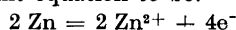


## On the Kinetics of the Zn/Zn<sub>aq</sub><sup>2+</sup> Electrode

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Investigations have been made on the anodic dissolution and cathodic deposition of zinc in acid chloride solution at 20°C by means of a slow galvanostatic technique, allowing the "true" rate of these reactions to be determined from the weight change of the electrodes. The reactions have been found to exhibit a combined concentration and activation polarization under the conditions applied, to have mutually symmetric activation controlled Tafel lines with slopes of numerically 2.303  $RT/2F$ , and to be independent of the pH of the solution. The activation controlled rate of deposition is moreover found to be proportional to the square of the zinc ion activity. This indicates the kinetic unit equation to be:



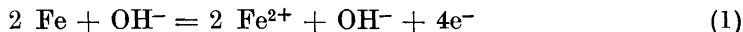
In strong chloride solutions, where the polarization behaviour is simplest, the exchange current is found to be:

$$i_0 = 0.7 a_{\text{Zn}^{2+}} \text{ A/cm}^2$$

Comparisons are made to previous results on zinc and to results of analogous experiments on iron and copper.

### 1.0 INTRODUCTION

It has previously been shown that the reactions of the Fe/Fe<sub>aq</sub><sup>2+</sup> electrode<sup>1</sup> and the Cu/Cu<sub>aq</sub><sup>2+</sup> electrode<sup>2</sup> under stationary conditions seem best represented by the "kinetic unit equations":



indicating that the anodic and cathodic reactions are second order with respect to the metal and the metal ions, respectively, and that there in the case of iron (but not in the case of copper) is a first order "catalytic" interaction of hydroxyl ions.

As these results were somewhat surprising, it was assumed desirable to carry out the same type of slow amperostatic polarization measurements on some further metals. In the present paper, results thereby obtained on *zinc* in various pure and mixed solutions of hydrochloric acid, potassium chloride, and zinc chloride at 20°C are presented and discussed.

The experimental method applied is especially useful in this case as it allows the rate of the zinc electrode reactions to be determined from the weight change of the electrodes. Account is thereby made of a possible simultaneous corrosion of the electrodes and of a possible current consuming hydrogen evolution accompanying the deposition process.

## 2.0 PREVIOUS WORK

The anodic dissolution and cathodic deposition of metals have recently been reviewed and discussed by Vetter<sup>3</sup>, Hoar<sup>4</sup>, Bockris<sup>5</sup>, and Fischer<sup>6</sup>. General reference may also be given to the monograph by Mathewson<sup>7</sup>. All these reviews include references to zinc, but do not reveal much data appropriate for a modern analysis of the kinetics of the *active* dissolution and deposition of this metal.

One of the most direct investigations is due to Rojter, Polujan and Jusa<sup>8</sup>. From oscillographically obtained anodic and cathodic potential transients for single crystal zinc in 0.25 M solutions of zinc sulphate in water and in 0.005—0.008 N sulphuric acid at 30°C, they found the Zn/Zn<sub>aq</sub><sup>2+</sup> electrode to behave symmetrically and the polarization at constant current to reach a maximum after about 10<sup>-2</sup> sec and then to decrease towards a stationary value. Both the maximum values and the stationary values obey the Tafel relationship and give numerical Tafel slopes of approximately 2.303  $RT/F$  and 2.303  $RT/2F$ , respectively. This is the same as found for iron<sup>9,10</sup> in experiments of the same type, and the Tafel slope for the stationary potentials also agrees with what is obtained from other types of stationary-state measurements both on iron<sup>1,11</sup> and on copper<sup>2</sup>. Rojter, Polujan and Jusa could moreover find no effect of pH on the Zn/Zn<sub>aq</sub><sup>2+</sup> electrode reactions, which thus seem more analogous to those of the Cu/Cu<sub>aq</sub><sup>2+</sup> electrode<sup>2</sup> than to those of the Fe/Fe<sub>aq</sub><sup>2+</sup> electrode<sup>1,10</sup>. From the maximum polarization values, these authors further estimate the exchange current of the Zn/Zn<sub>aq</sub><sup>2+</sup> electrode to be of the order of 10<sup>-5</sup> A/cm<sup>2</sup> under the conditions given. This seems to be the only value so far available for the exchange current of this electrode.

Of other polarization studies on the Zn/Zn<sub>aq</sub><sup>2+</sup> electrode reactions may especially be mentioned those of Röntgen and Buchkremer<sup>12</sup>, Müller and Barchmann<sup>13</sup>, and Piontelli and Poli<sup>14</sup>. The former of these investigations deals with the deposition process and with hydrogen evolution on zinc cathodes. The two latter are mainly concerned with the effect of anions on the deposition and the dissolution process. All three show a rather low Tafel slope for the zinc electrode reactions (not more than 2.303  $RT/2F$ ) and a very low overvoltage even at current densities of the order of 10<sup>-3</sup> A/cm<sup>2</sup> at zinc ion concentrations of 0.5 M (see especially Ref.<sup>14</sup>). This may possibly indicate an appreciably higher exchange current for the polycrystalline zinc used by these authors (see also the early work of Allmand and Cocks<sup>15</sup>) than for the single crystals used by Rojter, Polujan and Jusa. The interpretation of the results is impeded, however, by the investigations having been made in acid solutions of low pH without account having been made of the free corrosion of the electrodes.

The rate of corrosion at various crystallographic planes of zinc single crystals in acid solution has been studied by Aminoff<sup>16</sup> and Straumanis<sup>17</sup>, both of which have found the close-packed hexagonal basal planes to corrode more slowly than less closely packed planes. The orientation and morphology of electrodeposited zinc have recently been studied by Sato<sup>18</sup>.

Much work has been done on the reduction and dissolution of zinc at zinc amalgam electrodes. As this is slightly outside the scope of the present work, no detailed review will be made. However, it may be of interest to give a brief reference to the recent work of Horiuti and Matsuda<sup>19</sup> based on experimental results of Losev. These authors found the mutually reverse reactions of the  $\text{Zn}_{\text{am}}/\text{Zn}_{\text{aq}}^{2+}$  electrode to have very nearly symmetric Tafel lines with slopes of numerically  $2.303 RT/F$  (see Figs. 1 and 2 in Ref.<sup>19</sup>). This is twice that mentioned above for the stationary reaction on solid zinc electrodes.

### 3.0 EXPERIMENTAL

The experimental technique has been exactly the same as previously described for analogous experiments on iron<sup>1</sup> and copper<sup>2</sup>. It is a slow amperostatic technique which allows the "true" rate of the dissolution and deposition reaction to be determined from the weight change of the electrodes.

The circular sheet electrodes used were made from *p.a.* zinc rods (E. Merck) by cold-rolling and punching. Prior to use, the electrodes were degreased in chloroform, etched in 1 N hydrochloric acid for 15 min, washed in distilled water and acetone, dried, and weighed. The electrolytes were prepared from A.R. quality acid and salts and were pre-saturated with purified hydrogen.

The experiments were performed in a thermostated room at about 20°C. The saturated calomel electrodes used have been ascribed a potential of 0.245 V on the normal hydrogen scale (NHS) at this temperature. No attempts have been made to correct for possible liquid junction potentials. When stirring was applied, this was performed with a magnetic stirrer which was placed close to the electrode studied. This stirring was found to raise the limiting deposition current by a factor of about five (see Fig. 4).

### 4.0 RESULTS

Preliminary experiments showed 0.001 N hydrochloric acid solutions of zinc chloride and potassium chloride to give most suitable pH-conditions for correlating studies to be made on the mutually reverse reactions of the  $\text{Zn}/\text{Zn}_{\text{aq}}^{2+}$  electrode. The pH of these solutions seems low enough to exclude difficulties from zinc ion hydrolysis, and high enough to make the corrosion rate negligible as compared to the reaction rates imposed by the applied current ( $10^{-4}$ – $10^{-2}$  A/cm<sup>2</sup>). The latter was shown by the weight change of the electrodes used. The weight change measurements further showed the deposition efficiency in these solutions to be very nearly 100 %, except at current densities exceeding the limiting current for deposition. The main part of the present experiments have therefore been performed with solutions of this type.

*Potential-time curves.* Fig. 1 gives some examples of anodic potential-time curves at various constant current densities in unstirred 0.001 N hydrochloric acid + 2.999 M potassium chloride. Most of these curves show an initial rise in the potential to a stationary value. This initial rise was usually not observed in the zinc chloride containing solutions used (see below), nor in the initially

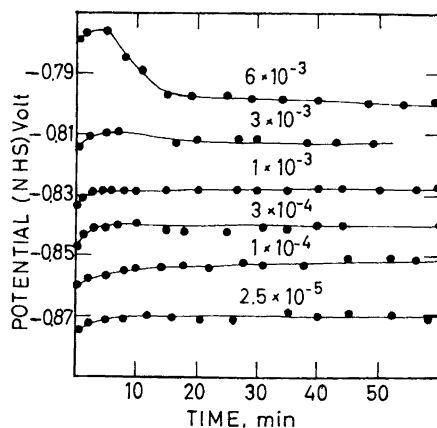


Fig. 1. Anodic potential-time curves for zinc in 0.001 M hydrochloric acid + 2.999 M potassium chloride at various current densities (A/cm<sup>2</sup>). 20°C.

zinc free solutions when stirring was applied at the anodes. In these cases, the stationary potential either prevailed from the very first reading or was reached after an initial fall in the potential (somewhat as shown by the highest curve in Fig. 1).

Fig. 2 gives some examples of cathodic potential-time curves at various constant current densities in unstirred (A) and stirred (B) 0.001 N hydrochloric acid + 0.05 M zinc chloride + 2.899 M potassium chloride. These curves are representative for those obtained for the deposition of zinc in the

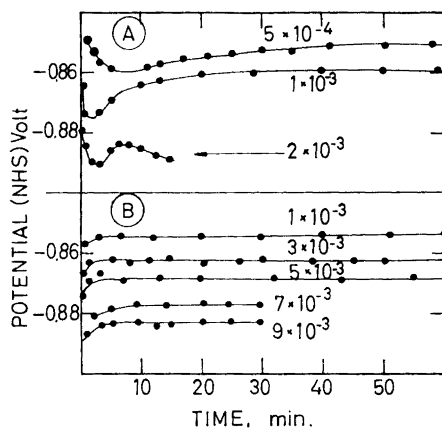


Fig. 2. Cathodic potential-time curves for zinc in unstirred (A) and stirred (B) 0.001 M hydrochloric acid + 2.899 M potassium chloride + 0.05 M zinc chloride at various current densities (A/cm<sup>2</sup>). 20°C.

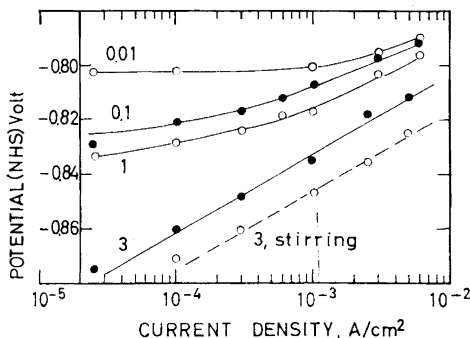


Fig. 3. Anodic polarization curves for zinc in 0.001 M hydrochloric acid solutions of potassium chloride at various total chloride molalities (0.01–3). 20°C.

present work at current densities not exceeding (or approaching too closely) the limiting current.

In constructing polarization ( $V/\log i$ ) curves from the potential-time curves and the weight change data, the potentials representing the lowest numerical polarization have been used (*i.e.* the lowest potentials shown by the anodic and the highest shown by the cathodic potential-time curves).

*Polarization curves.* Fig. 3 gives some examples of polarization curves obtained for the anodic dissolution of zinc in 0.001 N hydrochloric acid solutions of potassium chloride at various total chloride molalities (0.01–3). Except for one, these curves apply to unstirred solutions, for which case they show a distinct effect of the potassium chloride concentration on the dissolution polarization (especially at low dissolution rates). In stirred solutions, however, this effect is less distinct. This was shown by the application of stirring at anodes in the 1 M solution of this series displacing the corresponding polarization curve almost down to the one given for the stirred 3 M solution in Fig. 3. The author has so far no satisfactory explanation to give for the observed effect of the potassium chloride concentration.

The results in Fig. 3 further show the anodic polarization in the 3 M solution to obey the Tafel relationship with a slope of

$$b_a = 2.303 RT/2F \quad (3)$$

*i.e.* 29 mV per logarithmic rate unit at 20°C. This is in agreement with what is indicated above on the basis of previous work on zinc, and it is the same as previously found for the anodic dissolution of iron<sup>1</sup> and copper<sup>2</sup> to divalent ions.

Fig. 4 gives polarization data for the anodic dissolution and cathodic deposition of zinc in 0.001 N hydrochloric acid solutions of zinc chloride (0.01, 0.02 and 0.05 M) and potassium chloride at a total chloride molality of 3. The curves there drawn (solid for unstirred and dashed for stirred solutions) have been constructed from the formula:

$$i/i_0 = \pm \exp\left(\frac{n\alpha F(V-E_R)}{\nu RT}\right) \mp \left(1 \pm \frac{i}{i_{\text{lim}}}\right)^{1/\nu} \exp\left(\frac{n(\alpha-1)F(V-E_R)}{\nu RT}\right) \quad (4)$$

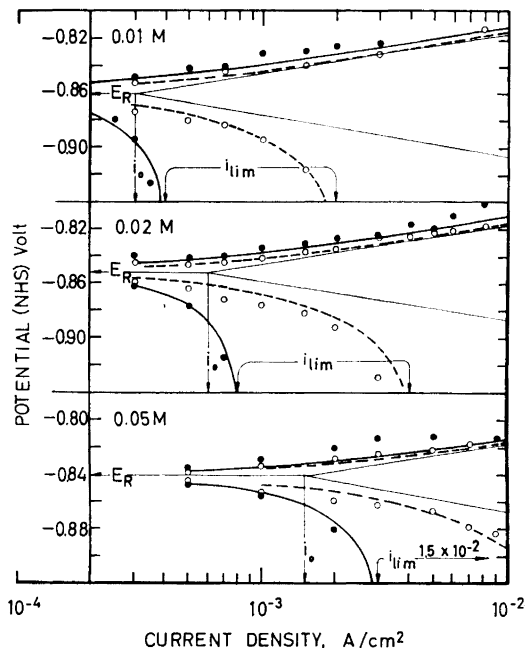


Fig. 4. Polarization curves for anodic dissolution and cathodic deposition of zinc in 0.001 M hydrochloric acid solutions of zinc chloride (0.01, 0.02, and 0.05 M) and potassium chloride at a total chloride molality of 3. The open circles apply to stirred and the closed to unstirred solutions. 20°C.

by use of the  $i_0$ ,  $i_{lim}$  and  $E_R$  values given in Fig. 4, the  $\alpha$  and  $\nu$  values corresponding to the symmetric Tafel lines there suggested, namely

$$\alpha = \nu = 1/2 \quad (5)$$

and a value of 2 for  $n$ . Where double signs are used in (4), the upper apply to dissolution and the lower to deposition. All reaction rates are thereby regarded positive, irrespective of the reactions being anodic or cathodic.

Eqn. (4) may be regarded a general polarization equation for simple metal/metal ion electrodes for which no other limiting current than the cathodic limiting diffusion current of the metal ions has to be considered<sup>5,20</sup>. It shows the combined effect of activation and concentration polarization and may, by  $i_0$  and  $\nu$ , possibly also account for what Vetter<sup>3</sup> calls crystallization polarization. The exchange current  $i_0$  must then be assumed to represent the rate of metal ion exchange between the metal lattice and the solution (and not only between possible adatoms and the solution). It is easily seen that (4) involves the simpler equations for pure activation control and pure diffusion control as special cases.

The Tafel lines drawn in Fig. 4 thus represent the absolute rate of the zinc electrode reactions at various potentials and electrolyte compositions (the

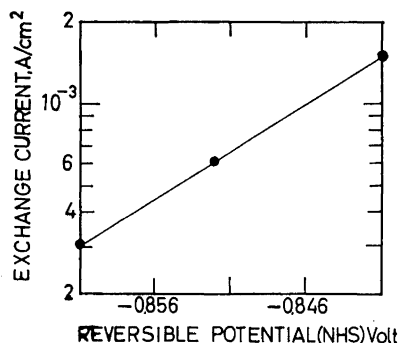


Fig. 5. Exchange current versus reversible potential for zinc in 0.001 M hydrochloric acid solutions of zinc chloride and potassium chloride at a total chloride molality of 3. 20°C.

bulk composition of the solutions applied). The relative position of these lines in the diagrams shows:

$$(d \log i_a / d \log a)_\nu = 0 \quad (6)$$

$$(d \log i_c / d \log a)_\nu = 2 \quad (7)$$

for the effect of the zinc ion activity (estimated from the reversible potentials given) on the absolute rate of the anodic and cathodic reaction, respectively. This is in accordance with what one should expect for a metal/metalion electrode with a stoichiometric factor ( $\nu$ ) of 1/2 (see eqn. (3) and Refs.<sup>3,5,20</sup>).

The relatively good fit of the experimental data in Fig. 4 to the calculated curves lends confidence to the validity of (4)–(7) in the present case and to the values suggested for the exchange current. These values are in Fig. 5 plotted versus the reversible potential of zinc in the corresponding solutions. Accepting the value of  $-0.763$  V for the standard potential of zinc<sup>21</sup>, the straight line drawn in Fig. 5 corresponds to

$$i_0 = 0.7 a \text{ A/cm}^2 \quad (8)$$

in the 3 M chloride solutions concerned. This shows the standard exchange current to be  $0.7 \text{ A/cm}^2$ . The reversible potential values given in Figs. 4 and 5 are the mean values of the potentials measured in the cell prior to application of current.

From measurements on the corrosion and the anodic dissolution of zinc in more acid solutions (to be published in a subsequent paper on the corrosion of zinc), the pH of the solution could not be found to have any direct effect on the zinc electrode reactions. This is in accordance with the results of Rojter, Polujan, and Jusa<sup>8</sup>.

## 5.0 DISCUSSION

The above results indicate the zinc electrode to exhibit combined diffusion and activation (including crystallization) polarization under the conditions applied, its polarization (at least in strong chloride solutions) being well

described by the "general" polarization equation (4). The equation is here called "general" by being assumed to cover all the mentioned types of polarization and *not* by being assigned general validity. It does, for instance, not account for possible electric field effects in the diffusion layer and the diffuse double layer, nor for possible effects of specific adsorption of ions on the metal surface. The obedience to this equation, as found in the strong (3 M) chloride solutions, may thus be an indication of such effects being negligible. This is what one should expect in the presence of a large excess inert electrolyte<sup>3</sup>. The polarization observed at lower chloride concentrations (see Fig. 3) may include such effects, however.

The way in which the term  $i/i_{lim}$  is used in (4), involves the approximation that the diffusion layer thickness is independent of the concentration difference over this layer. This approximation could formally be improved by raising the term to a power of 0.8 (see Ref.<sup>3</sup>, p. 172), but this will not have any great effect on the constructed polarization curves. Eqn. (4) also ignores a possible change in the activity coefficient of the zinc ions with their concentration in the diffusion layer. For the strong (3 M) chloride solutions, however, this may seem justified by the observed reversible potentials indicating proportionality between activity and concentration of zinc chloride (at least at zinc ion concentrations from 0.01 to 0.05 M).

The value of 1/2 used in the present case both for the symmetry factor ( $\alpha$ ) and the stoichiometric number ( $\nu$ ) gives a satisfactory fit to the experimental results. The experimental data are perhaps not accurate enough to prove the absolute correctness of this value for both factors, but they strongly indicate that it cannot be far from correct. It is at least easily seen that other simple values as 1 or 2 for the stoichiometric number do not fit the results at all. The double metal ion mechanism previously found to govern both the Fe/Fe<sub>aq</sub><sup>2+</sup> and the Cu/Cu<sub>aq</sub><sup>2+</sup> electrode reactions<sup>1,2</sup>, may thus seem to govern also the Zn/Zn<sub>aq</sub><sup>2+</sup> electrode reactions. The kinetic unit equation may thereby be written:



when also the independence of pH is remembered (compare to (1) and (2) for the iron and copper electrode reactions). This is in accordance with the stationary polarization data of Rojter, Polujan, and Jusa<sup>8</sup>.

Eqn. (9) implies that the chloride ions do not directly participate in the electrode reactions. This is substantiated by the relatively small difference shown in Fig. 3 for the anodic polarization of zinc at high current densities in unstirred solutions of widely different chloride concentrations, and also by the results of some preliminary measurements in sulphate solution (not given in this paper) showing the anodic polarization not to be very much different from what it is in chloride solution.

The present results show an appreciably higher exchange current than do the previous results of Rojter, Polujan, and Jusa<sup>8</sup>. It is so far difficult to say whether this is due to the different experimental conditions (polycrystalline zinc in chloride solution *contra* single crystal zinc in sulphate solution) or to the different experimental methods (slow galvanostatic *contra* oscillographic)



applied. The higher values may seem to be more in accordance with the polarization data reported by other authors<sup>12-15</sup>, however. These data are already discussed in the above description of previous work.

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