

FARADAIC IMPEDANCE STUDY OF Mn(II) REDUCTION MECHANISM IN NaClO₄ AND NaCl SOLUTIONS ON MERCURY ELECTRODEBarbara MARCZEWSKA^{1,*}, Andrzej PERSONA² and Marek PRZEGALIŃSKI³*Faculty of Chemistry, Maria Curie-Skłodowska University, PL 20-031 Lublin, Poland;**e-mail: ¹ bmarc@hermes.umcs.lublin.pl, ² persona@hermes.umcs.lublin.pl,**³ mprzegal@hermes.umcs.lublin.pl*

Received March 28, 2002

Accepted September 2, 2002

The electrochemical reaction of the Mn(II)/Mn(Hg) system on mercury electrode was studied in 1 M NaClO₄ and 1 M NaCl as supporting electrolytes of different complexing and adsorptive properties. The impedance measurements confirmed the two-stage electroreduction of the Mn(II) in investigated solutions. Both the apparent and the true rate constants of the second electron transfer in both supporting electrolytes are lower by one order of magnitude than the rate constant of the first electron transfer. Similar values of corrected rate constants in both electrolytes suggest the similarity in mechanism of the Mn(II) electroreduction.

Keywords: Two-step electroreduction; Faradaic impedance; Manganese; Kinetics; Electrochemistry.

The courses of electroreduction of Mn(II) in perchlorates, chlorides, bromides, iodides, thiocyanates, sulfates, formates or tartarates are similar under polarographic conditions in which a single two-electron reduction wave is observed¹⁻⁸. Galvanostatic single-pulse, chronopotentiometric and equilibrium measurements on the Mn(Hg)/Mn(II) electrode in chloride, iodide and thiocyanate solutions^{5,9-11} as well as chronocoulometric and cyclic voltammetry measurements of Mn(II)/Mn(Hg) in Ca(ClO₄)₂ electrolyte solution of a Ca(ClO₄)₂ concentration lower than 5 M and temperature lower than 85 °C² provided a basis for suggesting a mechanism with two consecutive one-electron transfers. Yet there still remained some doubts as to whether the obtained results are not affected by the structure of electric double layer at the electrode surface. For that reason it seemed relevant both to employ a different measurement technique for the investigation of this reaction and to check the influence of the double layer structure on electrode process. Hence, an attempt was made to examine the mechanism of the Mn(II) electroreduction on the mercury electrode employing electrochemical impedance spectroscopy as a measurement technique.

In the present study values of apparent and true rate constants were used for the determination and comparison of the mechanism of the Mn(II) electroreduction on the mercury electrode in two different supporting electrolytes: in NaClO₄ solution with a low complex-forming tendency and in NaCl regarded as a complexing electrolyte.

EXPERIMENTAL

Impedance measurements were carried out with a 9121 FR Analyser and 9131 electrochemical interface (Atlas Sollich, Gdańsk, Poland).

The working electrode was a controlled-growth mercury drop electrode (CGME, MTM Poland), with a surface area of 0.017 cm². As a reference electrode, Ag/AgCl with saturated NaCl solution was used. The reference electrode was connected to the electrolytic cell *via* an intermediate vessel filled with the investigated solution. The platinum wire served as a counter electrode.

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. MnSO₄·H₂O was used without further purification. The Mn(II) concentration in solution was 10⁻³ M. The concentration of NaClO₄ or NaCl in investigated mixtures was 1 M. Measurements were carried out at 298 ± 0.1 K. Solutions were deaerated using nitrogen. The gas was passed over the solution during measurements.

RESULTS

The complex cell impedance was obtained at 25 frequencies in the range from 20 Hz to 10 kHz with logarithmic frequency sweep at potentials in the Faradaic region at 10 mV intervals. Figures 1 and 2 present examples of impedance diagrams at 5 different values of the potential for the electroreduction of Mn(II) in 1 M NaClO₄ and 1 M NaCl.

Mathematical analysis of impedance spectra variables was carried out using mathematical models and equations describing equivalent circuits. The analysis yielded parameters of an equivalent electrical circuit corresponding to the phenomena taking place on the electrode surface. The method consists in the minimizing of the error function. The minimization is performed by the iterative method of non-linear regression using the algorithm of Marquardt. In this case the Randles equivalent circuit^{12,13} was employed, which is described in terms of ohmic resistance (R_{Ω}), double layer capacitance (C_d), charge transfer resistance (R_{ct}) and Warburg coefficient (σ). In agreement with the well-known irreversibility of Zn(II) reduction, it is known that $R_{ct} \gg \sigma\omega^{-1/2}$.

The results rely mainly on the analysis of the R_{ct} values as a function of the dc potential. The values k_f^a (forward apparent rate constants) were computed from R_{ct} according to ref.¹⁴

The values of the apparent rate constants, k_f^a , of the electroreduction of Mn(II) in the investigated solutions as a function of the potential are tabulated as $\ln k_f$ in Table I. Calculations employed values of D_{ox} , D_{red} , E_f^0 for NaClO_4 (ref.¹⁵) and for NaCl (ref.⁵) solutions.

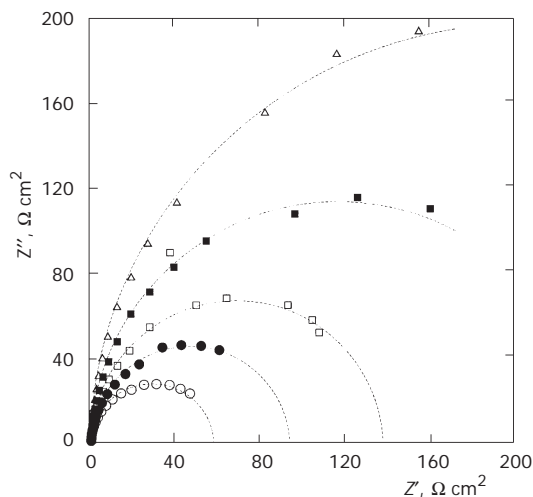


FIG. 1

Impedance diagrams measured at different values of Mn(II) electroreduction potential in 1 M NaClO_4 : ○ 1450, ● 1440, □ 1430, ■ 1410, △ 1400 mV

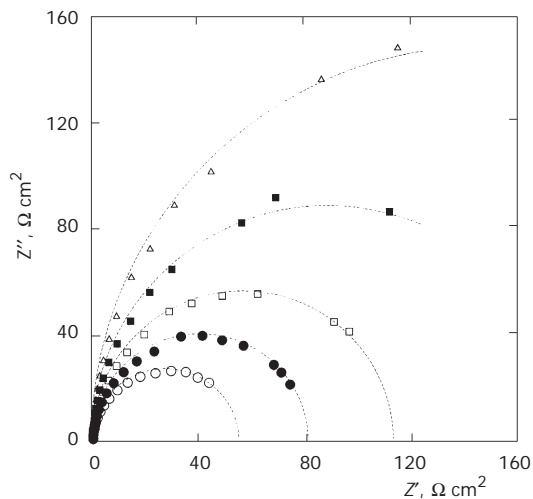


FIG. 2

Impedance diagrams measured at different values of Mn(II) electroreduction potential in 1 M NaCl : ○ 1450, ● 1440, □ 1430, ■ 1420, △ 1410 mV

Rate constants of Mn(II) were obtained on the assumption of Andreau *et al.*¹⁴. For the two-step electron transfer mechanism at the most negative potentials, the rate constant of the first-electron transfer is determined by $k_f = k_{\text{lim}} = k_1$, and, at the most positive potentials, the overall rate is determined by both steps simultaneously, according to the equation

$$1/k_f = 1/k_1 + K_1/k_2, \quad (1)$$

where k_2 is the rate constant of the second electron transfer; K_1 the equilibrium constant of the first-electron transfer reaction (at standard formal potential E_f^0 , $K_1 = 1$)

TABLE I

Natural logarithm of the apparent rate constant (in cm s^{-1}) of the Mn(II) electroreduction, $\ln k_f$, in 1 M NaClO₄ and 1 M NaCl at varied potentials

$-E$, mV	$-\ln k_f$	
	NaClO ₄	NaCl
1380	9.90	
1390	9.07	9.01
1400	8.40	8.57
1410	7.71	8.02
1420	6.96	7.33
1430	6.34	6.54
1440	5.66	5.81
1450	4.83	5.00
1460	4.28	4.27
1470	3.66	3.68
1480	3.56	3.16
1490	3.21	2.88
1500		3.01

The obtained values of the apparent rate constant of the first and second electron transfer in NaClO_4 and NaCl solutions are collected in Table II.

Taking into account the double layer effects and using the Frumkin correction, the true rate constants can be obtained by calculating

$$k_f^i(E - \varphi_2) = k_f^a(E) \exp [nF/RT]\varphi_2(E) . \quad (2)$$

The values of φ_2 were taken from our previous investigations and the data reported by Taraszewska *et al.*¹⁶ and ref.⁵. The course of the natural logarithms of the true rate constants vs $E - \varphi_2$ for the Mn(II)/Mn(Hg) system in 1 M NaClO_4 and 1 M NaCl is shown in Fig. 3. The obtained values of the true standard rate constant are collected in Table II.

TABLE II

Values of apparent (k^a) and true (k^i) rate constants of first (k_1) and second (k_2) electron transfer in 1 M NaClO_4 and 1 M NaCl solutions at E_r^0 potential

Solution M	$k_1^a \cdot 10^3$ cm s^{-1}	$k_2^a \cdot 10^3$ cm s^{-1}	$k_1^i \cdot 10^5$ cm s^{-1}	$k_2^i \cdot 10^5$ cm s^{-1}
NaClO_4	10.1	1.0	5.0	0.7
NaCl	12.9	0.7	6.1	0.5

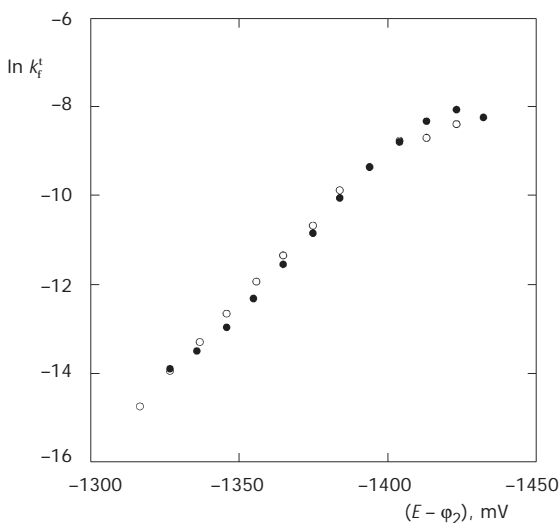


FIG. 3

The natural logarithm of the true rate constants (in cm s^{-1}) vs $E - \varphi_2$ for the Mn(II)/Mn(Hg) system in 1 M NaClO_4 (O) and 1 M NaCl (●)

DISCUSSION

Parameters of the electrode reactions of cations depend on the adsorption of ions or molecules, which modifies the structure of the double layer at the electrode surface and on the composition and structure of the electro-reduced species.

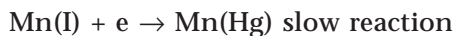
It seemed that the use of two supporting electrolytes of different complexing and adsorptive properties should result in different courses of the electrode process in these solutions.

Experiments with the impedance technique confirm the two-stage course of the Mn(II) electroreduction process. The plots of the $\ln k_f$ vs potential obtained by this method in both supporting electrolytes are not assumed to have the straight-line shape. This kind of dependence is usually associated with a step mechanism of the electrode reaction.

The values of the corrected rate constants of the first and second electron transfer were very similar in both electrolytes, which excludes the effect of potential ϕ_2 on the electrode process and suggests that it is the same form of Mn(II) that undergoes the reduction process in both solutions, which in turn excludes the participation of chloro complexes of Mn(II) in the electrode reaction in the NaCl solution. Both the apparent and the true rate constants (Table II) in both investigated supporting electrolytes indicate that the calculated value k_2 of the second electron transfer is smaller by one order of magnitude than that of the first electron. The obtained results suggest that in both examined solutions the electroreduction mechanism is identical and the Mn aqua-complex undergoes electroreduction.

The rate constant of the first electron transfer is higher by one order of magnitude than that of the second electron in both supporting electrolytes. These dependences are reverse to the electroreduction of Cd(II) or Zn(II)^{14,17} where the rate constant of the first electron transfer is lower by one order of magnitude than that of the second electron transfer. Therefore, the second electron transfer is the limiting step of the total rate of the electrode reaction.

The process of Mn(II) electroreduction may be described as two reactions, the first of which proceeds much faster than the other.



Cation electroreduction to amalgam requires to free solvent molecules from the cation coordination sphere. In electrochemical experiments the presence of a transient species may be determined if the rate of its formation is sufficiently low; this is the case of Ni(II) reduction¹⁸.

The slower stage of the first electron transfer in Zn(II) or Cd(II) electroreduction is associated with the process of partial dehydration of these ions. In the case of Mn(II) ions the faster process is the first electron transfer. It seems likely that the first electron transfer takes place without a change in the composition of the coordination sphere of Mn(II). However, it cannot be excluded that Mn(II) partly exchanges water molecules in the coordination sphere with water molecules present on the electrode surface. The sum of water molecules remains therefore unchanged. The slower process of the second electron transfer is accompanied by total dehydration of Mn(II).

A probable mechanism of the process may be presented as follows: (i) partial replacement of water molecules in the coordination sphere with water molecules adsorbed on the mercury electrode, (ii) first electron transfer, (iii) total dehydration of Mn(I), (iv) second electron transfer.

REFERENCES

1. Gaur J. N., Goswami N. K.: *J. Indian Chem. Soc.* **1969**, *46*, 1030.
2. Borodziński J. J., Galus Z.: *Electrochim. Acta* **1984**, *29*, 893.
3. Gupta J. K., Gupta C. M.: *Monatsh. Chem.* **1969**, *100*, 2019.
4. Reynolds G. F., Shalgosky H. J., Webber T. J.: *Anal. Chim. Acta.* **1953**, *9*, 91.
5. Eriksrud E.: *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *71*, 169.
6. Grenier J. W., Meites L.: *Anal. Chim. Acta.* **1956**, *14*, 482.
7. Jain D. S., Goswami N. K., Gaur J. N.: *Electrochim. Acta* **1968**, *13*, 1757.
8. Wang E., Vlček A. A.: *Collect. Czech. Chem. Commun.* **1960**, *25*, 2089.
9. Hurlen T., Smaaberg R.: *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *71*, 157.
10. Hurlen T.: *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *73*, 285.
11. Hurlen T.: *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *77*, 181.
12. Sluyters-Rehbach M., Sluyters J. H.: *Electroanalytical Chemistry* (J. Bard, Ed.), Vol. 4, p. 1. Dekker, New York 1970.
13. Sluyters-Rehbach M., Sluyters J. H.: *Comprehensive Treatise of Electrochemistry* (E. Yeager, J. O'. M. Bockris, B. E. Conway and S. Sarangapani, Eds), Vol. 9, p.177. Plenum, New York 1984.
14. Andreu R., Sluyters-Rehbach M., Remijnse A. G., Sluyters J. H.: *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *134*, 101.
15. Broda J., Galus Z.: *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *130*, 229.
16. Taraszewska J., Wałęga A.: *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *171*, 243.
17. Saakes M., Sluyters-Rehbach M., Sluyters J. H.: *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *259*, 265.
18. Gierst L., Hurwitz H.: *Z. Elektrochem., Ber. Bunsenges. Phys. Chem.* **1960**, *64*, 36.