

# Cyclic voltammetry of germanium dioxide in molten borax

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Using the method of cyclic voltammetry, the system  $\text{Na}_2\text{B}_4\text{O}_7\text{—GeO}_2$  (1.0 mole %) was studied at 800°C. The reaction  $\text{Ge}^{4+} + 4e \rightleftharpoons \text{Ge}^0$  is reversible and the reaction product can be regarded as soluble. A simple criterion of the reversibility of the electrode reaction was used. The criterion is independent of the number of the exchanged electrons and of temperature. It was verified using literature data reported for 300°C and confirmed experimentally at 800°C.

Методом циклической вольтамперометрии при температуре 800°C изучалась система  $\text{Na}_2\text{B}_4\text{O}_7\text{—GeO}_2$  (1,0 мол. %). Реакция  $\text{Ge}^{4+} + 4e \rightleftharpoons \text{Ge}^0$  является обратимой. Продукт восстановления можно считать растворимым. Было применено простое условие обратимости электродной реакции у циклической вольтамперометрии, которое не зависит от количества обменных электронов и от температуры. Это условие было проверено на основе литературных данных при температуре 300°C, а экспериментально подтвердилось при температуре 800°C.

In the linear and cyclic voltammetry for the linear diffusion and in the case of the formation of a soluble product, following criteria of reversibility of the electrode transfer reaction are usually used (1, 2):

$$E_{\text{pc}/2} - E_{\text{pc}} = 2.199 RT/nF, \quad (1)$$

$$E_{\text{pa}} - E_{\text{pc}} = 2.218 RT/nF, \quad (2)$$

where the symbols  $n$ ,  $F$ ,  $R$ ,  $T$  have their common meaning,  $E_{\text{pc}}$  and  $E_{\text{pa}}$  are potentials of the cathodic and anodic peaks, respectively,  $E_{\text{pc}/2}$  and  $E_{\text{pa}/2}$  are the half-peak potentials [1].

If an insoluble product is formed, for a shift of  $E_{\text{pc}}$  and  $E_{\text{pc}/2}$  it holds [2]

$$E_{\text{pc}/2} - E_{\text{pc}} = 0.77 RT/nF. \quad (3)$$

The formation of an insoluble product can be also confirmed by the logarithmic analysis.

For appreciation of the reversibility of a transfer reaction according to eqn (1) or (2) at temperatures from 25 to 1500°C, it is necessary to know about 60 values of the expressions  $2.20 RT/nF$  or  $2.22 RT/nF$  for  $n = 1$ , providing the stepwise

variation of these expressions by 5 mV. The number of the data may yet increase since in some cases  $n = 6$  [3]. Therefore, a temperature independent criterion appears to be desirable, especially for systems which can work in the temperature range up to 300°C.

From eqns (2) and (1) we get

$$E_{pa} - E_{pc/2} = 0.019 RT/nF \quad (4)$$

and analogically

$$E_{pc} - E_{pa/2} = -0.019 RT/nF. \quad (5)$$

Dividing eqn (4) or (5) by eqn (2), we obtain a constant 0.00857 or  $-0.00857$  which confirms that  $E_{pa}$  ( $E_{pc}$ ) is shifted by 0.857% of the value of  $\Delta E = E_{pa} - E_{pc}$  towards more positive (negative) potentials with respect to  $E_{pc/2}$  ( $E_{pa/2}$ ) independently of temperature and the number of exchanged electrons. With an accuracy of measurements of  $\pm 1\%$ , a perpendicular line drawn from the point  $E_{pa}$  ( $E_{pc}$ ) should pass through the point  $E_{pc/2}$  ( $E_{pa/2}$ ) on the potential axis. In a cathodic-anodic record, the cathodic wave is better shaped, hence eqn (4) is more convenient while eqn (5) is better suited for the anodic-cathodic record. With respect to conditions of the validity of eqns (1) and (2), the proposed criterion also indicates the linearity of the diffusion and the solubility of the product of the electrode reaction.

The criteria (4) and (5) can be verified on the basis of literature data. The reaction  $\text{Bi}^{3+} + 2e \rightleftharpoons \text{Bi}^+$  studied by means of the method of cyclic voltammetry in the  $\text{AlCl}_3\text{--NaCl}$  system at temperatures up to 300°C was found to be a reversible transfer reaction [4]. The shift  $E_{pa} - E_{pc/2}$ , ca 2 mV, represents 4% of  $\Delta E$ , determined from eqn (2). The value of  $\Delta E$  was determined with an accuracy  $\pm 10\%$ , thus  $E_{pa}$  and  $E_{pc/2}$  may be considered as practically identical. The criterion (4) can be verified also graphically [4].

## Experimental

A polarograph LP 60 with the scanning rate adjusted up to 1.6 V/min was used for measurements. Since the paper strip in recorder EZ-2 moves in one direction only, it was necessary to re-draw the voltammetric curves in the form shown in Fig. 1. The cylindrical cathode K consisted of a Pt wire (diameter 0.5 mm). A Pt crucible, used as anode A contained 25 g of the measured melt. With regard to the large surface of A as compared with K, it was assumed that the anode is unpolarizable and it served as a quasi-reference electrode. The immersion of K (5 mm) was ensured by a micrometer screw. A resistance furnace (Kanthal A 1) of own design was used. Temperature was measured by means of a thermocouple Pt/PtRh10 which was immersed together with the cathode into the same depth. Borax anal. grade was remelted at 1000°C and homogenized.  $\text{GeO}_2$  for semiconductors was used. The voltammetry in oxide melts was in more details described in a previous work [5].

## Results and discussion

The cyclic voltammetric curves of  $\text{GeO}_2$  (1.0 mole %) in molten borax at 800°C were recorded at the scanning rates  $v$  0.4, 0.8, and 1.6 V/min. The reproducibility of the measurements of the peak current  $i_{pc}$  decreased with a decreasing  $v$ . In a series

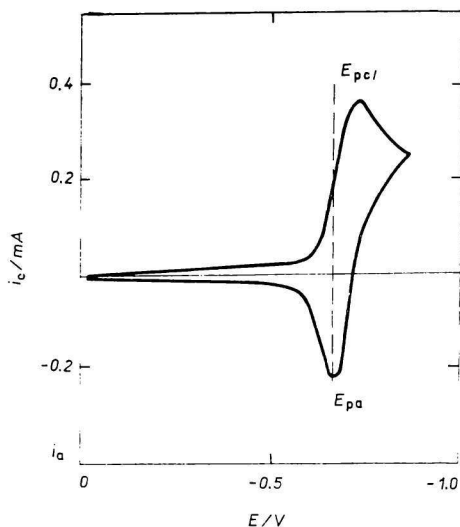


Fig. 1. Cyclic voltammogram of a reversible transfer reaction in molten borax.

1.0 mole % of  $\text{GeO}_2$ ,  $800^\circ\text{C}$ ,  $0.8 \text{ V/min}$ .

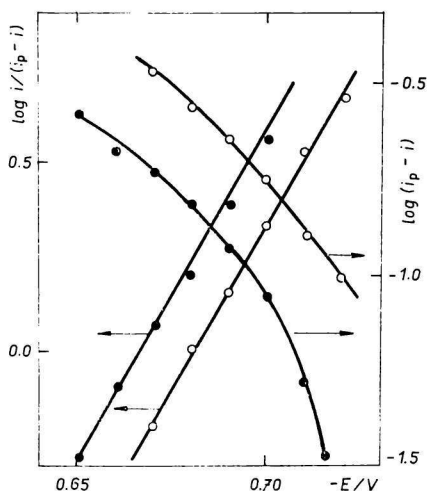


Fig. 2. Logarithmic analysis of voltammograms of  $\text{GeO}_2$  in molten borax.

●  $0.8 \text{ V/min}$ , ○  $1.6 \text{ V/min}$ .

of ten measurements the deviations were  $\pm 1\%$  and  $\pm 4.6\%$  at  $1.6 \text{ V/min}$  and  $0.4 \text{ V/min}$ , respectively. The peak current increased linearly with the  $\text{GeO}_2$  concentrations in the interval  $0.3$ – $1.0$  mole %. The dependence is not shown here since its course was the same as described in [3] where, however, the  $i$ – $E$  curves were interpreted as polarographic, in spite of their markedly formed peak. The peak and half-peak potentials were measured with an accuracy  $\pm 5 \text{ mV}$  which determined the reproducibility of results obtained by means of eqns (1), (2), and (4). The reproducibility was the same for all these relationships. When using the criteria (4) and (5) for very precise measurements in aqueous solutions at  $25^\circ\text{C}$ , it should be considered that  $E_{pa}$  ( $E_{pc}$ ) is shifted by  $0.5 \text{ mV}$  towards more positive (negative) potentials with respect to  $E_{pc/2}$  ( $E_{pa/2}$ ). The accuracy of the measurements in melts is lower already at  $300^\circ\text{C}$  [4], hence a  $0.857\%$  deviation of  $E_{pa}$  with respect to  $E_{pc/2}$  can be neglected.

The measured values are listed in Table 1 and the voltammogram at  $0.8 \text{ V/min}$  is shown in Fig. 1. Since  $n$  is close to 4 and it is the same from both eqns (1) and (2), the electrode reaction may be regarded as reversible with a soluble product. The product  $i_{pc} v^{-1/2}$  being independent of  $v$ , the electrode reaction is controlled by the diffusion of depolarizer to the electrode.

The logarithmic analysis, which was carried out for the voltammograms at  $0.8 \text{ V/min}$  and  $1.6 \text{ V/min}$  (Fig. 2), confirmed that the product of the electrode reaction may be regarded as soluble. For a better survey, the dependence of  $\log i/(i_p - i)$  vs.  $E$  is shown in Fig. 2. The number of electrons determined according to [2] from the slope of the tangent to the curve  $\log(i_p - i)$  vs.  $E$  for  $0.5$ – $0.9 i_p$  is less than one (for  $1.6 \text{ V/min}$   $n = 0.5$ , for  $0.8 \text{ V/min}$   $n = 0.9$ ). By means of eqn (3), a value  $n \sim 0.8$  was obtained for the scanning rates  $0.4$ – $1.6 \text{ V/min}$ . On the

Table 1

Dependence of the peak current of GeO<sub>2</sub> in molten borax on the polarization rate (800°C)

$i_{pc} \cdot 10^4$ A	$v \cdot 10^2$ V s <sup>-1</sup>	$i_{pc} v^{-1/2} \cdot 10^3$ A s <sup>1/2</sup> V <sup>-1/2</sup>	$E_{pc}$ V	$E_{pa}$ V	$E_{pc/2}$ V
3.0	0.667	3.60	0.735	0.675	0.675
4.0	1.333	3.48	0.730	0.670	0.670
5.7	2.667	3.50	0.730	0.670	0.675

other hand, the value of  $n$  determined from the slope of the dependence  $E$  vs.  $\log(i_p - i)/i$  approaches 4. This is in a good agreement with the results obtained from eqns (1) and (2) and with polarographic data [3]. The formation of a soluble product was found also in the case of the reduction of Ti(III) ions to metal in molten fluorides [9].

The realization of a flat indication electrode in oxide melts at high temperatures appears to be complicated. The validity of eqns (1) and (2) confirms that also at the used arrangement, the diffusion may be considered to be linear since both the peak potentials and the product  $i_{pc} v^{-1/2}$  for temperature 800–1000°C and various diameters of the Pt cathode (0.5 and 0.3 mm) are independent of the scanning rate [7]. Obviously, the conditions were fulfilled under which the diffusion towards a cylindrical electrode in the voltammetry may be regarded as linear [8]. Therefore, the criterion (4) was used for verifying the reversibility of the transfer reaction. From Fig. 1 and Table 1 it is apparent that the potential  $E_{pa}$  is practically identical with  $E_{pc/2}$ , which verifies eqn (4). This criterion may be found useful when working in fused media. Furthermore, it also supplements the routine proceedings in aqueous solutions where the experiments are carried out at room temperature and the number of exchanged electrons is given unambiguously. In melts the described procedure can be used in a broader temperature interval for a fast determination of the reversibility of the transfer reaction or the formation of a soluble product.

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