for the transfer of a smaller Sn(II) cation in comparison to a heavier and larger Pb(II) cation. Similar trend is observed in the activation enthalpy presented in Table 3. As for most electrode reactions, the activation entropy is negative and very much the same for the studied two electrode reactions.

References

1. Bard, A. J. and Faulkner, R. L., *Electrochemical Methods, Fundamentals and Applications*. J. Wiley, New York, 1980.
2. Galus, Z., *Fundamentals of Electrochemical Analysis*. Ellis Horwood, Chichester—Państwowe Wydawnictwo Naukowe, Warszawa, 1976.
3. Kiszka, A., *Pol. J. Chem.* 58, 307 (1984).
4. Kaźmierczak, J., *Pol. J. Chem.* 63, 597 (1989).
5. Kiszka, A. and Kaźmierczak, J., *Electrochim. Acta* 30, 57 (1985).
6. Kiszka, A., *Collect. Czechoslov. Chem. Commun.* 50, 2814 (1985).
7. Kiszka, A., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 33, 347 (1985).
8. Kiszka, A., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 33, 357 (1985).
9. Kiszka, A., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* 37, 263 (1989).
10. Kiszka, A., Kaźmierczak, J., and Miciór, E., *Collect. Czechoslov. Chem. Commun.* 55, 1478 (1990).
11. Kiszka, A. and Kaźmierczak, J., *Z. Phys. Chem.*, in press.
12. Delahay, P., *J. Chem. Phys.* 66, 2204 (1962).
13. Reinmuth, W. H., *Anal. Chem.* 34, 1272 (1962).

14. Boukamp, B. A., *Equivalent Circuit*. University of Twente, the Netherlands, 1989.
15. Laitinen, H. A., Tischer, R. P., and Roe, D. K., *J. Electrochem. Soc.* 107, 546 (1960).
16. Randles, J. E. B. and White, W., *Z. Elektrochem.* 59, 666 (1955).
17. Kiswa, A. and Grzeszczuk, M., *J. Electroanal. Chem.* 91, 115 (1978).
18. Lelievre, D., De Guibert, A., and Plichon, V., *Electrochim. Acta* 24, 1243 (1979).
19. Liu, C. H., Johnson, K. E., and Laitinen, H. A., in *Molten Salt Chemistry*. (Blander, M., Editor.) Interscience, New York, 1964.
20. Laitinen, H. A. and Osteryoung, R. A., in *Fused Salts*. (Sundheim, B. R., Editor.) McGraw-Hill, New York, 1964.
21. Funk, K. W. and Mamantov, G., in *Advances in Molten Salt Chemistry*. Vol. 2. (Braunstein, J., Mamantov, G., and Smith, G. P., Editors.) Plenum Press, New York, 1973.