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IMPEDANCE MEASUREMENTS OF ZINC AND AMALGAMATED ZINC ELECTRODES IN ALKALINE ELECTROLYTE

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Abstract—The behaviour of zinc and amalgamated zinc electrodes in alkaline zincate electrolytes was studied with the impedance technique in the frequency range 0.01–65,000 Hz. The impedance spectra of the amalgamated zinc electrode can be adequately described with a kinetic and diffusion controlled reaction. The results are not affected by the method of amalgamation. The zinc electrode shows a different impedance spectrum indicating that surface processes in which intermediate species such as $\text{Zn(OH)}_2$, $\text{Zn(OH)}_3^-$, $\text{Zn(OH)}_4^{2-}$ are involved, play a more important role. The $i_C$-values that can be derived from the impedance data were found to be in good agreement with the values obtained with the galvanostatic pulse technique.

1. INTRODUCTION

The use of the impedance technique for the study of electrode processes has expanded rapidly over the last three decades. With this technique information has been obtained on deposition and dissolution phenomena of the zinc electrode[1–7]. However, the interpretations of the results differ, in particular with respect to the kind and number of adsorbed intermediate species. Much work has been carried out on the kinetics of the zinc reaction at a mercury electrode, but the amalgamated zinc electrode has not been investigated. Because of the application of zinc in batteries where mostly amalgamated zinc electrodes are employed, the behaviour of zinc and amalgamated zinc electrodes in alkaline zincate electrolyte was studied with the impedance method.

2. EXPERIMENTAL

2.1. Electrodes and cell

The impedance measurements of the disc electrodes were carried out in the three-compartment cell, as given earlier[8]. The electrolyte was an alkaline solution with concentrations ranging from 1.5–10 M KOH and 0.01–0.1 M ZnO. The measurements were performed at 0 and 2000 rpm. The latter rotation frequency was chosen in order to minimize the convective diffusion of the chemical species towards the electrode.

The counter electrode 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 working electrode 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).

The electrodes. Several zinc and amalgamated zinc disc electrodes (area 0.28 cm²) were investigated.

The electrode consisted of a polycrystalline zinc rod (99.9 % Merck), machined to 6 mm diameter and embedded in KelF. This type of electrode construction was also used for the amalgamated zinc electrodes, which consisted of a proprietary zinc rod containing 1 and 6 wt. % mercury, respectively. These pre-amalgamated zinc alloys are manufactured with a special production technique[9] by Metallurgy Hoboken-Overpelt, Belgium. The electrodes with 1 and 6 wt. % mercury are nominated Zn(Hg, I) and Zn(Hg, II) respectively.

A third amalgamated electrode [Zn(Hg, III)] was prepared as follows: the zinc electrode was polished using SiC paper 600 and then diamond paste 3 μm. The electrode was amalgamated by immersing 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.

Electrode pretreatment. The zinc and the amalgamated zinc electrodes [Zn(Hg, I) and Zn(Hg, II)] were 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 to five 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.

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2.2. Instrumentation

The apparatus used for the impedance measurements incorporates a frequency response analyser (Solartron 1250), an electrochemical interface (Solartron 1186) and a microcomputer (HP 9816), which completely controls the experiment. The complete set-up is given in Fig. 1.

Measurements were made at frequencies from 0.01 Hz to 65 kHz; the amplitude of the sinusoidal potential perturbation is 1 mV (rms).

Most of the impedance diagrams were determined at the rest potential of the zinc electrode; some experiments were carried out with anodic or cathodic polarization.

3. RESULTS

3.1. Amalgamated zinc electrodes

In Fig. 2 a typical impedance spectrum of the Zn(Hg, III)-electrode is shown at its rest potential in 7 M KOH/0.1 M ZnO in quiescent solution. The spectra of the Zn(Hg, I)- and Zn(Hg, II)-electrodes are similar. This diagram can be described with the Randles equivalent circuit[10, 11] for a simple charge transfer and diffusion-controlled reaction. From the impedance plot the exchange current density ($i_0$), the capacity of the double layer ($C_{dl}$), the Warburg coefficient ($\sigma$) and the diffusion coefficient of the zincate ion ($D$) can be calculated, using the formulas[11]

\[
(R_{ct})_{rev} = \frac{RT}{nF} \left( \frac{c_{ox}^n}{c_{ox}^s} \right)^{1-\sigma} \quad [\Omega] 
\]

\[
(\sigma)_{rev} = \frac{RT}{n^2F^2A} \left( \frac{1}{2D} \right)^{1/2} \quad [\Omega^{-1/2}]
\]

where

$A$ = surface area of the electrode [cm$^2$]
$D$ = diffusion coefficient of the metal ion [cm$^2$ s$^{-1}$]
$c_{ox}^n$ = concentration of metal ion at the electrode surface [mol cm$^{-2}$]
$c_{ox}^s$ = concentration of metal ion in the bulk phase [mol cm$^{-3}$]
$I_0$ = exchange current [A]
$n$ = electrons per molecule oxidized or reduced
$\sigma$ = cathodic transfer coefficient.

As is clear from Fig. 2 the simulated impedance plot for the Zn(Hg, III) electrode, shown by the drawn line, is in good agreement with the measured values.

In Table 1 the results of all experiments are tabulated as a function of the electrolyte composition and the kind of amalgamated surface. The table shows that the kind of amalgamation and the concentration of the electrolyte do not noticeably influence the $i_0$ and $C_{dl}$-values.

When the disc electrode is rotated, the low frequency domain of the impedance diagram changes. A typical diagram is shown in Fig. 3. (The three amalgamated electrodes produce similar diagrams.) These diagrams can also be described with the Randles circuit, in which now the Warburg impedance has to be corrected for convective transport. This in particular affects the low
Impedance measurements of zinc electrodes

Table 1. \( i_0 \), \( C_{dl} \), \( \sigma \) and \( D \) as function of the solution composition and the type of amalgamated surface

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrode</th>
<th>( i_0 ) (A cm(^{-2})) \times 10^4</th>
<th>( C_{dl} ) (( \mu )F cm(^{-2}))</th>
<th>( \sigma ) (( \Omega ) s(^{-1/2}))</th>
<th>( D ) cm(^2) s(^{-1} \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, I)</td>
<td>200-290</td>
<td>28-34</td>
<td>1.16-1.23</td>
<td>1.9-2.1</td>
</tr>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, II)</td>
<td>240-270</td>
<td>30-33</td>
<td>1.02</td>
<td>2.7</td>
</tr>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, III)</td>
<td>200-210</td>
<td>25</td>
<td>1.12</td>
<td>2.3</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, I)</td>
<td>190-260</td>
<td>23-25</td>
<td>1.09</td>
<td>2.4</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, II)</td>
<td>240-294</td>
<td>30-32</td>
<td>1.08</td>
<td>2.4</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, III)</td>
<td>160-250</td>
<td>23-24</td>
<td>1.08</td>
<td>2.4</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, I)</td>
<td>330-650</td>
<td>53-68</td>
<td>0.97</td>
<td>3</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, II)</td>
<td>50-250</td>
<td>23-32</td>
<td>0.92</td>
<td>3.3</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>Zn(Hg, III)</td>
<td>175-650</td>
<td>44-66</td>
<td>0.89</td>
<td>3.6</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>Zn(Hg, I)</td>
<td>66-102</td>
<td>31-32</td>
<td>8.2</td>
<td>4.2</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>Zn(Hg, II)</td>
<td>63-115</td>
<td>28-39</td>
<td>5.2</td>
<td>10.4</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>Zn(Hg, III)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 3. Measured impedance plot (•) of Zn(Hg, III)-electrode in 7 M KOH/0.1 M ZnO at the rest potential \( (E_r = -1.382 \text{ V vs Hg/HgO}) \) at 2000 rpm. Simulated impedance plot (——). Frequency range: 0.02 Hz to 65 kHz (multiplication factor: 2).

frequency part. It can be shown[11] that at decreasing frequency the real part becomes

\[
\lim_{\omega \to 0} Z'_\omega = \sigma \delta (2/D)^{1/2},
\]

where \( \delta = \text{thickness of the Nernst diffusion layer} \).

The value of \( \delta \), obtained from the real part of the Warburg impedance, can be compared with the value calculated from the Levich equation

\[
\delta = 1.61 D^{1/3} \omega_{r}^{-1/2} \sqrt[6]{n/6}
\]

In Table 2 the \( \delta \)-values are summarized.

The agreement between the \( \delta \)-values is good. The simulated impedance diagram (Fig. 3) also agrees well with the measured data.

Superposition of ac-signals on a dc-current, whether anodic or cathodic, results in similar diagrams as

Table 2. The Nernst diffusion layer \( \delta \) as calculated with Equations (3) and (4) \((D \text{ and } \sigma \text{ are obtained from Table 1 and } \nu \text{ from [12]})\)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>( \lim_{\omega \to 0} Z'_\omega )</th>
<th>( \sigma ) (( \Omega ) s(^{-1/2}))</th>
<th>( D ) cm(^2) s(^{-1} \times 10^6 )</th>
<th>( \sqrt[6]{n/6} ) (( \text{cm}^2 \text{s}^{-1} \times 10^2 ))</th>
<th>( \delta ) (cm) \times 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>0.8-0.9</td>
<td>1.1</td>
<td>2.3 \times 10^{-6}</td>
<td>1.84</td>
<td>7.9-8.8</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>0.7-0.9</td>
<td>0.9</td>
<td>3.3 \times 10^{-6}</td>
<td>1.23</td>
<td>10.0-11.4</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>0.7-0.8</td>
<td>0.9</td>
<td>3.3 \times 10^{-6}</td>
<td>1.23</td>
<td>10.0-11.4</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>3.3-4.2</td>
<td>6</td>
<td>6 \times 10^{-6}</td>
<td>1.10</td>
<td>9.5-12.1</td>
</tr>
</tbody>
</table>

where

\( D = \text{diffusion coefficient of zincate [cm}^2\text{s}^{-1}] \)
\( \omega_r = \text{angular frequency of rotation [s}^{-1}] \)
\( \nu = \text{kinematic viscosity [cm}^2\text{s}^{-1}] \).
observed at the rest potential. A typical diagram, at anodic dc-current of 10 mA cm$^{-2}$, is shown in Fig. 4. However, due to the dissolution or deposition process, the surface of the electrode changes continuously, thus affecting the impedance measurements. A striking example is given in Fig. 5: at longer deposition times an inductive loop is observed in the impedance diagram, which was found to be typical for a non-amalgamated zinc electrode as will be shown in Section 3.2.

Therefore, it is not justifiable to obtain kinetic parameters from such measurements. The galvanostatic pulse method[8] is more apt for this purpose.

3.2. Non-amalgamated zinc electrode

The impedance spectrum of the pure zinc electrode in 7 M KOH/0.1 M ZnO is given in Fig. 6 at the rest potential in quiescent solution. This spectrum is quite different from that of an amalgamated electrode (Fig.

---

![Fig. 4](image1.png)

**Fig. 4.** Measured impedance plot of Zn(Hg, II)-electrode in 7 M KOH/0.1 M ZnO at 2000 rpm. Numbers indicate frequency; $i_a = 10$ mA cm$^{-2}$.

![Fig. 5](image2.png)

**Fig. 5.** Measured impedance plot of Zn(Hg, II)-electrode in 5 M KOH/0.1 M ZnO at 2000 rpm; $i_c$: 10 mA cm$^{-2}$; o: directly after pretreatment; ●: after ca. 20 min deposition.

![Fig. 6](image3.png)

**Fig. 6.** Measured impedance spectrum of the zinc electrode in 7 M KOH/0.1 M ZnO at 0 rpm (●); simulated impedance plot (—-); numbers indicate frequency.
Impedance measurements of zinc electrodes

2. The small semicircle at high frequencies is followed by a pattern consisting of a semicircle and a straight line. This part often masks the semicircle at high frequencies.

In the case of heterogeneous reactions, surface processes (such as adsorption, surface diffusion and lattice formation) can play an important role. Based on the adatom mechanism for metal-ion exchange reactions[13], Fleischmann et al.[14] have proposed an analogous circuitry in which additional components expressing surface adsorption, surface diffusion and lattice formation are included (Fig. 7).

In this circuit $C_d$ represents a pseudo-capacitance, $Z_s$ the adatom diffusion impedance and $R_{lat}$ the impedance due to lattice formation. At equilibrium potential these are defined[14] by

$$C_d = \frac{z^2F^2A}{RT} \cdot \sigma$$  

$$Z_s = \frac{k_2 L}{D_a} \cdot \frac{RT}{zF \ell_0} \cdot \frac{1}{1 + j\omega/k_2},$$

where

$C_d$ = pseudo capacitance [F]

$\sigma$ = adatom concentration [mol. cm\(^{-2}\)]

$k_2 = I_0/(\alpha F \sigma A)$ [s\(^{-1}\)]

$Z_s$ = adatom diffusion impedance [\(\Omega\)]

$D_a$ = diffusion coefficient along the surface [cm\(^2\) s\(^{-1}\)]

$2L$ = distance between two parallel steplines on the surface [cm].

When $\omega/k_2 \ll 1$, the $Z_s$-term can be simplified to

$$Z_s = \frac{k_2 L}{D_a} \cdot \frac{RT}{zF \ell_0}.$$  

Further, we can define $R_x$ as

$$R_x = Z_s + R_{lat}. \quad (8)$$

The simulated curve based on this equivalent circuit is shown in Fig. 6 by the drawn line. The agreement is reasonable taking into account that the surface of the zinc electrode changes somewhat during the measurement. The values of $I_0$, $\sigma$, $R_x$, $C_d$, $C_s$, $C_{lat}$ and $\sigma$ can be calculated.

In Table 3 all data are summarized for different solutions for a series of experiments.

Comparing Tables 3 and 1, it appears that the $I_0$-values are somewhat higher for the zinc than for the amalgamated electrodes, though the scatter is rather large. The double layer capacity is about twice that of the amalgamated zinc electrode. The impedance diagram at a rotating zinc-disc electrode, shown in Fig. 8, is quite similar to that of a non-rotating electrode (Fig. 6). Only the Warburg impedance at low frequencies is not observed and it appears that the resistance in the RC-circuit, which relaxes at low frequencies, is about 2-5 times larger than in the absence of rotation.

![Fig. 7. Equivalent circuit in which additional components expressing surface processes are included in the Randles circuit (see text).](image)

![Fig. 8. Measured impedance spectrum of the zinc electrode in 3 M KOH/0.1 M ZnO at 2000 rpm; numbers indicate frequency.](image)

### Table 3. $I_0$, $C_{dl}$, $R_x$, $C_s$ and $C_{A}^{0}$ as function of the solution composition at a zinc electrode

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$I_0$ (A cm(^{-2}) $\times 10^4$)</th>
<th>$C_{dl}$ ((\mu F) cm(^{-2}))</th>
<th>$R_x$ ((\Omega) cm(^2))</th>
<th>$C_s$ (mF cm(^{-2}))</th>
<th>$C_{A}^{0}$ (mol cm(^{-2}))</th>
<th>$\sigma$ ((\Omega) s(^{-1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>120-290</td>
<td>60-80</td>
<td>3-28</td>
<td>60-70</td>
<td>4-5</td>
<td>2-6</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>200-750</td>
<td>70-180</td>
<td>4-20</td>
<td>20-80</td>
<td>2-5</td>
<td>2-6</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>500-1500</td>
<td>50-100</td>
<td>4-11</td>
<td>44-120</td>
<td>3-8</td>
<td>2-6</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>50-150</td>
<td>60-75</td>
<td>24-34</td>
<td>0.6-1.0</td>
<td>0.04-0.07</td>
<td>10-20</td>
</tr>
</tbody>
</table>
Superposition of ac-signals on a dc-current changes the impedance diagrams drastically. Figure 9 shows the spectra obtained with an anodic dc-current of 3.5 (a) and 35 (b) mA cm$^{-2}$. Increase of the dc-current leads to a strong reduction of the large semi-circle observed at the rest potential. It seems that this reduced semi-circle overlaps the semi-circle due to the relaxation of the $R_C$-diode circuit. Also, an inductive and an additional capacitive loop are observed.

With a cathodic dc-current similar diagrams are

Fig. 9. Impedance spectra of a zinc electrode in 7 M KOH/0.1 M ZnO at 2000 rpm; numbers indicate frequency. a: $i_\text{c} = 3.5$ mA cm$^{-2}$. b: $i_\text{c} = 35$ mA cm$^{-2}$.

Fig. 10. Impedance spectra of a zinc electrode in 7 M KOH/0.1 M ZnO at 2000 rpm; numbers indicate frequency. a: $i_\text{c} = 3.5$ mA cm$^{-2}$. b: $i_\text{c} = 35$ mA cm$^{-2}$. 
observed (Fig. 10). Here also, the large semi-circles shrink with increasing current and an inductive and an additional capacitive loop are observed.

4. DISCUSSION

The total impedance of the amalgamated electrodes can be adequately described with a model consisting of a kinetic and a diffusion controlled part, if necessary corrected for forced convection. Since no difference was found between the impedance spectra for Zn(Hg, I–II–III)-electrodes, it can be concluded that the kind of amalgamation has no effect, ie at all three electrodes sufficient mercury is present to cover the surface completely. Probably, as a result of the electrode pretreatment, in which more zinc dissolves than deposits, concentration of mercury on the surface takes place, leading to a complete coverage.

The $i_0$-value obtained with the impedance technique can be compared with $i_0$-data measured by the authors with the galvanostatic pulse technique.[8]

In Table 4 these $i_0$-values are compared, showing a fair agreement.

The hydroxyl concentration has no appreciable influence on the $i_0$-values, as was the case in the galvanostatic pulse technique. If the $i_0$-values are obtained in direct sequence with the two different techniques at the same Zn(Hg, III)-electrode, the agreement is excellent. The $\sigma$-values (Table 1) change satisfactory either, because from the impedance measurements in the presence of a dc-current (Fig. 9) it can be deduced that the resistance decreases strongly with increasing dc-current or overpotential. This is rather unlikely for a resistance due to lattice formation, particularly in view of the already very high surface adatom concentration. For this reason, another process which is dependent on the activation potential must be responsible for the resistance $R_e$.

Using an anodic or cathodic dc-current we observed an extra inductive and capacitive loop, cf Figs 9 and 10. This would suggest, according to Epelboin et al.[1, 16] that intermediates are involved in the total reaction. In their model this is mathematical described by

$$Z_f = \frac{\delta i}{\delta E} = \left( \frac{\delta i}{\delta E} \right)_{\theta_1, \ldots, \theta_n} + \sum_{i=1}^{n} \left( \frac{\delta i}{\delta \theta_i} \right)_{\theta_{i,E}} \frac{\delta \theta_i}{\delta E} (i \neq i)$$

(9)

for $n$ intermediates with surface coverage $\theta_1, \ldots, \theta_n$.

Epelboin et al.[1] observed, during zinc electrocystallization, an impedance diagram with an inductive Faradaic part, characterized by at least three time constants. These are ascribed to the involvement of

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Impedance technique</th>
<th>Galvanostatic pulse technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>200–290</td>
<td>80–520</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>60–300</td>
<td>50–100</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>50–650</td>
<td>50–270</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>60–120</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 5. Comparison of $i_0$-values, obtained with two different techniques at the same electrode surface [Zn(Hg, III)]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Impedance technique</th>
<th>Galvanostatic pulse technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 M KOH/0.1 M ZnO</td>
<td>200–290</td>
<td>160–200</td>
</tr>
<tr>
<td>7 M KOH/0.1 M ZnO</td>
<td>200–270</td>
<td>30–250</td>
</tr>
<tr>
<td>3 M KOH/0.1 M ZnO</td>
<td>500–1500</td>
<td>100–350</td>
</tr>
<tr>
<td>1.5 M KOH/0.01 M ZnO</td>
<td>50–120</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Comparison of $i_0$-values, obtained with two different techniques.
three intermediate species in the total reaction \[ \text{H}_\text{ad}, \ Zn_\text{ad} \text{ and } ZnA_\text{ad} (A \text{ is an anion}) \]. Cachet, Ströder and Wiart\[6\] pointed out four Faradaic relaxation processes in the impedance diagrams during steady-state polarization measurements. From these results they concluded to at least four adsorbed intermediate species at the interface. The intermediate species, however, were not identified. Following the same reasoning, our data would point to two intermediate species, these intermediates are likely to be zinc-species that are involved in the reaction mechanism\[8\], such as \( ZnOH, Zn(OH)_2, Zn(OH)_3 \).

It has been shown by Cachet et al.\[17\], that nucleation and growth lead also to an impedance spectrum with both capacitive and inductive loops. Kinetic measurements at zinc and amalgamated zinc electrodes\[8\] revealed a difference in reaction mechanism. This was explained by a difference in adsorption behaviour: adsorbed species at zinc while at the amalgamated electrode only \( H_2O \)-molecules are present.

The observed impedance spectra likewise indicate a pronounced change of the interface for zinc with respect to amalgamated zinc.

For the explanation of the impedance behaviour therefore a model based on the adsorption of intermediates is preferred.

The relaxation processes, observed in\[1, 6\], take place partly in the very low frequency region (< 0.1 Hz). The question here is whether the impedance data measured at such low frequencies (requiring very long measuring times) are not influenced by the change of the interface as a result of the deposition or dissolution process. This change can be seen very clearly during the deposition of zinc onto an amalgamated zinc surface (Fig. 5). Therefore, not much value should be attached to very low frequency measurements (< 0.1 Hz).

5. CONCLUSIONS

The impedance diagrams of zinc and amalgamated zinc electrodes show a remarkable difference. The impedance diagrams of amalgamated disc electrodes are not influenced by the method of amalgamation and can be adequately described with a kinetic- and diffusion-controlled reaction. They indicate that no adsorption of hydroxyl ions or intermediate species takes place at the amalgamated zinc electrode.

The impedance diagrams at the zinc disc electrode indicate that surface processes in which intermediate species such as \( Zn(OH), Zn(OH)_2, Zn(OH)_3 \) are involved play a more important role. For both the zinc and the amalgamated zinc electrodes the derived kinetic parameters are in good agreement with those obtained from the galvanostatic pulse technique.

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REFERENCES