THE ELECTRODEPOSITION AND DISSOLUTION OF ZINC AND AMALGAMATED ZINC IN ALKALINE SOLUTIONS

J. HENDRIKX, A. VAN DER PUTTEN, W. VISSCHER and E. BARENDRECHT

Laboratory for Electrochemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 23 May 1983)

Abstract—The reaction mechanism of zinc and amalgamated zinc was investigated with the galvanostatic transient technique in the concentration range 1.5-10 M KOH. The Tafel slopes of the zinc electrode were 40 mV anodically and 120 mV cathodically. The cathodic reaction order in zincate was found to be +1. From the Tafel slopes and the dependence of the exchange current density on the activity of the KOH, the reaction orders in OH- were calculated, yielding values of 2.3 ± 0.8 in the anodic and −0.8 ± 0.2 in the cathodic direction. These results are consistent with the suggested mechanism of Bockris et al.[16] for the zinc electrode. The Tafel slope in cathodic direction of the amalgamated zinc electrode was a function of the KOH concentration (120 mV at KOH concentrations up to 3 M; about 60 mV in 10 M KOH); the anodic Tafel slope was 30 mV over the whole concentration range. These results and measurements at constant ionic strength suggest a mechanism which involves the participation of water. The difference in behaviour of the zinc electrode and the amalgamated zinc electrode is probably caused by changes in the adsorption characteristics due to amalgamation.

NOMENCLATURE

a activity (moles per l)
b constant in the Davies equationc Tafel slope (mV)
c concentration (moles per l)CDL double-layer capacity (F m-2)
CE counter electrodeE potential (V)Eo standard electrode potential (V)E 0 restpotential (V)
l ionic strength (moles per l)i current density (A m-2)i 0 exchange current density (A m-2)k rate constantnhe normal hydrogen electrode n total number of transferred electronsR molar gas constant (kJ mole-1 K-1)RDS rate determining stepRE reference electrode p reaction orderT temperature (K)WE working electrode z number of electrons in the RDS z+ - valency of cation and anion respectively

Greek characters

αa anodic transfer coefficientαc cathodic transfer coefficientγ activity coefficientη overpotential (V)νj stoichiometric coefficient for species j

INTRODUCTION

Zinc is used in a variety of alkaline batteries because of its high energy density and its ability to be discharged at high current densities[1, 2]. One of these battery systems is the secondary nickel-zinc battery, which approaches the power and energy density required for electric traction. The commercial application of this battery is hindered mainly by a limited cycle life, caused by dendrite formation and shape change of the zinc electrode. It has been found that amalgamation of the zinc electrode accelerates shape change[3-6]. The function of the amalgamation, however, is to hinder the formation of hydrogen. As discussed below, several mechanisms have been proposed for the zinc reaction, based on contradictory experimental results. For the amalgamated electrode as used in actual battery systems even less information is available. In order to gain more insight in the effect of the amalgamation on the kinetic behaviour of the zinc electrode, both the zinc electrode and the amalgamated zinc electrode were studied with the galvanostatic transient technique in 1.5-10 M KOH.

REVIEW OF PREVIOUS WORK

Several mechanisms for the zinc electrode were proposed. One of them, that of Dirkse and Hampson, is as follows[7-14]:

\[
\begin{align*}
\text{Zn}^{\text{e}} + \text{OH}^- & \rightarrow \text{Zn(OH)}_\text{ad}^\cdot, \\
\text{Zn(OH)}_\text{ad}^- & \rightarrow \text{Zn(OH)}_\text{ad}^\cdot + e^-; \\
\text{Zn(OH)}_\text{ad}^- + \text{OH}^- & \rightarrow \text{Zn(OH)}_2^+ + e^-;
\end{align*}
\]

In this mechanism, written for the anodic process, reaction (D.II) is rate-determining at very short times. On a longer time scale (> 10 μs) or at high overpotentials, the formation of kink sites, associated with reaction (D.I), becomes rate-determining. The mechanism is based on galvanostatic transient measurements at very low overpotentials (< 10 mV) in.
1-10 M KOH. It was found that the exchange current density, $i_0$, decreased as the measuring time increased. The authors did not correct for the ohmic potential drop, because in their view this drop may be neglected in such concentrated electrolytes. They also performed potentiostatic measurements at high overpotentials, but observed a maximum in the transient[14]. In double pulse measurements the maximum disappeared, but no straight Tafel lines were obtained. According to Dirkse, this behaviour is caused by adsorption of an intermediate[14].

Dirkse has also pointed out that the ionic strength of the electrolyte must play an important role[12, 15]. At high KOH concentration (>4 M) there is almost no "free" water because it is almost totally attached to the ions present. This will have a strong effect on the activity coefficient of the OH$^-$ ion. Dirkse therefore has carried out some measurements at constant ionic strength (with the aid of KF, for $F^-$ is isoelectronic with OH$^-$) in order to maintain the water activity constant.

A second mechanism is that of Bockris et al.[16]:

$$\text{Zn} + \text{OH}^- \rightarrow \text{ZnOH}^- + e^- \quad \text{(B.I)}$$
$$\text{ZnOH} + \text{OH}^- \rightarrow \text{Zn(OH)$_2^-$} \quad \text{(B.II)}$$
$$\text{Zn(OH)$_2^-$} + \text{OH}^- \rightarrow \text{Zn(OH)$_3$}^- + e^- \quad \text{(B.III)}$$
$$\text{Zn(OH)$_3$}^- + \text{OH}^- \rightarrow \text{Zn(OH)$_4$}^{2-} \quad \text{(B.IV)}$$

In this mechanism, reaction (B.III) is the rate-determining step (RDS), both in anodic and cathodic direction. The first two steps of the mechanism (B.I + B.II) are derived from theoretical arguments. Bockris et al. come to their conclusions on the basis of galvanostatic and potentiostatic transient measurements in 0.1-3 M KOH, both at very low and high overpotentials. Compensation for the IR-drop was found to be necessary even using a special reference electrode construction in which this electrode could be placed as close as 0.0025 cm to the working electrode. The results of the potentiostatic and the galvanostatic experiments were identical. Bockris et al. also determined reaction orders with respect to OH$^-$ and Zn(OH)$_2^-$, in both anodic and cathodic direction. In their opinion the formation of kink sites is not rate-determining because the $i_0$ obtained from extrapolation of the Tafel line was identical with the value from experiments at very low overpotential. The same mechanism was also found by other workers from steady state measurements[17]. Their results from transient measurements, however, were not consistent with this mechanism. This is a good example of the contradictory information regarding the kinetics of the zinc electrode.

About the amalgamated electrode as used in actual battery systems, almost no kinetic information is available. Dirkse has performed some experiments [18] in order to prove that in this case charge transfer is rate-determining, and not the formation of kink sites. The amalgamated electrode must then be regarded as a "liquid", which implies that kink site formation cannot play a role in the electrode processes. He found that indeed the amalgamated electrode gave rise to higher current densities than the zinc electrode for a given overpotential. The resulting mechanism has the same reaction sequence as for the zinc electrode, only the RDS is now shifted to reaction D.II. More information is available about the mechanism of the zinc amalgam electrode. The question arises, however, if these results can be applied to the amalgamated zinc electrode; amalgam experiments make use of a mercury drop in which a small amount of zinc is dissolved, being the reverse of an amalgamated electrode, in which a small amount of mercury is introduced onto solid zinc. Even the proposed mechanisms for zinc amalgam are contradictory, Payne and Bard[19] suggest a similar mechanism as that of Dirkse and Hampson (Zn amalgam written as Zn), with conclusions drawn from potential step chronocoulometry, d.c. polarography and potential sweep voltammetry experiments, followed by thorough mathematical analysis. However, Despic et al.[20] suggest a mechanism with a chemical step between two electron transfer reactions as the RDS. Moreover, they consider water as a reaction partner.

**EXPERIMENTAL**

The zinc electrode and the amalgamated electrode were studied by means of the galvanostatic transient technique in alkaline solutions with concentrations ranging from 1.5 to 10 M KOH and in KOH-KF electrolytes at constant ionic strength. The zincate concentration was varied from 0.011 to 0.4 M.

**The cell**

All experiments were performed in the cell given in Fig. 1. The total cell volume was approx. 60 ml. The counter electrode (CE) was made of zinc (99.9% Merck) in order to maintain the zincate concentration as constant as possible. As a reference electrode (RE) a Hg/HgO-electrode was used having the same electrolyte as used in the cell. All potentials are given with respect to this electrode. In general, the distance between the WE and the tip of the Luggin capillary-RE system was 2 mm in order to avoid shielding of the electrode. Before each measurement nitrogen was bubbled through the cell to remove dissolved oxygen. All experiments were performed at room temperature (20°C).

---

**Fig. 1. The cell.**
The electrode

The electrode consisted of a polycrystalline zinc rod (99.9 %, Merck) machined to 6 mm diameter and embedded in KEL-F. This type of electrode construction was used both for the zinc electrode and the amalgamated electrode.

Electrode pretreatment

The zinc electrode was first mechanically polished using SiC paper 600. After this treatment, the electrode was electrochemically etched in the electrolyte under investigation by varying the potential three times from −800 to −1600 mV vs Hg/HgO and back (scan rate 50 mV s⁻¹). During this scan much more zinc dissolved into the solution than was deposited on the surface. The result was a shiny electrode in which the separate grains could be clearly discerned. The amalgamated electrode was prepared as follows; the electrode was polished using SiC paper 600 and then diamond paste 3 µm. The electrode was amalgamated by immersing it for 60 s into a solution of 0.3 g HgCl₂ in 10 g acetone. The resulting black film on the electrode surface was wiped off, the electrode was rinsed with double distilled water and electrochemically etched in the same way as the zinc electrode. Before each experiment the electrode was amalgamated and pretreated anew.

Solution preparation

The zincate solutions were prepared from analytical grade chemicals (p.a. Merck) and double distilled water. For the experiments at constant ionic strength KF (p.a. Merck) was used.

Measuring technique

The galvanostatic pulse technique was used, with a pulse time of 5 ms or shorter. The set-up is based on a concept of Bockris et al.[21]. The cathodic set-up is depicted in Fig. 2.

RESULTS FOR THE ZINC ELECTRODE

E–t transients

In both the anodic and cathodic Tafel region a distinct plateau (after charging of the double-layer) was observed for the transients. The ohmic potential drop, which could be read directly from the oscilloscope screen, could not be neglected since it occasionally exceeded several times the values for the activation overpotential; the transients obtained at very low current densities did not reach a constant value after charging of the double-layer. This makes extrapolation to zero-time hazardous, thus, no values for i₀ were calculated from these experiments. At very high current densities the overpotential increased linearly with time after charging of the double-layer, due to concentration polarization[22]. In this case the linear region was extrapolated to zero-time and the zero-time value was used for calculating the activation overpotential. Sometimes a small maximum was observed in the transient. The possibility of the appearance of such a maximum in the transient for multistep reactions was evaluated by Pionski[23] for several theoretical models. According to Selinger[24] the maximum can be explained by polymerization of zinc species at the electrode surface. The appearance of the maximum had almost no effect on the extrapolated value of the activation overpotential.

It was noted that the activity of the zinc electrode appeared to be a function of the waiting time at the restpotential. This activity, reflected in the i₀ value, decreased with increasing waiting time. It was tried to find a pretreatment which would yield a reproducible electrode surface; applying a high anodic prep)e of 5000 A m⁻² did not have the desired result, nor did cathodic reduction with hydrogen evolution in 1 M KOH as recommended by Bockris et al.[16]. It seems, therefore, that the activity of the electrode is determined by its actual surface state. Consequently, in order to get as reproducible results as possible, it was decided to perform the measurements after 30 min waiting time at the restpotential. Within a single measurement the Tafel slope did not depend on i₀. Values for the capacity of the double-layer, calculated from the slope of the tangent at the very beginning of the transient, were very high (several hundreds µF cm⁻²) and showed little variation with solution composition.

Tafel lines

In general, the applied current densities did not exceed 5000 A m⁻². Measurements at higher i were not possible due to fast occurring concentration polarization, making the extrapolation to zero-time impossible. Examples of results for the zinc electrode in the anodic and cathodic directions are given in Figs 3 and 4. As can be seen from these figures the Tafel lines are linear over one decade of current density. Results of
the experiments as a function of KOH concentration
are given in Table 1. The anodic Tafel slope is 41
± 7 mV, the cathodic one 118 ± 8 mV.

Restpotentials
In Table 2 the restpotentials of zinc vs Hg/HgO are
given as a function of KOH concentration. The zincate
concentration was 0.1 M. The restpotentials showed
some fluctuations, probably due to the interference of
hydrogen evolution. Because the corrosion current is
low and \( i_0 \) of the zinc/zincate couple is high, the
restpotentials will differ only slightly from the equilib-
rium potentials. These equilibrium potentials were
calculated according to the Nernst equation, using the
Davies equation[25] for the activity coefficients, since
the activity coefficients of KOH and \( KZn(OH)_4 \), in
the presence of each other, are not known:
\[
-\log \gamma_+ = 0.509 z_+ z_- \left( \frac{\sqrt{I}}{\sqrt{I + 1}} - B \frac{I}{I + 1} \right),
\]
where \( I \) is the ionic strength of the solution, \( \gamma_+ \) the
activity coefficient and \( B \) a constant. Although this
empirical equation is valid only for concentrations up
to 1 M, Boden et al.[25] calculated values of the
activity coefficients for KOH solutions up to 10 M,
which almost coincided with the measured values of
Akerlof and Bender[26]. The best agreement was
found for \( B = 0.275 \). The values for the activity
coefficients of zincate were also calculated with this
equation. For the activity of water, values obtained for
NaOH solutions were adopted[27]. The activity of the
solids (Zn, Hg, HgO) was considered to be unity. The
calculated equilibrium potentials are presented in
Table 3.
From Tables 2 and 3 one can see that the agreement
is excellent. The restpotentials as a function of zincate
concentration in 7 M KOH are given in Table 4. In this
table are also shown the calculated values using, again,
the Davies equation. From Table 4, one can see that
there also the agreement between the measured and the
calculated restpotentials is good.

Reaction order in hydroxyl ions
Because the fluctuations of \( i_0 \) are a function of the
surface state of the electrode, reaction orders have to
be determined from measurements at the same elec-
trode. At each concentration, a galvanostatic run was
made to obtain the Tafel lines. After completion of the
experiment, the first solution was tested again; indeed
the Tafel line was not shifted more than 10 mV. The
reaction order with respect to species \( j \) is defined as
follows:
\[
P_j = \left( \frac{\partial \log i}{\partial \log a_j} \right)_{E,E_0}.
\]
It is necessary to use activities (so to know the activity
coefficients) instead of concentrations as done by most
authors, because here very high concentrations were
used. The fact that the reaction order is defined at
constant potential \( E \) causes difficulties in the measure-
ment of \( \mu \) with respect to OH\(^-\); in order to plot the
Tafel lines with respect to the same reference electrode,
the change in equilibrium potential must be known as a
function of KOH activity. This change cannot be
measured directly since the potential of the RE also
changes with the KOH activity. To use a pH in-

Table 1. Measured values of Tafel slope \( b \) and \( i_0 \) of the zinc electrode as a function of
KOH concentration

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Anodic</th>
<th>Cathodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH/O.1M ZnO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 M KOH/O.1M ZnO</td>
<td>30-100</td>
<td>120-160</td>
</tr>
<tr>
<td>3 M KOH/O.1M ZnO</td>
<td>100-350</td>
<td>180-300</td>
</tr>
<tr>
<td>7 M KOH/O.1M ZnO</td>
<td>30-100</td>
<td>100-250</td>
</tr>
<tr>
<td>10 KOH/O.1M ZnO</td>
<td>100-110</td>
<td>200-280</td>
</tr>
<tr>
<td></td>
<td>38-40</td>
<td>117-125</td>
</tr>
<tr>
<td></td>
<td>40-43</td>
<td>110-125</td>
</tr>
<tr>
<td></td>
<td>40-43</td>
<td>120-125</td>
</tr>
</tbody>
</table>
dependent RE is not desirable, since unknown liquid-
junction potentials are so introduced by the different
electrolytes in the RE and the WE compartment. Therefore, direct measurement of \( p \) is not possible.

An alternative is the calculation of \( p \) from the
dependence of \( i_0 \) on KOH activity. For the anodic
process

\[
i_0 = k \Pi_a \exp \left( \frac{\alpha_o z F E_r}{RT} \right),
\]

(3)

\[
\left( \frac{\partial \log i_0}{\partial \log a} \right) = p_j + \frac{\alpha_o z F}{2.3RT} \left( \frac{\partial E_r}{\partial \log a_j} \right).
\]

(4)

Consequently, for the cathodic process:

\[
\left( \frac{\partial \log i_0}{\partial \log a_j} \right) = p_j - \frac{\alpha_o z F}{2.3RT} \left( \frac{\partial E_r}{\partial \log a_j} \right).
\]

(5)

Now, \( \left( \frac{\partial E_r}{\partial \log a_j} \right) \) can be obtained from the Nernst
equation (\( E_r \) in V vs nhe):

\[
E_r = -1.184 + \frac{RT}{2F} \ln \frac{\gamma_{K\text{ZnOH}} \gamma_{K\text{ZnOH}^+}}{\gamma_{KOH} \gamma_{KOH}^+}.
\]

(6)

The activity coefficients can be obtained from
Equation (1). In Table 5 the calculated activities of KOH and the restpotentials vs nhe are given for
the different solutions. From these data it follows that
\( \left( \frac{\partial E_r}{\partial \log a_{\text{KOH}}} \right) = -87.3 \text{ mV} \). According to
Equation (4) a value of 2.3 \pm 0.8 can be calculated for
the anodic reaction order. [The measured value of
\( \left( \frac{\partial E_r}{\partial \log a_{\text{KOH}}} \right) \) was 0.1.] In cathodic direction
[Equation (5)] the calculation yields a value of \(-0.8 \pm 0.2 \).

Reaction orders in zincate

In contrast to the experiments at different KOH
concentrations the reaction order in zincate can be measured directly. In these experiments the zincate concentration was varied from 0.011 to 0.4 M, in 7 M
KOH. Again activities have to be used instead of concentrations. However, since the ionic strength is
about the same for the different solutions, the activity coefficient of zincate should not vary with the zincate concentration. Therefore, we suppose it makes no difference now, whether activities or concentrations are used for the determination of the reaction orders in zincate. The results in the cathodic direction are given in
Fig. 5. The measured cathodic \( p \)-value in zincate is
1.3. The same experiment in anodic direction gave a
value of 0.

**Experiments at a constant ionic strength**

In order to eliminate the effect of changes in the
activity of water as a function of the KOH concentra-
tion, experiments were performed at a constant
ionic strength of 10 M. As a supporting electrolyte KF
was used. Although the changes in the activity of water
can be significant, the results showed that these
changes did not make any difference for the zinc
electrode reaction. The Tafel slopes remained con-
stant; \( i_0 \) kept the same order of magnitude.

**RESULTS FOR THE AMALGAMATED
ELECTRODE**

The transients of the amalgamated electrode were
different from those obtained at the zinc electrode. First of all, the rise time of the transients was much
smaller, caused by a smaller value of \( C_{DL} \) and not by an
increase of \( i_0 \). In general, the values for \( C_{DL} \) were
about ten times smaller than in the case of the zinc
electrode. Another difference was the behaviour at very
low \( i \). In contrast to the zinc electrode a distinct plateau
in the \( E-t \) transient was observed, thus values for
\( i_0 \) could also be obtained from measurements at low
overpotential. In Fig. 6 the results of three separate
experiments at low overpotential are presented. It can
be seen that, again, the activity of the electrode (\( i_0 \)) is a
function of the actual surface state.

**Tafel lines**

The Tafel lines were measured for four different
KOH concentrations. Typical examples of these ex-
periments are given in Figs 7 and 8 (for the anodic and
cathodic situation respectively). The deviation of the
linear region from the anodic Tafel line was probably
brought about by a change in the surface state of the
electrode caused by the passage of such a high current.
The results of the complete series of experiments are
summarized in Table 6. The anodic Tafel slope is 30
\pm 5 mV; the cathodic one appears to depend on the
KOH concentration. At concentrations up to 3 M, 115

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( a_{H_2O} )</th>
<th>( \gamma_{KOH} )</th>
<th>( \gamma_{K_2ZnOH} )</th>
<th>( E_r ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M KOH/0.1 M ZnO</td>
<td>0.95</td>
<td>0.9</td>
<td>0.8</td>
<td>-1332</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>0.88</td>
<td>1.3</td>
<td>1.7</td>
<td>-1352</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>0.62</td>
<td>4.2</td>
<td>17.7</td>
<td>-1368</td>
</tr>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>0.38</td>
<td>10.6</td>
<td>113</td>
<td>-1372</td>
</tr>
</tbody>
</table>
Table 4. Measured and calculated restpotentials of zinc in 7 M KOH as a function of zincate concentration

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_r$ (measured) (mV)</th>
<th>$E_r$ (calculated) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 M ZnO</td>
<td>-1353</td>
<td>-1350</td>
</tr>
<tr>
<td>0.1 M ZnO</td>
<td>-1367</td>
<td>-1368</td>
</tr>
<tr>
<td>0.04 M ZnO</td>
<td>-1375</td>
<td>-1379</td>
</tr>
<tr>
<td>0.11 M ZnO</td>
<td>-1386</td>
<td>-1394</td>
</tr>
</tbody>
</table>

Table 5. Calculated activities of KOH and restpotentials of the zinc electrode vs Hg as a function of KOH concentration; the zincate concentration was 0.1 M

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\gamma_{KOH}$</th>
<th>log $a_{KOH}$</th>
<th>$E_r$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M KOH</td>
<td>0.9</td>
<td>0.1</td>
<td>-1222</td>
</tr>
<tr>
<td>3 M KOH</td>
<td>1.3</td>
<td>0.6</td>
<td>-1270</td>
</tr>
<tr>
<td>7 M KOH</td>
<td>4.2</td>
<td>1.4</td>
<td>-1345</td>
</tr>
<tr>
<td>10 M KOH</td>
<td>10.6</td>
<td>2.0</td>
<td>-1386</td>
</tr>
</tbody>
</table>

Fig. 5. Determination of the cathodic reaction order in zincate for the zinc electrode in 7 M KOH.

$= \pm 15$ mV and at high concentrations (10 M) $= 55 \pm 8$ mV was found.

Restpotentials

In Table 7 the restpotentials of the amalgamated electrode are given as a function of KOH concentration. It can be seen that these values are approx.

Table 6. Measured values of Tafel slope $b$ and $i_0$ of the amalgamated electrode as a function of KOH concentration; the zincate concentration was 0.1 M

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$i_0$ (A m$^{-2}$)</th>
<th>$b_a$ (mV)</th>
<th>$i_0$ (A m$^{-2}$)</th>
<th>$b_c$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M KOH</td>
<td>50–200</td>
<td>27–32</td>
<td>50–200</td>
<td>103–129</td>
</tr>
<tr>
<td>3 M KOH</td>
<td>50–230</td>
<td>27–29</td>
<td>50–270</td>
<td>118–120</td>
</tr>
<tr>
<td>7 M KOH</td>
<td>50–90</td>
<td>27–29</td>
<td>80–100</td>
<td>60–120</td>
</tr>
<tr>
<td>10 M KOH</td>
<td>80–420</td>
<td>29–34</td>
<td>100–520</td>
<td>50–60</td>
</tr>
</tbody>
</table>
Electrodeposition and dissolution of zinc and amalgamated zinc

Table 7. Measured restpotentials vs Hg/HgO of the amalgamated electrode as a function of KOH concentration

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_r$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M KOH/0.1 M ZnO</td>
<td>$-1342 \pm 2$</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>$-1362 \pm 6$</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>$-1383 \pm 3$</td>
</tr>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>$-1390 \pm 8$</td>
</tr>
</tbody>
</table>

15 mV more negative than the values for zinc. This is probably caused by a change in $E^0$ and/or the activity of Zn, due to amalgamation.

**Reaction orders in hydroxyl ions**

In this case too, the reaction orders cannot be measured. The $i_0$ was virtually pH independent:

$$\frac{\partial \log i_0}{\partial \log c_{OH^{-}}} = -0.1 \text{ to } +0.2.$$

The reaction orders in the hydroxyl ion can be calculated according to Equations (4) and (5). The resulting values are $3.1 \pm 1.1$ for the anodic $p$. The cathodic $p$ was $-0.8 \pm 0.3$ for KOH concentrations up to 3 M, and $-1.6 \pm 0.6$ for 10 M KOH.

**Reaction orders in zincate**

Since the cathodic Tafel slope is a function of the KOH concentration, the $p$ in zincate was measured both in 3 M and 10 M KOH in the same way as for the zinc electrode. Both experiments gave a value of $+0.9$ for the cathodic $p$. In the anodic direction this value was 0.

**Experiments at constant ionic strength**

In contrast to the results for zinc, the ionic strength had a distinct influence on the kinetics of the amalgamated electrode. The anodic Tafel slope remained the same, but the cathodic slope was 50–59 mV for the whole KOH concentration region. The $i_0$ was pH independent.

**CHARACTERIZATION OF THE AMALGAMATED ELECTRODE**

To characterize the amalgamated electrode two facts are of importance, viz. the total amount of mercury on the surface and the distribution of the mercury over, and in, the zinc. The total amount of mercury on the electrode surface was measured as follows; ten thin circular zinc discs (diameter 8 mm) were amalgamated under the conditions given above. Thereafter, the discs were dissolved in 25 ml concentrated nitric acid and the mercury concentration of this solution was measured by atomic absorption. The mercury content of the zinc electrode was 0.9 mg cm$^{-2}$. Second, it was investigated whether the mercury forms alloys with the zinc on a time scale of a few h. The X-ray diffractograms (Cu, Kα) of the zinc electrode and the amalgamated electrode did not show any difference. Moreover, the calculated values for the lattice constants almost coincided with the values on the ASTM card of zinc, thus the lattice was not stretched due to possible diffusion of mercury into the zinc lattice.

The distribution of the mercury over the zinc surface was investigated by electron probe micro-analysis. This technique did not reveal segregation of the mercury. Therefore, it must be assumed that mercury is distributed regularly over the surface. These findings agree with the results of Swift et al.[28]. Moreover, they showed that on a time scale of a few h, no mercury will diffuse into the grains. Such diffusion had only to be taken into account after a period of four months.

**DISCUSSION**

The results are summarized in Table 8. The interpretation of the results for the zinc electrode is rather straightforward. The results are in full agreement with the mechanism suggested by Bockris et al. for KOH concentrations up to 3 M and hence in conflict with the mechanism of Dirkse and Hampson. Tafel-slopes of 40 mV in anodic and 120 mV in cathodic direction and the calculated reaction orders for OH$^-$ indicate the following reaction as RDS, in both anodic and cathodic direction.

$$\text{Zn(OH)}_2^+ + \text{OH}^- \rightarrow \text{Zn(OH)}_3^+ + e^- \quad \text{(B.III)}$$

**Table 8. Results of the kinetic experiments for the zinc electrode and the amalgamated electrode**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Anodic</th>
<th>Cathodic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc electrode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tafel slope $b$ (mV)</td>
<td>$41 \pm 7$</td>
<td>$118 \pm 8$</td>
</tr>
<tr>
<td>$i_0$ (A m$^{-2}$)</td>
<td>$30-350$</td>
<td>$100-300$</td>
</tr>
<tr>
<td>$p$ (OH$^-$)</td>
<td>$2.3 \pm 0.8$</td>
<td>$-0.8 \pm 0.2$</td>
</tr>
<tr>
<td>$p$ (Zn(OH)$_2^+$)</td>
<td>$0$</td>
<td>$1.3$</td>
</tr>
<tr>
<td>Effect of ionic strength</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Amalgamated electrode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tafel slope $b$ (mV): $c_{OH^-}$ up to 3 M</td>
<td>$30 \pm 5$</td>
<td>$115 \pm 15$</td>
</tr>
<tr>
<td>$i_0$ (A m$^{-2}$)</td>
<td>$50-420$</td>
<td>$55 \pm 8$</td>
</tr>
<tr>
<td>$p$ (OH$^-$): $c_{OH^-}$ up to 3 M</td>
<td>$3.1 \pm 1.1$</td>
<td>$-0.8 \pm 0.3$</td>
</tr>
<tr>
<td>$p$ (Zn(OH)$_2^+$)</td>
<td>$0$</td>
<td>$1.6 \pm 0.6$</td>
</tr>
<tr>
<td>Effect of ionic strength</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>
The calculated anodic reaction order in OH\(^-\) (2.3 \pm 0.8) is somewhat lower than three. However, this value lies within the error bars. Since the electroactive species is Zn(OH)\(^2\)-, the first two steps in the cathodic direction are

\[
\begin{align*}
\text{Zn(OH)}^2- & \rightarrow \text{Zn(OH)}^3+ OH^- , \\
\text{Zn(OH)}^3+ e^- & \rightarrow \text{Zn(OH)}^2+ OH^- .
\end{align*}
\]

The remaining steps of the mechanism of Bockris et al. are based on theoretical arguments.

Although \(i_0\) cannot be determined exactly from our experiments at low overpotentials one may conclude that the value for \(i_0\) from these experiments, and from experiments at high overpotential (Tafel region) did not differ by more than a factor of three. This is in agreement with the findings of Bockris et al., who concluded from this information that kink site formation is not rate-limiting. Unfortunately, direct measurement of the reaction orders in OH\(^-\) is not possible. It has become clear in our experiments that \(i_0\) is virtually pH independent. This is again in agreement with the findings of Bockris et al. and contradicts measurements of Dirkse, who obtained a maximum at 7 M KOH.[10]

The same applies to the measurement of the reaction orders in zincate, Fig. 5, which reveal that \(i_0\) depends on the zincate concentration. Dirkse and Hampson, however, observed that \(i_0\) was practically independent of the zincate concentration[10, 13].

The differences in the \(i_0\) values from our work and that of others must be attributed to differences in electrode pretreatment and the measuring period. The highest values for \(i_0\) were obtained when short measuring periods (\(\mu s\) range) were used. Bockris et al. reported values of 80–3700 A m\(^{-2}\) in electrolytes from 0.1 to 3 M KOH. The fact that Dirkse et al. did not obtain straight Tafel lines at high overpotentials[14] is probably caused by the fact that the ohmic potential-drop was not taken into account. Our experiments showed that the 1-k dropped certainly cannot be neglected. The ionic strength has no influence on the mechanism and the kinetics of the zinc electrode.

The explanation of results for the amalgamated electrode is not equally straightforward. The formation of kink sites is of no importance since \(i_0\) values measured in experiments at low and very high overpotentials are the same. The results at constant ionic strength suggest that water participates as a reaction partner. On the basis of this assumption, and the obtained Tafel slopes, we propose the following mechanism in which the reacting species, adsorbed at the electrode, is the water-containing species Zn[OH]_{2}(H_{2}O)_{n}]^{2-}:

\[
\begin{align*}
\text{Zn[OH]_{2}(H_{2}O)_{n}]^{2-}} & \rightarrow \text{Zn[OH]_{3}(H_{2}O)_{k}]^{-} + OH^{-} + (a-b)H_{2}O,} \\
\text{Zn[OH]_{3}(H_{2}O)_{k}]^{-} + e^{-} & \rightarrow \text{Zn[OH]_{2}(H_{2}O)_{k}]^{-} + OH^{-} + (b-c)H_{2}O,} \\
\text{Zn[OH]_{2}(H_{2}O)_{k}]^{-} & \rightarrow \text{Zn[OH]_{3}(H_{2}O)_{n}]} + OH^{-} + (c-d)H_{2}O,} \\
\text{Zn[OH]_{3}(H_{2}O)_{n}] + e^{-} & \rightarrow \text{Zn(Hg) + OH^{-} + dH_{2}O.}
\end{align*}
\]

In anodic direction reaction (P.I) is rate-determining, independent of the ionic strength. The shift in the cathodic Tafel slope from 120 to 60 mV, when going to high KOH concentrations, can be explained if \((c-d)\) is smaller than \((b-c)\). At high KOH concentrations, there is almost no free water present, so reaction (P.III) will proceed faster than reaction (P.II). Consequently, the Tafel slope changes from 120 to 60 mV. At a constant ionic strength of 10 M there is no free water available in each solution, thus reaction (P.III) will be the RDS over the whole concentration range. The question arises what causes the different behaviour of the zinc and the amalgamated zinc electrode, since the ionic strength does not have any influence on the behaviour of the zinc electrode. In our view, this change is caused by a difference in adsorption because the double-layer capacities differ by a factor of ten. The high double-layer capacity of the zinc electrode suggests that the electrode is covered with adsorbed OH\(^-\) ions. The capacity of the amalgamated electrode approaches the value for pure mercury. This implies that the surface of this electrode is mainly covered with adsorbed water molecules. Consequently, the water activity only influences the amalgamated electrode and at the zinc electrode only OH\(^-\) is involved. Thus, the difference in the mechanism of the zinc electrode and the amalgamated electrode is caused by a change in adsorption behaviour, rather than by easier formation of kink sites due to the amalgamation.

Acknowledgment—The authors wish to thank Prof. J. R. Selman, on leave from the Illinois Institute of Technology, Chicago, Illinois, for helpful discussions and suggestions.

REFERENCES

Electrodeposition and dissolution of zinc and amalgamated zinc