1. Introduction

1.1. Motivation

Functional corrosion-protection coatings are one of the major industrial applications for electroplated Zn coatings. Besides the suitability of the produced coating for corrosion protection, it is also of major interest under which configurations these Zn coatings can be produced efficiently. In addition to the question of the evaluation and scaling of the actual plating process at the cathode, the electrochemical dissolution processes at the anodes have a major effect to the development of the whole process.

As industrial-scale experiments are very complicated and not affordable in practical applications, there is a major interest for simulations, for which measurements at a laboratory scale are sufficient. In this article, a mathematical model and a numerical scheme for the simulation of the dissolution of zinc anodes are presented, which only use impedance spectra as an input.
For the evaluation of the dissolved mass of zinc at a point in time $m(t)$, one can use Faraday’s law, cf. [1, 2], given through $m(t) = \frac{M \cdot j \cdot t}{z \cdot F}$, where $M$ is the molar mass of zinc, $z$ the corresponding valence of Zn and $F$ is Faraday’s constant, and $j$ is the current density, which is the only part in the formula which is not known and thus needs to be simulated.

As described in section 1.2., the simplest and most common ways to simulate the current density is based on a model with the Poisson equation of electrostatic, cf. [3], in its core. As to be seen, the corresponding models assume constant electric potentials or constant charge transfer currents on the anode, resp. cathode. This assumption will be omitted at the cathode where neither the current nor the electrical potential are fixed but the relation of exchange current and exchange voltage, which is connected via the classical Ohm’s law and the charge-transfer resistance. Hence in this paper, polarization data, as in [4] are used, for which good experimental results were obtained already.

### 1.2. State of the art

Most models of the current density in electroplating rely on the simulation of the electric field in the bath, which itself relies on the description of a static electric fields $E_B$, cf. [1, 3, 5]. The assumption of a static electric field simplifies the setting as static electric fields are conservative, i.e. they can be interpreted as gradient field of an electric potential $\phi_B$, i.e. one assumes $E = \nabla \phi_B$.

Assuming as in [1, 6], that the bath is homogenously electrical neutral, i.e. that for the charge density $\rho_B$, the equation $\rho_B = 0$ holds true, the classical Ohm’s law yields a description for the electric potential $\phi_B$ through the following Poisson equation:

$$\sigma_E \Delta \phi_B = 0. \tag{1}$$

Where $\sigma_E$ is the permittivity of the electrolyte in the bath, i.e. the reciprocal of the resistance of the electrolyte. The two most common models for the current density are the primary and the secondary current distribution, cf. [7], [3] which define the boundary data of the Poisson equation (1) but differ in their boundary data on the anodes and cathodes. In both models, one splits the boundary $\partial \Omega_B$ of $\Omega_B$ into three sub-surfaces: an isolation part $\Gamma_I$, an anodic part $\Gamma_A$ and a cathodic part $\Gamma_C$. In both models it is assumed that over the isolation $\Gamma_I$ no current flows, i.e. one assumes that the Neumann boundary condition $\nabla \phi_B |_{\Gamma_I} \cdot n = 0$ is fulfilled, where $n$ is the outer unit normal on $\Gamma_I$.

The primary current density interprets the conditions on the electrodes as Dirichlet boundary conditions for the electric potential $\phi_B$. On the cathode the potential $\phi |_{\Gamma_C} = E_{Cell} - E_{0,C}$, and on the anode, the potential $\phi |_{\Gamma_A} = E_{Cell} - E_{0,A}$, is assumed, where $E_{0,C}$ is the equilibrium potential of the cathode, $E_{0,A}$ is the equilibrium potential on the anode and $E_{Cell}$ is the cell potential. In this section, it is assumed that the overpotential on cathode and on anode $\eta$ vanishes.
The secondary current density interprets the conditions on the electrodes as Neumann boundary conditions for the electric potential \( \phi \). Additionally, it is assumed that the overpotentials \( \eta \) do not vanish. Furthermore, it is assumed that the charge transfer current \( j_{CT} \) is given through the Butler-Volmer equation, cf. [1]

\[
i_{ct} = i_0 \left( \exp \left[ \frac{(1-\beta)F\eta}{RT} \right] - \exp \left[ \frac{\beta F\eta}{RT} \right] \right)
\]

In the formula (2) \( i_0 \) is the exchange current density, \( \beta \) is the charge exchange coefficient, \( R \) the universal gas constant and \( T \) is the absolute temperature. Thus on the electrodes, the following Neumann boundary condition is given by:

\[
\nabla \phi \cdot n |_{\Gamma_E}, \text{ with } E \in \{A, C\}.
\]

Both models, primary and secondary current density, then evaluate the current density \( j \) on the anode and on the cathode via

\[
|\nabla \phi_B|_2, \text{ where } |\bullet|_2 : \mathbb{R}^3 \rightarrow \mathbb{R}_{\geq 0} \text{ denotes the Euclidean norm.}
\]

Note that the boundary data are assumed to be homogenous along the electrodes and furthermore note that the corresponding mathematical formulations of the boundary value problems are uniquely solvable, cf. [8].

2. On a mathematical model and a numerical scheme

2.1. Mathematical Background

Before a model for the dissolution of the zinc anodes is discussed in section 2.2 and the numerical strategy in section 2.3, some notation and mathematical notions have to be introduced.

First let \( \Omega, D \subset \mathbb{R}^3 \) be open, connected, bounded Lipschitz domains and let a decomposition \( \mathcal{Z} := \{\Omega_1, \ldots, \Omega_N\} \) into \( N \) open bounded and domains, with \( \overline{\Omega} = \bigcup_{j=1}^{N} \Omega_j \) and \( \Omega_j \cap \Omega_k \), for \( j \neq k \) be given. For an open set \( D \), the set \( \overline{D} \) denotes the topological completion of \( D \). First denote with \( L^p(D) \) the Banach space of \( p \)-integrable functions, with \( 1 \leq p \leq \infty \), cf. [9]. In the following, one denotes, as in [9] and in [10], the spaces \( W^{k,p}(\Omega) \) the space of functions \( v \in L^p(D) \) for which the weak derivative \( \frac{\partial^n v}{\partial x_j^n} \) exists for all \( j = 1, 2, 3 \) and each \( 1 \leq n \leq k \). For the notion of weak differentiability that is used in this section, a definition can be found in [9, 10, 11], for example. Weak differentiability basically states that for a weak differentiable function \( v \in L^p(\Omega) \) partial integration is well defined. The Banach spaces \( L^p(\Omega) \) and \( W^{k,p}(\Omega) \) are considered with their usual norms, cf. [9, 10]. Furthermore, note that \( L^2(\Omega) \) and \( H^1(\Omega) := W^{1,2}(\Omega) \) are even Hilbert spaces.

Furthermore, let the broken space of once weakly differentiable functions w.r.t. the decomposition \( \mathcal{Z} \) be given by cf. [12]:

\[
H^1(\Omega; \mathcal{Z}) := \{ v \in L^2(\Omega) \mid \forall D \in \mathcal{Z} : v|_D \in H^1(D) \} = \prod_{D \in \mathcal{Z}} H^1(D).
\]
Furthermore, let \( u^{(j)} = u|_{\Omega_j} \) additionally define the jump over an interface be define through \([u]_{j,k} := (\gamma_{\partial \Omega_j} u^{(j)} - \gamma_{\partial \Omega_k} u^{(k)})\), where for all \( 1 \leq j \leq n \), the operator is the trace operator \( \gamma_{\partial \Omega_j} \), as defined in [10].

2.2. A model for the current density

In this section, a new mathematical model for the dissolution of soluble anodes will be discussed. For that, consider an industrial galvanic bath as in figure 1a and figure 1b and the test volume \( \Omega \), filled with an electrolyte in the subdomain \( \Omega_B \subset \Omega \), where the box inside the box does not belong to the domain. In this context the surface of the inner box represents the cathode surface, cf. figure 1c. Furthermore, let zinc anodes, be placed in the path, cf. figures 1a and 1d, the corresponding subdomain is denoted by \( \Omega_A \subset \Omega \). In industrial applications, the zinc anodes are contacted over a titanium conductor, cf. figure 1e, the corresponding subdomain is denoted by \( \Omega_Z \subset \Omega \).

Firstly, it is assumed, as in section 1.2 that during the electroplating, the electric field is static in each domain. It directly follows that for all \( S \in \{A, C, Z\} \), the electric field \( E^{(S)} \) in \( \Omega_S \) can be represented as the gradient field of the electric potential \( \phi^{(S)} \) in \( \Omega_S \), i.e. one has \( E^{(S)} = \nabla \phi^{(S)} \). Then, the corresponding Ohm’s laws in the separate domains can be formulated as in the following:

\[
\begin{align*}
\sigma_B \Delta \phi^{(B)} &= 0, & \text{in } \Omega_B \\
\sigma_A \Delta \phi^{(A)} &= 0, & \text{in } \Omega_A \\
\sigma_Z \Delta \phi^{(Z)} &= 0, & \text{in } \Omega_Z
\end{align*}
\]

As described in section 1.2, the boundary and interface conditions must be fixed. Firstly, note, cf. [13], that the electric field is continuous over a common interface of two conductors. On \( \partial \Omega^{(A)} \cap \partial \Omega^{(Z)} \), inside the anode in figure 1e, the following identity is assumed:

\[
\nabla \phi^{(Z)} - \nabla \phi^{(A)}, \quad \text{on } \partial \Omega^{(A)} \cap \partial \Omega^{(Z)}
\]

At the interface of bath and anode, cf. figure 1d, i.e. on \( \partial \Omega^{(A)} \cap \partial \Omega^{(B)} \), one assumes that Ohm’s law \( U = R_{CT} I \) is assumed, where \( R_{CT} \) is the charge-transfer resistance, \( U \) the potential jump on the interface and \( I \) is the current on the interface. In this article, the following is assumed:

\[
R_{CT} (\nabla \phi^{(B)} - \nabla \phi^{(A)}) \cdot n - (\phi^{(B)} - \phi^{(A)}) = 0, \quad \text{on } \partial \Omega^{(A)} \cap \partial \Omega^{(B)}
\]

On the cathode surface \( \Gamma_K \), cf. figure 1c, one assumes the following identity as in section 1.2.:

\[
\phi^{(B)} = -E_{0,C}, \quad \text{on } \Gamma_K.
\]

Furthermore on the power supply of the Ti parts of the anodes \( \Gamma_{SZ} \), cf. figure 1d, is given by:

\[
\phi^{(Z)} = E_{Cell}, \quad \text{on } \Gamma_{SZ}
\]
Additionally, it is assumed that the other boundaries are insulating. As in section 1.2., one assumes that there is no current that flows over the insulation, i.e. the following boundaries are assumed:

\[
\begin{align*}
\nabla \phi^{(B)} \cdot n &= 0, & \text{on } \partial \Omega_B \cap \partial \Omega, \\
\nabla \phi^{(A)} \cdot n &= 0, & \text{on } \partial \Omega_A \cap \partial \Omega, \\
\nabla \phi^{(Z)} \cdot n &= 0, & \text{on } \partial \Omega_Z \cap \partial \Omega \setminus \Gamma_{SZ},
\end{align*}
\] (11) (12) (13)

Furthermore, note that the permittivity of the Ti kernels of the zinc anode is given by \(\sigma_Z = 2.5 \cdot 10^6 \text{ Sm}^{-1}\) and the permittivity of the zinc anodes is given by \(\sigma_A = 16.7 \cdot 10^6 \text{ Sm}^{-1}\).

2.3. Numerical strategy

For the numerical strategy, a generalized mathematical formulation of (4)-(13) was considered. For the description of the solver, let \(\Omega \subset \mathbb{R}^3\) be an open, bounded, polyhedral Lipschitz domain and let a decomposition \(\mathcal{Z}\), as described in section 2.1., of \(\Omega\) be given. Furthermore, let \(N \in \mathbb{N}\) be the number...
of elements in \( \mathcal{X} \). Furthermore, let \( \Gamma_j := \partial \Omega_j \partial \Omega \) and \( \Gamma_{j,k} = \partial \Omega_j \partial \Omega_k \). Additionally, let an set of indices \( J \) with \( \emptyset \neq J \subset \{(j,k) \mid \Gamma_{j,k} \neq \emptyset \} \) be fixed and let \( I := \{(j,k) \mid \Gamma_{j,k} \neq \emptyset \} \setminus J \) be defined.

Furthermore, for all \( 1 \leq j, k \leq N \) let the values \( 0 < \sigma_j \) be arbitrary fixed, let \( f_j \in L^2(\Omega_j) \), \( a_j, b_j, g_j \in L^\infty(\Gamma_j) \) and \( a_{j,k}, b_{j,k}, g_{j,k} \in L^\infty(\Gamma_{j,k}) \) be arbitrary fixed. Then, the in this subsection considered, generalized problem will be given as:

Find \( \phi \in H^1(\Omega; \mathcal{X}) \) such that

\[
\begin{align*}
-\sigma_j \Delta \phi^{(j)} &= f_j \quad \text{in} \ \Omega_j, \quad \forall 1 \leq j \leq N, \quad (14) \\
a_j \phi^{(j)} + b_j \nabla \phi^{(j)} &= g_j \quad \text{on} \ \Gamma_j, \quad \forall 1 \leq j \leq N, \quad (15) \\
a_{j,k} \phi^{(j,k)} + b_{j,k} \nabla \phi^{(j,k)} &\cdot n = g_{j,k} \quad \text{on} \ \Gamma_{j,k}, \quad \forall (j,k) \in J, \quad (16) \\
\nabla \phi^{(j)} - \nabla \phi^{(k)} &= 0 \quad \text{on} \ \Gamma_{j,k}, \quad \forall (j,k) \in I. \quad (17)
\end{align*}
\]

As it can be easily seen, the model problem (14)-(17) generalizes the model (4)-(13) and even the models for the primary and the secondary current density described in section 1.2. Based on the weak formulation for the system of Partial Differential Equations, the numerical approximation searches for a weak solution of (14)-(17), which is given as the solution of the variation problem below, cf. [8, 11]:

Find \( \phi \in H^1(\Omega; \mathcal{X}) \) such that for all \( v \in H^1(\Omega; \mathcal{X}) \), the following identity holds true

\[
a(\phi, v) = b(v), \quad v \in H^1(\Omega; \mathcal{X}).
\]

In the notation above, the bilinear form \( a : H^1(\Omega; \mathcal{X}) \times H^1(\Omega; \mathcal{X}) \to \mathbb{R} \) is defined by

\[
a(\phi, v) := \sum_{j=1}^{N} \left[ \sigma_j (\nabla \phi^{(j)}, \nabla v^{(j)})_{L^2(\Omega_j)} + (a_j \phi^{(j)} + b_j \nabla \phi^{(j)} \cdot n, v^{(j)})_{L^2(\Gamma_j)} \right] \\
+ \sum_{(j,k) \in J} (a_{j,k} \phi^{(j,k)} + b_{j,k} \nabla \phi^{(j,k)} \cdot n, \phi^{(j,k)})_{L^2(\Gamma_{j,k})} \\
+ \sum_{(j,k) \in I} (\nabla \phi^{(j)} - \nabla \phi^{(k)} - \nabla v^{(j)} - \nabla v^{(k)})_{L^2(\Gamma_{j,k})}
\]

and the linear functional \( b : H^1(\Omega; \mathcal{X}) \to \mathbb{R} \) is given by

\[
b(v) := \sum_{j=1}^{N} \left[ (f_j, v^{(j)})_{L^2(\Omega_j)} + (g_j, v^{(j)})_{L^2(\Gamma_j)} \right].
\]

For the numerical treatment of (18), a discretization \( X_h \) of \( H^1(\Omega; \mathcal{X}) \) has to be fixed. In this paper, a conforming discretization was chosen, i.e. \( X_h \subset H^1(\Omega; \mathcal{X}) \). Due to the definition of \( H^1(\Omega; \mathcal{X}) \), a discretization of \( H^1(\Omega_j) \) suffices to be defined for each \( 1 \leq j \leq N \). For the definition
of a discretization, let $\mathcal{T}$ be a triangulation, for a definition c.f. [14], of $\Omega$ given such that for each $1 \leq j \leq N$, there exists a subtriangulation $\mathcal{T}_j \subset \mathcal{T}$ such that $\mathcal{T}_j$ is a triangulation of $\Omega_j$. For the discretization of $H^1(\Omega_j)$, the linear space of spines $S^1(\mathcal{T}_j)$ is used. Where $S^1(\mathcal{T}_j)$ is, as in [15], defined as

$$S^1(\mathcal{T}_j) = P^1(\mathcal{T}_j) \cap C^0(\Omega).$$

In the notation above the space of piecewise affine functions $P^1(\mathcal{T}_j)$ is defined as

$$P^1(\mathcal{T}_j) = \{v \in L^2(\Omega_j) \mid \forall T \in \mathcal{T}_j \exists a, b \in \mathbb{R}^3 : v|_T \equiv b \cdot x + a\}.$$  \hspace{1cm} (20)

In this paper $X_h$ is defined as $X_h := \prod_{j=1}^N S^1(\mathcal{T}_j)$.

An important step of the numerical scheme is the application of an adaptive algorithm, which allows to work very efficiently since it generates a mesh $\mathcal{T}$, which is fine where it needs to be to minimize the error of the numerical scheme. The adaptive FEM loop that is used in this paper, is given through the following steps, given as in [16, 17]:

1. **Input:** Initial triangulation $\mathcal{T}^0$ as well as problem data w.r.t. (14)-(17) and define $k := 0$.

2. **Solve:** Solve the discrete problem:

   Find $\phi_h \in X_h$ such that for all $v_h \in X_h$ the following equality holds true:

   $$a(\phi_h, v_h) = b(v_h).$$  \hspace{1cm} (21)

3. **Estimate:** Estimate the error $\|\phi - \phi_h\|_X$ with $\eta^2 := \sum_{T \in \mathcal{T}} \eta^2_T$, where $\eta^2_T$ is analogous to the discussion in [18], defined through

   $$\eta^2_T := |T|^{1/3} \sum_{j=1}^N \left[ \sum_{F \in \mathcal{T}_j} \|\sigma_j (\nabla \phi_h^{(j)}) \cdot n\|_{L^2(F)}^2 + \sum_{F \in \mathcal{T}_j \cap \partial T} \|a_j \phi_h^{(j)} + b_j \nabla \phi_h^{(j)} \cdot n - g_j\|_{L^2(F)}^2 \right] + |T|^{1/3} \sum_{(j,k) \in J} \sum_{F \in \mathcal{T}_j \cap \partial T} \|a_{j,k} \phi_h^{(j)} + b_{j,k} \nabla \phi_h^{(j)} \cdot n - g_{j,k}\|_{L^2(F)}^2 + |T|^{1/3} \sum_{(j,k) \in J} \sum_{F \in \mathcal{T}_j \cap \partial T} \|\nabla \phi^{(j)} - \nabla \phi^{(k)}\|_{L^2(F)}^2.$$

4. **Mark:** Mark the elements with Dörfler marking, cf. [19], with associated bulk parameter $\theta = 0.5$.

5. **Refine:** Refine the triangulation $\mathcal{T}^{k+1} := $Refine($\mathcal{T}^k$), with the newest vertex bisection, cf. [20].
(6) **Break:** If \( \eta^2 \) is lower than a given tolerance \( \varepsilon \) or if the number of degrees of freedom is higher than a given lower bound then break the condition. Else go to (2) and set \( k = k + 1 \).

Note that in step (2), the problem (21) corresponds to a linear system of equations, which can be solved with standard software.

### 2.4. Numerical Validation of the Software

Since the numerical scheme for the approximation of the solution of (14)-(17) was programmed in Matlab and no commercial software was used, hence, a numerical validation of the software is necessary. For the numerical validation let \( \Omega := [0,1]^3 \) be fixed, with a decomposition \( \mathcal{K} = \{ \Omega_1, \Omega_2, \Omega_3 \} \), where \( \Omega_1 = \{ x \in \Omega \mid x_1 < 1/4 \} \), \( \Omega_2 = \{ x \in \Omega \mid 1/4 < x_1 < 3/4 \} \) and \( \Omega_3 = \{ x \in \Omega \mid x_1 > 3/4 \} \), cf. figure 2a. Furthermore, let an exact solution of (14)-(17) be defined through \( u(x,y,z) = x(1-x)y(1-y)z(1-z) \). Furthermore, let \( \sigma_1 = 1/2, \sigma_2 = 1/3 \) and \( \sigma_3 = 1/4 \) are fixed for this problem. Furthermore, it is assumed that the identities \( u|_{\partial \Omega} = 0, [\nabla u]|_{1,2} \cdot n = [\nabla u]|_{2,3} \cdot n = 0 \). Additionally \( f \in L^2(\Omega) \) is chosen such that \( u \) is the exact solution to the corresponding problem (14)-(17). An approximation of the solution of (14)-(17) yields the approximation given in figure 2b and one obtains the convergence graph given in figure 2c. As it can be seen from the convergence graph, the numerical scheme chosen seems to converge and reaches an asymptotic phase. The formal proof of convergence and calculation of the order of convergence will be omitted in this paper.

**Figure 2:** Splitted domain, approximate solution and error estimate for the verification of the solver.
Table 1: Parameters for the EIS measurements with a zinc anode and a steel cathode.

| Parameter         | Setup                                                                 |
|-------------------|----------------------------------------------------------------------|
| Process time      | 4h, continuous measurement of impedance spectra in ongoing time      |
| Mode              | Galvanostatic, constant anodic current density of 2 A/dm²             |
| Working electrode | Zinc, 99.995 %                                                       |
| Reference electrode | Ag/AgCl (saturated KCl)                                              |
| Cathode           | Steel                                                               |
| Frequency         | 100 kHz – 10 mHz                                                     |
| Amplitude         | 10 mV                                                               |

3. Experimental, materials and simulations

To apply the model given in section 2.2, it suffices to measure the conductivity of the electrolyte, or equivalently the electrolyte resistance, as well as the charge-transfer resistance. A common and intelligent way to determine the charge-transfer resistance and the electrolyte resistance is to measure impedance spectra, cf. [21], and fit the corresponding measurement results to an equivalent circuit. The corresponding measurements are given in subsection 3.1.

3.1. Electrochemical impedance spectroscopy (EIS) measurements

For the impedance measurement, the experiment parameters are given in table 1 for a weakly sour electrolyte.

As mentioned in table 1, the measurements of the impedance spectra were done over 4 h. In figure 3a and 3b, the results for the first measured impedance spectrum are shown. As it can be seen in the Nyquist-plot, the results do not represent a half cycle, as one could expect. When evaluating the other spectra, one obtains a very similar behavior, which is known in the literature, cf. [22]. As discussed in [22], the spectra can be interpreted as the overlap of two semi-cycles which can be identified with the reactions $\text{Zn} \rightarrow \text{Zn}^+ + \text{e}^-$ (I) and $\text{Zn}^+ \rightarrow \text{Zn}^{2+} + \text{e}^-$ (II). Furthermore as described in [22], the equivalent cycle for the situation discussed above is given by two constant-phase elements, parallel to a resistor, and in series with another resistor $R_{DW}$ representing the electrolyte resistance. The resistor associated to the reaction (I) is denoted by $R_{CP_1}$ and the resistance associated to the reaction (II) is denoted by $R_{CP_2}$. Then, the total charge-transfer resistance is given by $R_{ct} = R_{tot} = R_{CP_1} + R_{CP_2}$. 


Nyquist plot of the first EIS-Spectrum associated to the measurements gained with the parameters defined in table 1.

(b) ZHIT-approximation of the impedance, in the Bode plot associated to the first measurement in time associated to the parameters defined in table 1.

Figure 3: Nyquist plot and ZHIT approximation in the Bode-plot.

Figure 4: Equivalent circuit for the EIS spectrum given for the anode reactions $\text{Zn} \rightarrow \text{Zn}^+ + e^-$ (I) and $\text{Zn}^+ \rightarrow \text{Zn}^{2+} + e^-$ (II) for the measurements obtained for the parameters given in table 1. $R_{DW}$ represents the electrolyte resistance, $R_{CP_1}$ the resistance of the electrode reaction (I) and $R_{CP_2}$ the resistance of the electrode reaction (II).

When evaluating the measurements over time with the equivalent circuit above, one obtains the resistances shown in figure 5a and figure 5b. As it can be seen in the figures, the resistance $R_{DW}$ and $R_{ct}$ can be considered almost constant during the process.

3.2. Simulation results for the model

For the comparison of models the primary current density was simulated with COMSOL as references for the anodic current density, cf. figure 6a and the cathodic current density, cf. figure 6c, In the figures 6b and 6d the results of the new model are presented.

As it can be seen in both figures for the primary current density, especially in figure 6a vertex and edge effects can be observed, which corresponds to experimental observations. Furthermore, it can be seen that the calculated anodic current density is highly homogeneous. No gradient
Development of the Electrolyte resistance $R_{DW}$ over the measurement-time from the EIS – spectra measured with the parameters defined in table 1.

(a) Development of the Electrolyte resistance $R_{DW}$ over the measurement-time from the EIS – spectra measured with the parameters defined in table 1.

(b) Development of the resistances $R_{ct} = R_{tot}" = R_{CP1} + R_{CP3}$, $R_{CP1}$, and $R_{CP3}$, over the measurement time from the EIS – spectra measured with the parameters defined in table 1.

Figure 5: Fits of the electrolyte resistance $R_{DW}$ and the charge transfer resistance $R_{ct}$ with the equivalent circuit given in figure 4.

from the power supply to the end of the anode can be observed. This behavior can be expected from the model described in section 1.2, but it is not quite the behavior one could expect from observations that are commonly known in the real process: The anodes dissolve predominantly in a neighborhood of the power supply.

Furthermore, it can be seen that on the cathode surface, one obtains a highly homogeneous current density, with maxima directly opposite to the anodes. In addition, the cathodic current density is higher than the anodic current density.

Note, that the new model, simulated with the numerical scheme described in section 2.3 and implemented in Matlab, cf. figure 6b and 6d, predicts a more inhomogeneous current density than the model of the primary current density, cf. figure 6d. The inhomogenities on the cathode can be explained by the anodic current density, cf. figure 6b. As it can be seen from figure 6b, the anodic current density is highest in the proximity of the power supply. At the lower end of the anodes a further local maximum of the calculate current density can be observed, as result of the known edge-effects. While the high anodic current densities in the neighbourhood of the power supply can immediately be explained by the power supply, the higher current densities at the other end of the anode can be explained by edge and vertex effects. The high current densities at the power supply directly lead to the high current densities at the cathode surface.
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(a) Anodic current density for the primary current density, with $\sigma_B = 1/1.6 \cdot 10^6$ Sm$(-1)$, $E_{Cell} = 1.75$ V, $E_{0,C} = -0.04$ V and $E_{0,A} = -0.76$ V.

(b) Anodic current density for the new model, with $\sigma_B = 1/1.6 \cdot 10^6$ Sm$(-1)$, $\sigma_Z = 2.5 \cdot 10^6$ Sm$(-1)$ and the permittivity of the zinc anodes is given by $\sigma_A = 16.7 \cdot 10^6$ Sm$(-1)$, $E_{Cell} = 1.75$ V, $E_{0,C} = -0.04$ V and $E_{0,A} = -0.76$ V.

(c) Cathodic current density for the primary current density, with $\sigma_B = 1/1.6 \cdot 10^6$ Sm$(-1)$, $E_{Cell} = 1.75$ V, $E_{0,C} = -0.04$ V and $E_{0,A} = -0.76$ V.

(d) Cathodic current density for the new model, with $\sigma_B = 1/1.6 \cdot 10^6$ Sm$(-1)$, $\sigma_Z = 2.5 \cdot 10^6$ Sm$(-1)$ and the permittivity of the zinc anodes is given by $\sigma_A = 16.7 \cdot 10^6$ Sm$(-1)$, $E_{Cell} = 1.75$, $E_{0,C} = -0.04$ V and $E_{0,A} = 0.76$ V.

Figure 6: Comparission of the anodic current densities and cathodic current densities calculated with the new model and the primary current density.

4. Conclusion

Concluding the results of the paper, one obtains an alternative model for the current density on the anode and on the cathode, which reflects the electric current in the anode and the cathode, as described in section 2.2. Furthermore in section 2.3, a solver for a generalized problem was discussed and verified in section 2.4.

In section 3, impedance measurements for a weakly sour zinc electrolyte and the evaluation of the spectra were discussed. In section 3.2, the simulations for the secondary current density and the new model were discussed. The differences between the simulations were significant, but could be explained by physical considerations. In contrast to the models described in section 1.2, the model presented in section 2.2 is devoted to the simulation of large-scale electrodepositions, using polarization data to enhance the effectiveness of the model.

In the core of this article a strategy was described to implement the charge transfer resistance $R_{ct}$ at the interface regions of electrode and electrolyte in a model for galvanic cells basing on static electric fields and the Ohms law on multiple neighboring domains. Furthermore an adaptive conforming Courant FEM was described to approximate the new models.

The usage of charge transfer resistances gives the theoretical work on a huge number of
physical processes in galvanic cells available or give a more holistic frame on the process, such as the dissolution of large scale zinc anodes discussed in this article, the actual electroplating process at the cathode, corrosion and processes in lithium-ion batteries or fuel cells etc.

Furthermore it can be seen in this article that the new model for the current density gives a more complete overview over the currents in the complete process, as the currents in the electrodes are contained in the model in contrast to the primary and secondary current density. This gives the chance to simulate the current densities on large scale structures more accurate than it could be done until now, since the resistances in the electrodes are respected. This can lead to answers to questions like where to contact large scale anodes and cathodes most effectively in galvanic cells.

Although the model in this article is described for the electrochemical dissolution of zinc, it can be immediately applied to the electroplating of zinc as well as adjusted to other settings, e.g. other electrolytes, corrosion. Additionally, the model allows for the prediction of suitable positions of electric contacts on more complex anodes like wire-shaped anodes.

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