*On the Dismutation Process of Zinc Ion**

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In the current-potential curve of the Ševčik type oscillographic polarograph a quantitative relation between the cathodic and anodic currents of zinc ion was found.

Under the high rate of variation of the applied voltage (20 c. p. s., 50 v./s) the cathodic branch of zinc ion consists of two peaks in the solution containing iodide ions or bromide ions. On the contrary, a single peak can be observed in the anodic branch, as is illustrated in Figs. 1 and 2. Since the first cathodic peak is symmetrical with the anodic one, the first reduction is assumed to be reversible, and the second reduction to be irreversible. In this case the cathodic currents superposed on each other were estimated by the modified method developed by the present authors(1) (cf. Breyer et al.(2)).

The cathodic currents and the anodic currents thus estimated are plotted against the concentration of KI and KBr in Fig. 3 or 4, respectively. In this case the ionic strength of the supporting electrolyte is maintained at a constant value as much as 4 mol./l. by adding KNO_3 solution. In Fig. 3 it is easy to see that the value of $R_1+1/2\,R_2$ is, in any case, equal to the anodic current. This rela-

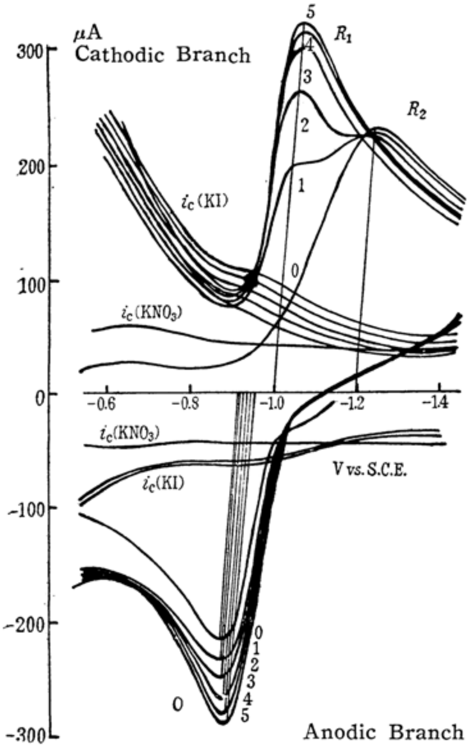

Fig. 1. Current-potential oscillograms of 0.37 mM Zn^{++} in various concentrations of KI (O-OM KI, 1-0.45 M KI, 2-0.9 M KI, 3-1.8 M KI, 4-2.7 M KI, 5-3.6 M KI, i_c-charging current).

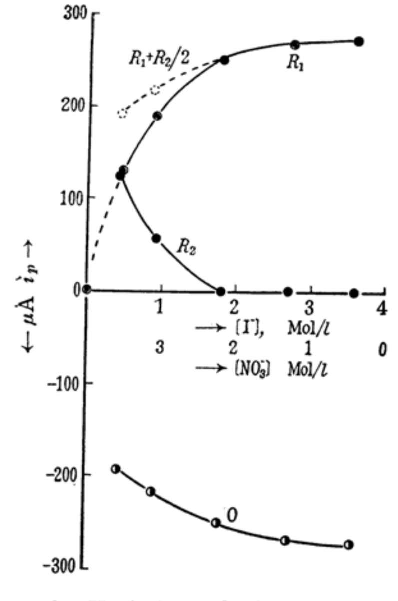

Fig. 3. Variation of the peak current with the concentration of KI.

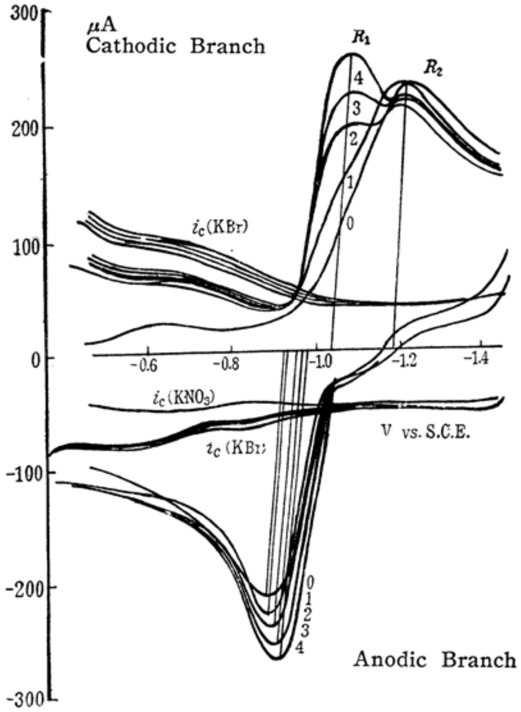

Fig. 2. Current-potential oscillograms of 0.73 mM Zn^{++} in various concentrations of KBr (O-OM KBr, 1-0.59 M KBr, 2-1.77 M KBr, 3-2.95 M KBr, 4-4.0 M KBr, i_c-charing current).

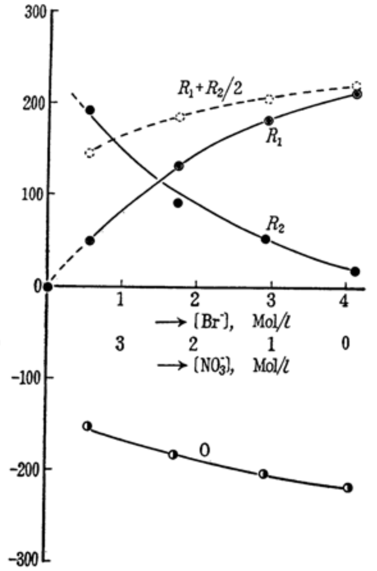

Fig. 4. Variation of the peak current with the concentration of KBr.

tion is better realized in Fig. 4.

From these results it can be reasoned that a half of the irreversible peak current corresponds to the reversible one in yielding the anodic current. Supposing that the dismutation process proposed by Heyrovský[3] is the case mentioned above, the reversible process, in which the electron transfer is facilitated by the catalytic action of anions such as iodide or bromide ions, results from the repetition of a cycile process, $2Zn^{++}+$

$$\begin{tikzcd}
 & 2Zn^{+} \arrow[ld] \arrow[dd] \\
2e \arrow[rd] & \\
 & Zn^{++}+Zn
\end{tikzcd}$$

, and yields the reduced metal the concentration of which is equivalent to that of the oxidant. Virtually this process is party limited except in the case of the solution containing more than 2 mol./l. I^-, and the residual oxidant is reduced in the second reduction when the applied potential shifts toward the more negative potential.

The irreversible process (R_2), however, is limited in the reaction, $2Zn^{++}+2e \rightarrow 2Zn^{+} \rightarrow Zn^{++}+Zn$. In this case the concentration of the reduced metal will be invariably as much as a half of the concentration of the oxidant. Since the peak current is linearly proportional to the concentration of a depolarizer, it is now easy to see why we obtain the above-mentioned characteristic relation between two cathodic peak currents (R_1, R_2) and the anodic peak current (0). In other words, these results seem to endorse the validity of the dismutation process assumed by Heyrovský. A more detailed investigation is now in progress.

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[1] M. Shinagawa, H. Imai and H. Sunahara, *J. Chem. Soc. Japan* (in press).

[2] B. Breyer, F. Gutman and S. Hacabian, *Australian J. Sci. Resear.*, 3, 567 (1950).

[3] J. Heyrovsky, *Z. Elektrochem.*, 59, 820 (1955).