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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 7(1), 19-23
Issue Date	1959-09
Doc URL	http://hdl.handle.net/2115/24690
Type	bulletin (article)
File Information	7(1)_P19-23.pdf

Instructions for use

THE STOICHIOMETRIC NUMBER OF ZINC
AMALGAM ELECTRODE REACTION

By

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(Received July 23, 1959)

V. V. Losev[1] has recently observed by means of radioactive zinc
the unidirectional anodic or cathodic current density $\vec{i}$ or $\overleftarrow{i}$ and the
directly measurable overall current density i simultaneously inclusive
of the exchange current i_0 at zero polarization of a zinc amalgam
electrode in contact with 0.1 N $ZnSO_4$ solution mixed with a small amount
of tetrabutyl ammonium sulphate (5.10 M) which remarkably reduces
the current i and in consequence the concentration polarization[2].

These experimental results enable us to determine the stoichio-
metric number $\iota(r)$ of the rate-determining step of the electrode process

$$Zn,am = Zn^{2+} + 2e , \qquad (1)$$

as shown below. Simultaneous values of $\vec{i}$ and $\overleftarrow{i}$ are determined at
different overvoltages from concurrent measurements of i and $\vec{i}$ or $\overleftarrow{i}$ according to the relation

$$i = \vec{i} - \overleftarrow{i} , \qquad (2)$$

where i is positive or negative at the anodic or cathodic polarization respectively. Fig. 1 and 2 reproduce the results of Losev and Table I and II show the concurrent values of i, η, $\vec{i}$ and $\overleftarrow{i}$ derived from Fig. 1 and 2 respectively, where $\varphi_{n.h.e}$[**]

$\varphi_{n.h.e}$ mv

-0.80
-0.75
-0.70

-6   -5   -4

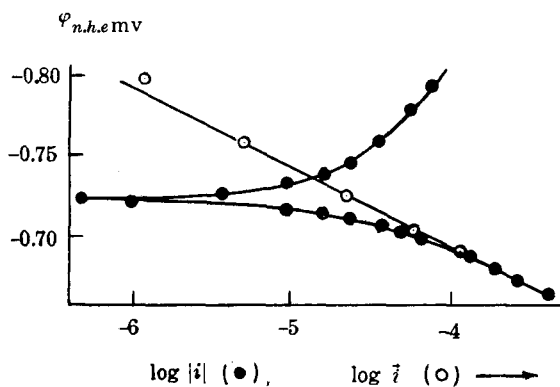log $|i|$ (●),   log $\vec{i}$ (○) ⟶

Fig. 1. Current-potential curves of zinc amalgam.
$\varphi_{n.h.e}$: potential of the electrode referred to
the normal hydrogen electrode. $\vec{i}$: unidirec-
tional anodic current density. i : overall
current density.

is the potential of the test electrode referred to the normal hydrogen electrode and $\eta = \varphi_{n.h.e} - (\varphi_{n.h.e})_{i=0}$.

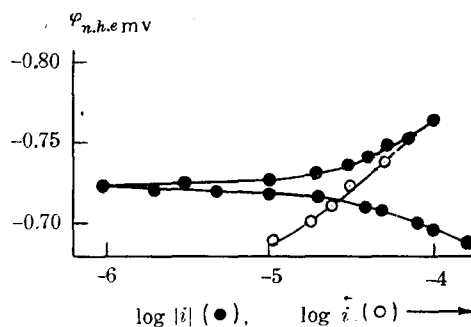Fig. 2. Current-potential curves of zinc amalgam. $\varphi_{n.h.e}$: potential of the electrode referred to the normal hydrogen electrode. $\vec{i}$: unidirectional cathodic current density. i: overall current density.

TABLE I.

Concurrent values of η, i, $\vec{i}$ and $\overleftarrow{i}$ derived from LOSEV's results in Fig. 1.

η (mv)	$i \cdot 10^5$ (a/cm²)	$\vec{i} \cdot 10^5$ (a/cm²)	$\overleftarrow{i} \cdot 10^5$ (a/cm²)
21.8	4.82	5.72	0.90
18.9	3.80	4.78	0.98
14.5	3.03	4.10	1.07
11.4	1.95	3.39	1.44
7.3	1.13	2.88	1.75
0	0	2.14	2.14
— 0.7	— 0.10		
— 3.3	— 0.40		
— 7.3	— 0.97	1.49	2.45
— 11.2	— 1.41		
— 14.5	— 1.94	1.03	2.97
— 15.2	— 1.97		
— 21.8	— 2.68	0.77	3.45
— 29.1	— 3.44	0.55	3.99
— 36.4	— 4.27	0.40	4.67
— 43.6	— 5.22	0.28	5.50
— 50.9	— 6.24	0.20	6.44
— 58.2	— 7.11	0.15	7.26
— 65.4	— 8.14	0.10	8.24

TABLE II.

Concurrent values of η, i, $\vec{i}$ and $\overleftarrow{i}$ derived from LOSEV's results in Fig. 2.

η (mv)	$i \cdot 10^5$ (a/cm²)	$\vec{i} \cdot 10^5$ (a/cm²)	$\overleftarrow{i} \cdot 10^5$ (a/cm²)
— 16.0	— 3.94		
— 11.4	— 3.02		
— 6.4	— 2.02		
— 3.6	— 1.00		
0	0	3.47	3.47
2.5	0.50		
4.6	1.02		
7.1	2.07		
8.5	2.72		
11.7	3.98	2.57	6.55
15.0	5.22	2.26	7.48
23 5	8.71	1.92	10.63
26.4	10.20	1.60	11.80
35.6	17.90	1.11	19.01

The ratio $\vec{i}/\overleftarrow{i}$ derived from Table I and II is now related with the stoichiometric number $\nu(r)$ of the rate-determining step[*] according to the general theory of reaction rate as[3]

$$\vec{i}/\overleftarrow{i} = \exp\left(-\Delta F/\nu(r)\,RT\right). \tag{3}$$

ΔF is the free energy increment of the whole system associated with the overall reaction or, particularly for (1),

$$\Delta F = 2\mu^{e} + \mu^{Zn^{2+}} - \mu^{Zn,am}, \tag{4}$$

where μ^{e}, $\mu^{Zn^{2+}}$ and $\mu^{Zn,am}$ are the chemical potentials of metal electron e, zinc ion Zn^{2+} in the solution and amalgamated zinc Zn,am respectively. Let μ^{e}_{eq} be the particular value of μ^{e}, when (1) is in equilibrium. We have from (4) by definition

$$0 = 2\mu^{e}_{eq} + \mu^{Zn^{2+}} - \mu^{Zn,am},$$

so that

$$\Delta F = 2\,(\mu^{e} - \mu^{e}_{eq}) \quad \text{or} \quad \Delta F = -2F\eta, \tag{5}$$

where η is the potential of the electrode in question referred to that in equilibrium.

We have now from (3) and (5)

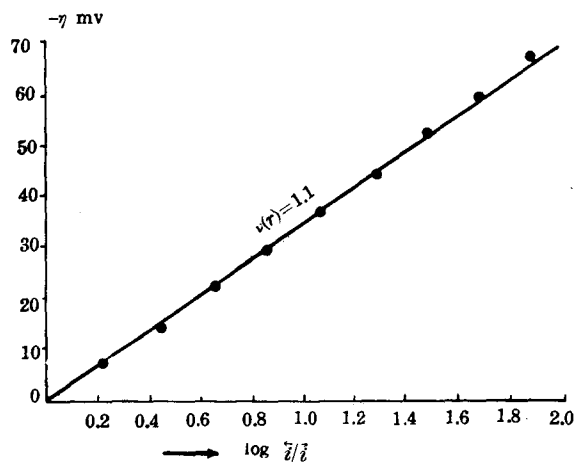$$\nu(r) = \frac{2F\eta}{RT \ln \vec{i}/\overleftarrow{i}}. \tag{6}$$

Fig. 3.

The $\eta, \log \vec{i}/\overleftarrow{i}$-curve at cathodic polarization $(\eta<0)$. $\vec{i}$ or $\overleftarrow{i}$: the unidirectional anodic or cathodic current density.
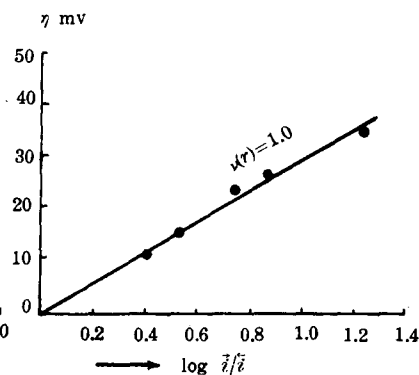
Fig. 4.

The $\eta, \log \vec{i}/\overleftarrow{i}$-curve at anodic polarization $(\eta>0)$. $\vec{i}$ or $\overleftarrow{i}$: the unidirectional anodic or cathodic current density.

*) The number of times of the rate-determining step to occur for every act of t overall reaction. The similar concept the "molecularity of a reaction" has be independently introduced by BORESKOW[5].

The η is plotted against $\log \vec{i}/\overleftarrow{i}$ in Fig. 3 and 4 as derived from Table I and II respectively.

Excellent straight lines through origin show that $\nu(r)$ derived from the results according to (6) is practically perfectly constant independent of η. We have from Fig. 3 and 4 $\nu(r)=1.1$ and 1.0 respectively.

The $\nu(r)$ is alternatively determined as follows from the exchange current i_0 at the electrochemical equilibrium, where $\nu(r)$ is indeterminate as expressed by (6). Expanding $\ln \vec{i}/\overleftarrow{i}$ in the latter equation with respect to $i/\overleftarrow{i}$ referring to (2) as $\ln \vec{i}/\overleftarrow{i} = \ln \ (1+i/\overleftarrow{i}) = i/\overleftarrow{i} - 1/2 \cdot (i/\overleftarrow{i})^2 + \cdots$, we have in the limiting case of $\eta = 0$[4],

$$\nu(r) = \frac{2F\,i_0}{RT(\partial i/\partial \eta)_{\eta=0}}, \qquad (7)$$

where $i_0 = \vec{i}_{\eta=0} = \overleftarrow{i}_{\eta=0}$. The $\nu(r)$ is determined by (7) from the values of i_0 and $(\partial i/\partial \eta)_{\eta=0}$ of the inclination of i against η at the electrochemical equilibrium. Table III shows the values of i_0
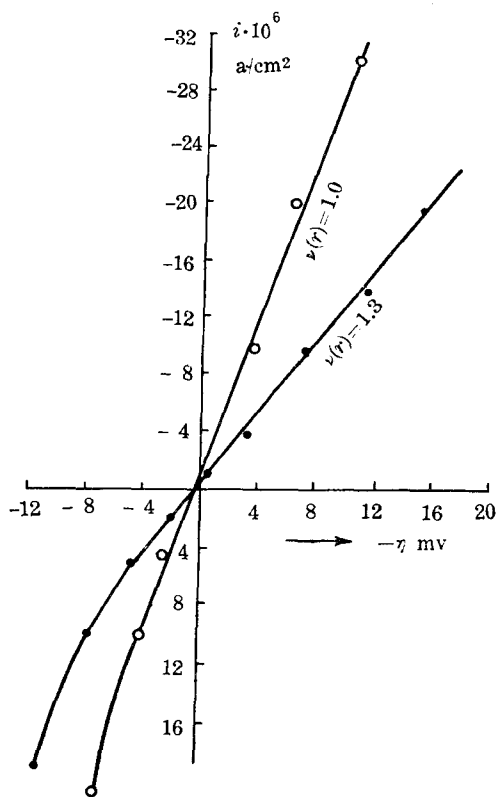

Fig. 5. The i, η-curves in the neighbourhood of electrochemical equilibrium.
● : derived from Fig. 1,
○ : derived from Fig. 2.

observed by LOSEV, $(\partial i/\partial \eta)_{\eta=0}$ determined from the plot in Fig. 5 of i against η in the neighbourhood of the equilibrium as derived from Fig. 1 and 2 and $\nu(r)$ calculated from these data by (7).

TABLE III. The i_0, $(\partial i/\partial \eta)_{\eta=0}$ and $\nu(r)$.

Source of Data	i_0 a/cm²	$\left(\dfrac{\partial i}{\partial \eta}\right)_{\eta=0}$ a/cm²mv	$\nu(r)$
Fig. 1	$2.14 \cdot 10^{-5}$	$1.30 \cdot 10^{-6}$	1.3
Fig. 2	$3.47 \cdot 10^{-5}$	$2.75 \cdot 10^{-6}$	1.0

The stoichiometric number is further evaluated by differentiating (6) with respect to η as

$$\nu(r)(\alpha_a + \alpha_c) = 2 , \qquad\qquad (8)$$

where

$$\alpha_a = \frac{RT}{F} \frac{\partial \ln \vec{i}}{\partial \eta} , \qquad \alpha_c = -\frac{RT}{F} \frac{\partial \ln \overset{\leftarrow}{i}}{\partial \eta} ,$$

are Tafel's constants for the forward and backward current and evaluated from Table I as
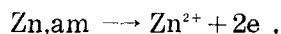
$$\alpha_a = 1.2 , \qquad \alpha_c = 0.6 .$$

We have according to (8)

$$\nu(r) = 1.1 .$$

The latter method of finding $\nu(r)$ would be expedient, when the isotopic difference of rates is pronounced as in the case of hydrogen isotopes.

It is thus concluded that $\nu(r)$ is unity.

The rate-determining step of the overall reaction (1) may be

$$Zn,am \longrightarrow Zn^{2+} + 2e ,$$

or the overall reaction (1) may consist in the above single step in accordance with the above conclusion.

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