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A computational multi-reaction model of a Cu electrolysis cell

A. Pohjoranta*, R. Tenno

Helsinki University of Technology, Control Engineering, P.O. Box 5500, FIN-02015 TKK, Finland

**A R T I C L E   I N F O**

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**A B S T R A C T**

A computational model for quantitatively describing the behavior of four simultaneous chemical reactions taking place on two copper electrodes in a Cu–Cu electrolysis cell is formulated. The individual reaction rates, corresponding current densities and total cell current and voltage are obtained as direct model output. The model parameters are found based on cyclic voltammetry experiments done in a Cu–Cu electrolysis cell with CuSO₄ (aq) concentrations between 0.1 M and 1 M. The model is fit against the data of one experiment and compared against a series of other measurements. A full set of model parameters is given and the effect of selected parameters on the simulated current–time response is analyzed.

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1. Introduction

The aim of this paper is to present a computational model that describes the behavior of a system of electrochemical and chemical reactions taking place during electrolysis, on a metallic copper electrode immersed in an aqueous electrolyte containing Cu(II) ions during electrolysis. Mass transfer and electric field effects are included in the model. By combining different physical subsystems, the model attempts to describe such phenomena that are encountered in real voltammetric experiments conducted on the Cu–Cu system, but cannot be described using simplified, reduced models. Furthermore, the paper aims to reproducibly document a model and a set of parameters that produce estimates fitting well with the measured data. In order to parameterize and to verify the model, experiments are carried out on electrolytes with high concentrations of copper. However, as the experiments are done with electrolytes not containing a supporting electrolyte, the reported model is not directly applicable to industrial applications.

The primary reaction considered is the copper RedOx reaction (1), where Δφₑₒᵣₙ is the standard electrode potential for the system.

\[ \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)}, \quad \Delta\phi_{\text{eq}}^{o} = +0.34 \text{V} \]  

The full reaction in (1) consists of the transfer of two unit charges. However, all charge transfer reactions are considered to occur on unit charge at a time, and, therefore, also (1) may be divided into two reaction steps, each containing the transfer of one unit charge as in (2a)–(2b).

\[ \text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^{+}, \quad \Delta\phi_{\text{eq},1}^{o} = +0.16 \text{V} \]  

\[ \text{Cu}^+ + e^- \rightleftharpoons \text{Cu(s)}, \quad \Delta\phi_{\text{eq},2}^{o} = +0.52 \text{V} \]

(2a) (2b)

In addition to (2), the Cu(I) and Cu(II) ions at the copper metal–electrolyte interface also “interchange” through the copper disproportionation reaction, (3) from left to right. The reaction from right to left is called comproportionation. \(K_{\text{dc}}\) is the equilibrium constant of (3), which is obtained based on the sum of the equilibrium potentials of the reactions forming the disproportionation/comproportionation (D/C) reaction, namely (2a) backward and (2b) forward.

\[ 2\text{Cu}^+ \rightleftharpoons \text{Cu}_2^+ + \text{Cu(s)}, \quad K_{\text{dc}} = 1.49 \times 10^{6} \]  

(3)

Even though the copper D/C reaction includes charge transfer and occurs on the very same interface as the other charge transfer reactions, no net current flows over the metal–electrolyte boundary during the D/C reaction. Unless in equilibrium, net mass transfer of species does, however, and the D/C reaction tends to maintain the Cu(I) and Cu(II) ion concentrations in the proportion determined by the reaction rates of the D/C partial reactions.

Finally, CuSO₄, though very soluble in water, dissociates only sparingly—the association constant logarithm, i.e., \(\log K_{\text{da}}\) for (4) at infinite dilution and 298 K being around 2.3 [1–3]. Therefore, the copper sulfate dissociation/association (D/A) reaction (4) is also...
considered in the model.

\[
\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}, \quad \log_{10} K_{\text{diss}} = 2.3
\]  

(4)

Numerous studies regarding the subject system have been reported. For instance, an impedance analysis-based study for empirically determining the standard reaction rate constants of (2) in a perchlorate medium is reported in [4]. A numerical simulation model based on the CuSO₄ and H₂SO₄ dissociation reactions is reported, e.g., in ref. [2] and the role of copper disproportionation in the system is examined, e.g., in refs. [5,6]. Generally, an equilibrium condition can be reliably determined empirically but a harder problem is to find the absolute rates of individual forward and backward reactions. However, since several sources for the equilibrium potentials of (2) [7] and equilibrium constants of (3) and (4) do exist, even for electrolytes with ionic strengths above 0 M [1], the emphasis when modeling is directed in examining the coefficients’ interrelations. A good model also enables examining the range of possible coefficient parameter values when other physical factors are fixed.

One motive for the model created in this paper is to enable estimating the behavior of directly unobservable processes, namely the step reaction rates, based on the developed model and the available measurable quantities, namely the electrolysis cell current and cell potential. As a by-product, the model enables studying the effects of ionic species’ activity, the CuSO₄ dissociation rate and equilibrium potentials in the none-equilibrium system [5] formed by the two step reactions in (2).

Most of the studies examined by the authors reduce the two-step Cu Red/0x reaction to a single-step reaction with two unit charges transferred simultaneously. Such an electrode model loses the information of individual step reactions and does not enable full capture of the nonlinearities that are observed when the copper electrolysis cell is examined empirically. One purpose of the model described in this paper is to better capture such nonlinearities of the Cu–Cu electrolysis system that are observed when the system is examined with cyclic voltammetry (CV). CV measurements are made and reported to parametrize and to verify the created models.

A cell model is formulated in order bring the electrode model into a practical context. The purpose is to be able to estimate the cell current upon only the cell potential without depending on a reference potential (device). Not needing a reference electrode is certainly an advantage when utilizing the model for control of an industrial production system where a reference potential device may easily break, wear out or become so contaminated that it is unusable. The cell voltage is also of further interest to industrial electrolysis applications since it is the cell voltage – not the electrode potential vs. a reference – and the cell current that determine the cell power consumption.

In what follows, in order to obtain the desired model of a Cu–Cu electrolysis cell, the two-step copper RedOX reaction (1) model along with the co-reactions (3), (4) is developed first on one electrode. Then the electrolysis cell, consisting of two identical copper electrodes immersed in aqueous CuSO₄ is created and the reaction rates at individual electrodes are coupled to each other via the cell current. CV measurements are used to fit the model with measurement data and the obtained model parameters are given (Table 1). Finally, an analysis of parameter effects on the system current–voltage behavior is carried out.

2. The equations

2.1. The electrode model

2.1.1. Designations

Rates of reactions are denoted by \( r_{\text{a},s} \) (mol m⁻² s⁻¹), s is either 1, 2, dc or da denoting the reaction in question—either (2a), (2b), (3) or (4), respectively. However, the subscript symbols are omitted when not necessary, for example, when the main symbol meaning is clear based on the context or based on another symbol. d is either a or c for reactions (2a) and (2b), denoting the reaction direction—either anodic or cathodic, respectively.

The reactions in (2) from left to right are considered to proceed in the cathodic direction. This is the direction where the net change of the Cu(II) and Cu(I) ions’ mass is negative, them being reduced into Cu(I) and Cu(s) ions and atoms, respectively. For example, \( r_{\text{a},2} \) denotes the reaction rate associated with the oxidation of metallic Cu into Cu(I).

For the copper D/C reaction (3) and copper sulfate dissociation reaction (4), the anodic and cathodic directions are not descriptive and, therefore, the reaction direction is denoted by either dp or dc,
for disproportionation and comproportionation and \textit{diss} or \textit{ass} for dissociation and association, respectively.

There are three electrochemically reacting species in the system, namely the aqueous cupric and cuprous ions, and metallic copper, which are denoted by \( \text{Cu(II)}, \text{Cu(I)} \) and \( \text{Cu} \). The copper sulfate species and sulfate species are denoted by \( \text{CuSO}_4 \) and \( \text{SO}_4 \), respectively.

### 2.1.2. Reaction rate equations on the electrodes

The rate of each reaction in (2) depends on the system temperature, \( T \) (K), and on the activity of the associated species, \( a_i \) (no unit). With the notations detailed above, the reaction rates \( r_{d,s} \) for reactions in (2) are modeled with (5).

\[
r_{d,s} = k_{d,s}^{\circ} a_i e^{\left(\alpha_i (\Delta \phi - \Delta \phi_{\text{eq,s}})\right)}
\]

In (5), \( k_{d,s}^{\circ} \) denotes the reaction rate coefficient (mol s\(^{-1}\) m\(^{-2}\)) and \( k = F/R/T \) (V\(^{-1}\)), where \( F \) is the Faraday constant (96,485 A s mol\(^{-1}\)) and \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). \( \Delta \phi \) is the electrode potential versus a reference potential, and the term \( \Delta \phi - \Delta \phi_{\text{eq,s}} \) refers to overpotential, or surface overpotential, and is further in the text denoted by \( \eta_{d,s} \). \( \alpha_i \) is the apparent transfer coefficient of the reaction, describing the symmetry in respect to the species and reactions.

Combining the partial reaction rates of each step (from left to right, cathodic direction) into the net rates of two bidirectional single-step reactions, yields the reaction system in (7).

\[
\begin{align*}
\text{Cu}_{\text{r}} & := r_{\text{r,1}} - r_{\text{r,1}} = k_{c,1}^{\circ} a_{\text{Cu(II)}} e^{\left(\alpha_{\text{Cu(II)}} - \alpha_{\text{Cu(II)}} \right)} - k_{n,1}^{\circ} a_{\text{Cu(I)}} e^{\left(\alpha_{\text{Cu(I)}} - \alpha_{\text{Cu(I)}} \right)} \\
\text{r}_{\text{d,2}} & := r_{\text{r,2}} - r_{\text{r,2}} = k_{c,2}^{\circ} a_{\text{Cu(II)}} e^{\left(\alpha_{\text{Cu(II)}} - \alpha_{\text{Cu(II)}} \right)} - k_{n,2}^{\circ} a_{\text{Cu(I)}} e^{\left(\alpha_{\text{Cu(I)}} - \alpha_{\text{Cu(I)}} \right)}
\end{align*}
\]

The copper D/C reaction is accounted for by a first order chemical reaction system and since there is only one step, the index dc is omitted when not necessary. The net D/C reaction rate is expressed as (8).

\[
r_{\text{dc}} = r_{dp} - r_{cp} = k_{d,1}^{\circ} a_{\text{Cu(II)}}^2 - k_{c,1}^{\circ} a_{\text{Cu(II)}} a_{\text{Cu(I)}}
\]

The D/C reaction rate constants \( k_{dp} \) and \( k_{cp} \) (mol m\(^{-2}\) s\(^{-1}\)) are connected by the relation \( k_{dp} = k_{cp} K_{dp} \), to assure that the D/C reaction equilibrium condition holds.

Combining the above reaction rates directly yields the net mass fluxes at the electrolyte-metal interface; the reaction rate \( r_{d,s} \) is equal to the mass flux of the reacting species over a unit area of reaction domain. The net anodic reaction rates are, therefore, also the net mass fluxes \( N_i \) (mol m\(^{-2}\) s\(^{-1}\)) in (9), where \( n \) is the number of moles of associated species, passing over a unit area.

\[
\begin{align*}
N_{\text{Cu(II)}} & = \frac{dn_{\text{Cu(II)}}}{dt} = -r_{1} + r_{dc} \\
N_{\text{Cu(I)}} & = \frac{dn_{\text{Cu(I)}}}{dt} = -r_{2} + r_{1} - 2r_{dc}
\end{align*}
\]

Since a charge is passed over the metal–electrolyte interface during the reaction, the reaction rates also correspond to an electric current, specifically, each charge transfer reaction is associated with a current density \( i_{d,s} = F r_{d,s} \) (A/m\(^2\)). The positive direction of the current is considered to be the same as the direction in which the positively charged species move. By choosing the positive direction of mass flux from the metal to the electrolyte, it follows that the sign of the current associated with a reaction on the metal–electrolyte interface is that of the anodic reactions. Consequently, when considering a full bidirectional reaction in either step (2a) or (2b), the reaction net current density is given as \( i = i_{d,s} - i_{c,s} \). Considering the current density on an electrode with a known area, yields a quantity that can be measured from the system, i.e. the total net current density on the electrode, obtained as (10).

\[
i = i_1 + i_2 = -F(r_1 + r_2)
\]

Even though the rates of individual step reactions in the physical system cannot be observed, they can be estimated when both \( \Delta \phi \) and the model parameters are known, and it is possible to measure the electrolysis cell current. Because the direction of the current is defined to be that of the movement direction of positive ions, the current direction can also be associated with a net mass flux, though the net mass flux is formed by fluxes of several different species and reactions.

#### 2.1.3. Reaction rates in the electrolyte

The copper sulfate dissociation reaction (4) takes place within the whole electrolyte domain. The reaction rate \( r_{d,c} \) (mol m\(^{-3}\) s\(^{-1}\)) is modeled as a first order reaction system (11) with constant reaction rate parameters. However, similarly to the D/C reaction rates, the parameters are kept in such a ratio that the equilibrium condition always holds, resulting in \( K_{da,s} = k_{da,s} K_{dp} \).

\[
r_{da,c} = k_{dass,\text{CuSO}_4} - k_{ass,\text{Cu(II)}\text{SO}_4}/1000
\]

The mass fluxes \( \dot{N}_{a,c} \), of the species involved in the D/A reaction are obtained based on (4) as (12).

\[
\begin{align*}
\dot{N}_{\text{Cu(II)}} & = r_{da} \\
\dot{N}_{\text{Cu(I)}} & = r_{da} \\
\dot{N}_{\text{Cu},\text{SO}_4} & = -r_{da}
\end{align*}
\]

#### 2.1.4. Equilibrium potentials during electrolysis

The equilibrium potentials of each reaction at the electrode surface, full two-step reaction or a single-step reaction, depend on the activities of all associated species and the temperature according to the Nernst Eq. (13).

\[
\Delta \phi_{\text{eq,s}} = \Delta \phi_{\text{eq,s}}^{\circ} + \frac{1}{k} \ln \left( \prod_{\text{reactants}} a_i \right) - \frac{1}{k} \ln \left( \prod_{\text{products}} a_i \right)
\]

\[\Delta \phi_{\text{eq,s}} \quad \text{is} \quad \text{given in (1), (2), (13) are considered the potential differences measured between a copper electrode and the standard hydrogen electrode (SHE)} \]

In each step, the reactants and products are only one species; the \( \text{Cu(II)} \) and \( \text{Cu(I)} \) ions in step 1 and the \( \text{Cu(I)} \) ions and \( \text{Cu} \) metal in step 2, respectively.

The standard equilibrium potentials \( \Delta \phi_{\text{eq,s}}^{\circ} \) given in (1), (2), (13) are considered the potential differences measured between a copper electrode and the standard hydrogen electrode (SHE) in a solution where the \( \text{Cu(II)} \) ion activity is unity, at 25°C.

#### 2.1.5. Activities of species

Activities of the associated species are given a content by considering the equilibrium state of the system, described above in Section 2.1.4. The activity of a species describes how much the volumetric concentration of the species in question deviates, in a proportion given by the activity coefficient, from the reference state, which is here considered to be that when the \( \text{Cu(II)} \) concentration is 1000 mol m\(^{-3}\).
The activity of the Cu(II) species is computed with a correlation equation based on empirical data as $a_{\text{Cu(II)}} = (c_{\text{Cu(II)}}/c_{\text{Cu(II)}}^0)^{c_{\text{Cu(II)}}}$, where $c_{\text{Cu(II)}}$ is the Cu(II) ion concentration (mol m$^\text{-3}$) and $c_{\text{Cu(II)}}^0 = 1000$ mol m$^\text{-3}$ [8]. $v_{\text{Cu(II)}}$ describes the nonlinearity of the Cu(II) ion activity dependence on Cu(II) ion concentration. The value $v_{\text{Cu(II)}}$ is 0.445, determined in ref. [8], is used. The value is in good agreement with, for example [9], where data corresponding to $v_{\text{Cu(II)}} = 0.468$ is given.

The activity of the Cu(I) species is computed similarly, but now the reference concentration is obtained as the equilibrium state of the copper disproportionation reaction (3), in the reference system (i.e. when $c_{\text{Cu(II)}} = 1000$ mol m$^\text{-3}$). Because no data of the Cu(I) species activity–concentration relation was found and the concentration of Cu(I) ions is known to be small, the activity of Cu(I) is calculated by dividing its concentration with the reference concentration. The reference concentration $c_{\text{Cu(I)}}^0$ is obtained based on the equilibrium constant $K_{\text{Cu}}$ of (3), which is $K_{\text{Cu}} = 3 \times 10^{-7}$, when the system is in equilibrium [12]. Therefore, $c_{\text{Cu(I)}}^0 = 0.2620 \cdot (c_{\text{Cu(II)}}^0)^{1/2} = 0.819$ mol m$^\text{-3}$ and $a_{\text{Cu(I)}} = c_{\text{Cu(I)}}/c_{\text{Cu(I)}}^0$.

By convention the activity of metallic copper is considered unity, i.e. $a_{\text{Cu}} = 1$, and is, therefore, omitted from the equations from here on.

2.2. The cell model

2.2.1. Designations

In the electrolysis cell model, a distinction is made between the processes and variables on the electrodes included in the system. In this paper, cyclic voltammetry (CV) is applied to obtain experimental data for model parametrization and validation and, therefore, the electrodes in discussion are called the working electrode, the counter electrode and the reference electrode, denoted with subscripts WE, CE and REF, respectively.

2.2.2. Cell current

The electrode model described in Section 2.1 yields the current density (10) on one copper electrode immersed in an electrolyte containing copper ions. An electrolysis cell consists of two such electrodes and, therefore, the obtained electrode model is duplicated, and two identical electrode models are used to simultaneously describe the charge transfer and other reactions on the two separate electrodes. One hand, these two electrodes are connected with the electrolyte and the electric field, which are modeled by a Nernst-Planck-based mass transfer model including a reaction term, and an electric field model, as described below. On the other hand, the electrodes are also connected together externally by the cell power source. The model structure thus enables coupling reaction rates on both electrodes to the cell current and the cell electric potential to the mass transfer and charge transfer phenomena in the cell.

Since the electrodes are connected to each other, the same current must run through the electrodes and, therefore, the coupling in (14), where $A_J$ is the electrode area (m$^2$), is obtained.

$$i_{\text{WE}}A_{\text{WE}} + i_{\text{CE}}A_{\text{CE}} = 0$$

The choice of which electrode system is solved first is arbitrary, but in this model, the working electrode current density, $i_{\text{WE}}$ is first calculated with the model, based on a set electrode potential $\Delta \phi_{\text{WE}}$ versus a reference potential. When $i_{\text{WE}}$ is obtained and the electrode areas $A_{\text{WE}}, A_{\text{CE}}$ are known, the current density on the counter electrode, $i_{\text{CE}}$, is calculated. Finally, the counter electrode potential $\Delta \phi_{\text{CE}}$ is solved based on the obtained $i_{\text{CE}}$. After both electrode potentials and the current densities on them are known, the mass transfer model and electric field model are also solved. Note that, the equations in (7) applied to compute (10) are nonlinear and, therefore, the value of $\Delta \phi_{\text{CE}}$ at which (14) holds, is found by using a numerical search.

2.2.3. Cell potential, $E_{\text{CELL}}$

In CV experiments, as well as in the simulated cases, the cell power source adjusts the cell potential so that the working electrode potential $\Delta \phi_{\text{WE}}$ is set to the desired value. As a result, current passes through the cell, meaning that the counter electrode must also find a suitable potential, $\Delta \phi_{\text{CE}}$. Moreover, due to the resistivity of the electrolyte, an ohmic loss of potential, $U_{\Omega}$, occurs as current passes through the cell. The potential difference between the electrodes, added with the ohmic loss of potential occurring over the electrolyte, forms the cell potential, i.e., $E_{\text{CELL}} = \Delta \phi_{\text{CE}} - \Delta \phi_{\text{WE}} + U_{\Omega}$.

In the cell model, the electrode potentials $\Delta \phi_{\text{WE}}$ and $\Delta \phi_{\text{CE}}$ are obtained as given in Section 2.2.2, but the ohmic potential loss is computed based on a lumped system assumption made on the electrolyte bulk. The electrolyte bulk is assumed homogenous and considered as a resistor with a measurable conductivity $\sigma$ (S m$^{-1}$) and a constant geometry, so that the current passing through it travels a path with mean length $L_{\text{G}}$ (m) and mean cross-sectional area $A_{\text{G}}$ (m$^2$). Furthermore, the cell current is computed as $i_{\text{WE}}A_{\text{WE}}$ and, therefore, the ohmic loss of potential $U_{\Omega} = i_{\text{WE}}A_{\text{WE}}/\sigma A_{\text{G}}$. In practice, the geometry parameters are measured from the examined cell and electrolyte conductivity is measured with a conductometer. This model structure enables accounting for the ohmic potential drop without including it explicitly in the geometry of the model.

In small-scale laboratory cells, where currents are in the mA range and cell dimensions are small on an absolute scale, yet large in respect to electrode surface size, the ohmic potential loss can be close to insignificant. However, in industrial scale electrolysis process equipment, the absolute cell size and passed current is large and the electrode areas approach the cell cross-sectional area, and this results in the ohmic loss also becoming significant to such an extent that it may be considered a cell design parameter.

The voltammetric sweep potential is used as a control signal to set the potential $\Delta \phi_{\text{WE}}$ vs. reference. This corresponds to a system with potentiostatic control, but just as well, the control signal could be a given electrode current density, $i_{\text{target}}$, either constant or time-varying. This would then correspond to galvanostatic control. Under galvanostatic control, both the electrode current densities would be directly obtained based on the electrode areas ($i_{\text{WE}} = i_{\text{target}}, i_{\text{CE}} = k_s i_{\text{target}}$) and the electrode potentials ($\Delta \phi_{\text{WE}}, \Delta \phi_{\text{CE}}$) should then be solved based on the electrode model by using a numerical search.

2.3. Mass transfer in the electrolyte

When implementing the electrochemical cell model, the electrolyte is considered to consist of one continuous domain bounded by the electrode surfaces. As CV experiments are used to validate the model, no agitation is enforced and mass transfer in the electrolyte is modeled upon the Nernst-Planck system with electroneutrality condition. A determined mass flux given by (9) exists over the electrode–electrolyte interfaces.

Put into equations, the concentrations $c_i$ (mol m$^{-3}$) of all species $i$ in the electrolyte fulfill the mass transfer equation system (15) with the electroneutrality condition $\sum c_i = 0$ in effect.

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left(D_i \nabla c_i + z_i F D_i \frac{\nabla \phi}{RT} c_i \nabla \phi \right) + R_{\delta i}$$

In (15) $z_i$ is the electron number and $D_i$ is the diffusivity (m$^2$ s$^{-1}$) of species $i$. 
The mass transfer boundary conditions are obtained based on the mass fluxes (9) on the electrodes and are computed with (16).

\[ N_i = -n \cdot \left( -D_i \nabla c_i - F z_i \frac{D_i}{RT} c_i \nabla \phi \right) \]  

(16)

The condition (16) is set on both the WE and CE boundaries, \( n \) being the boundary outward normal vector. This boundary condition couples the electrode model (i.e. the reaction rates) with the mass transfer model.

The initial condition for mass transfer is \( c_i = c_{i,1} \) everywhere with \( c_{i,1} \) being the bulk solution concentration of species \( i \) (mol m\(^{-3}\)), which is obtained as the equilibrium concentrations of (4).

2.4. The electric field

Given that the working electrode and the counter electrode are in some (different) electric potentials \( \Delta \phi_{WE} \) and \( \Delta \phi_{CE} \), respectively, an electric field in between them is formed according to the electric field Eq. (17).

\[ \nabla \cdot (\sigma \nabla \phi) = 0 \]  

(17)

In (17), \( \sigma \) is the electrolyte conductivity (S m\(^{-2}\)) close to the electrodes and is computed as \( \sigma = F^2 / RT \sum z_i D_i c_i \).

The boundary condition on both boundaries is a fixed potential condition (18).

\[ \phi = \Delta \phi \]  

(18)

On the boundary describing the working electrode–electrolyte interface \( \phi = \Delta \phi_{WE} \), and on the counter electrode boundary \( \phi = \Delta \phi_{CE} \). The condition (18) couples the electric field potential \( \phi \) with the electrochemical potential \( \Delta \phi \) and emphasizes the meaning of \( \phi \) as the local potential in respect to a known reference.

Solving the Poisson Eq. (17) inside the diffuse electrolyte layer has only a minor effect, compared to estimating the electric field there by a linear approximation. It is done, however, in order to follow the electroneutrality condition.

The model is configured as a spatially one-dimensional partial differential equations (PDEs) system and solved with the finite elements method by using the Comsol Multiphysics and Matlab software tools [10,11]. Comsol was used as the PDE system solver and the numerical search algorithms utilized in the cell model were implemented based on the Nelder-Mead direct search algorithm provided by the Matlab computational software. The domain where the PDE system was solved spanned a depth of 5 mm, which was found adequate for even the longest sweep times. The computational mesh consisted of 333 elements and the solution was not found to change by refining the computation mesh. Second order Lagrangian quadratic shape functions were used to solve all dependent variables. When run on a desktop PC (2.4 GHz, 3.2GB, Windows XP) the model solves in ca. 20 s, solution time depending somewhat on the control signal and the model parameters.

The implemented Comsol Multiphysics model, complete with necessary Matlab scripts as well as the experimental data can be obtained in electronic form from the corresponding author.

3. Experimental

Cyclic voltammetry was utilized to create data for the parameter search and to validate the model. The experiment cell was constructed of a 100 ml beaker, two copper electrodes with a known surface area and a Ag/AgCl reference electrode with a KNO\(_3\) bridge electrolyte and standard potential of 0.2 V. Analytic grade copper sulfate (Riedel-de Haen, CuSO\(_4\)·5H\(_2\)O), dissolved in deionized water (< 0.2 mS m\(^{-1}\)) in various concentrations, was used as the electrolyte and a PC-connected data acquisition card (NI PCI 6030E) was utilized to control and log the voltage signals. A Consort C533 conductometer with an SK23T conductivity cell with Pt electrodes was used for conductivity measurements.

In the CV tests for the electrode model parametrization, the potential between the working electrode (WE) and the reference electrode (REF) was swept between approximately -0.5 V and 0.5 V vs. zero-current potential, with sweep rates of 100, 75 and 50 mV s\(^{-1}\). The experiments were conducted in electrolytes containing CuSO\(_4\) in concentrations of 1, 0.5 and 0.1 mol m\(^{-3}\). No electrolyte pretreatment or agitation was applied during the experiments.

To obtain data for the cell model validation, the CE area was varied by changing the electrode. Hence, the CV experiments were done with two different electrode configurations: (i) with both WE and CE being identical, teflon-embedded Cu electrodes and \( A_{WE} = A_{CE} \) and \( k_1 = 1 \), and (ii) with the CE being an exposed copper wire, which makes \( A_{CE} \gg A_{WE} \) and \( k_1 \gg 1 \). The electrodes were always within 1 cm from each other.

In addition to cell current and the WE potential (vs. REF), also the potential between WE and CE (i.e. the cell voltage) is measured in order to (i) determine the cell power consumption and (ii) to verify the cell voltage estimated by the model.

The experiment configuration with a total CuSO\(_4\) concentration of 0.5 mol m\(^{-3}\), a sweep rate of 100 mV s\(^{-1}\) and \( k_1 \gg 1 \) was chosen as the reference case. The reference case results were used for model fitting and parameter search and the other experimented cases were used for model validation.

4. Results

4.1. Measurements

The experiment results are mostly shown in context with the corresponding simulation results, but the following measured data are shown here to highlight the cell configuration effects. The concentration of total CuSO\(_4\) in the electrolyte is 0.5 mol m\(^{-3}\) and the sweep rate is 100 mV s\(^{-1}\) in both experiments.

1. The control voltage signal, i.e. \( \Delta \phi_{WE} \) vs. \( \Delta \phi_{REF} \) when \( k_A \) is varied (Fig. 1 solid lines)
2. The output voltage signal, i.e. \( \Delta \phi_{WE} \) vs. \( \Delta \phi_{CE} \) when \( k_A \) is varied (Fig. 1 dashed lines)
3. The measured WE current density in cases 1 and 2 (Fig. 2)

The effect of CE size is clearly observed in Fig. 1: the required cell current decreases significantly when the counter electrode size is increased.

Fig. 2 illustrates how the WE current density is affected by the CE size during the anodic sweep due to changes in the chemical processes occurring on the CE at \( t = 4, \ldots, 6 \) s, when the cell potential approaches 1.2 V (as seen in 1, at \( t = 4, \ldots, 6 \)).

Note that, when comparing the cell voltage curves in Fig. 1 and the current density curves in Fig. 2, the cell power consumption (which is the product of cell voltage and current) is notably higher in the case when \( k_A = 1 \) is notably higher than when \( k_A \gg 1 \).

4.2. Simulation results in the reference case

As it is already clear, a significant number of parameters is required to be in place for the system to function. Many of these parameters, such as the species’ diffusivities and electrolyte conductivity can be estimated based on the literature and measurements [8,7,4,9,1]. Several other, however, cannot be estimated but...
Fig. 1. Potential measurements during two CV experiments. The first two curves (nearly coinciding) are the controlled potential between the WE and the REF. The last two, with dashed lines, are the potential between the WE and the CE. $k_A$ in each case is given in the legend and the effect of the counter electrode size is clearly observable.

Fig. 2. Measured WE current density during two CV experiments. The curve colors correspond to those of the voltage curves shown in Fig. 1.

Fig. 3. The $i-t$ curve predicted by the model (solid line) and measured in the experiment (dashed line) in the reference case.

Fig. 4. The $i - \Delta \phi_{\text{WE}}$ curve predicted by the model (solid line) and measured in the experiment (dashed line) in the reference case.

Fig. 5. The measured and estimated cell potential, $E_{\text{CELL}}$, when $k_A = 1$ and $k_A \gg 1$. 

an appropriate set of parameters must either be identified from data or found in some other manner. In this paper, the parameters were sought for by first fixing parameters for which data could be found in the literature, and then adjusting the unknown parameters to fit the working electrode current density estimated by the electrode model with the reference case measurement.

It is obvious that no set of parameters matching some data is unique and the aim here is to only find at least one well-functioning set of data that enables easy replication of the work and further examination of the model. The parameters applied in the reference case model, against which all other cases are compared, are given in Table 1.

The WE $i-t$ response for the fitted reference case is given in Fig. 3 (solid line) and compared with the measured data (dashed line). (Also further in the text, the measured data are always plotted with a dashed line.)

It can be seen in Fig. 3 that the model corresponds quite well with the measurement data except for the final part of the cathodic sweep. If the curves are examined in the $i - \Delta \phi$ plot, Fig. 4, the model error is seen as over-hysteretic behavior of the simulated curve.

As one means of verifying the electrode model adequacy and to obtain the desired full Cu–Cu electrolysis cell model, such a model based on two identical electrode models was constructed and simu-
Fig. 6. Rates of individual step reactions on the working electrode boundary. The effect of the disproportionation reaction is clearly seen during the anodic sweep ($t = 2, \ldots, 5$ s).

$k_A = 1$. In the simulation, the cell potential soars and computation is aborted at $t \approx 5$ s, whereas in the experiment, cell potential rises just above 1.2 V, close to the standard potential of oxygen formation from H$_2$O. The smallest $A_{CE}/A_{WE}$ ratio at which the model functions reliably is 1.9, which is used to obtain the plotted curve.

Assuming, based on the compared model estimates and measurement data in Figs. 3–5 that the model is able to capture the most important processes underlying the measurable properties, a variety of information concerning the Cu–Cu electrolysis process can be extracted from the model. Most importantly, the model enables examining the rates of individual charge transfer reactions. For the reference case model, these are plotted in Fig. 6, where both the rate-determining step in effect, as well as the effect of the D/C reaction can be observed clearly.

The data in Fig. 6 is in correspondence with the literature, saying that reaction (2b) is essentially faster than (2a) and that the latter is the system rate-determining step. On the cathodic side, the rates of (2b) and (2a) clearly coincide, as the slower of them limits the overall reaction rate, but on the anodic side the step reaction rates diverge somewhat due to the disproportionation reaction consuming a part of the available Cu(I) species.

Along with the individual reaction rates, also activities of the involved species can be observed. The activities of the species directly affect the equilibrium potentials of the charge transfer reactions which may also be evaluated. The reference case model-estimated activities of both the Cu(II) and Cu(I) species, on both the WE and CE are plotted in Fig. 7.

In Fig. 7 the activities on the counter electrode vary only very little from the initial state. This is intuitive since in the reference case, the counter electrode is significantly larger than the working electrode and, therefore, the CE current density and corresponding mass fluxes there are very small. In the simulation, a value of $k_A = 20$ was used and it was found that after $k_A \geq 10$, increasing the parameter has very little effect. A small deviation in the activity curves on the CE can be seen in Fig. 7 though theoretically, if $k_A$ was infinite and CE infinitely large, the current density there would be zero and no mass flux and thus no deviation on species activity should occur. The deviation is due to the implementation of the model, where infinity is approximated with 20.

The equilibrium potentials of reactions (1)–(2) corresponding to the activities on the WE are shown in Fig. 8.

4.3. Effects of parameters

Effects of various parameters can be easily evaluated with the model and selected parameter effects are discussed below.

4.3.1. Effect of the copper D/C reaction rate, $k_{dp}$, $k_{cp}$

The copper disproportionation/ comproportionation reaction rate has a significant effect on the electrode behavior when the electrode potential is on the anodic side. In CV experiments, however, the effects on the anodic sweep are also reflected on the cathodic side through mass accumulation in the electrolyte layer near the electrode. The effect of the D/C reaction rate variation can be seen in Fig. 9, where the reaction rate is varied between 0.1, \ldots, 10 times the reference rate.

Increasing the D/C reaction rate makes the electrode current behavior more linear on the anodic potential side and decreasing the rate makes the anodic curve more nonlinear again, i.e. the electrode equation dominates unless the D/C reaction is fast enough. However, while making the electrode current–potential behavior more linear, increasing the D/C reaction rate also affects the zero-current potential. Thus, a suitable D/C reaction rate must
be sought for along with other parameters of the main electrode equation.

4.3.2. Effect of CuSO₄ dissociation rate, \( k_{\text{diss}} \), \( k_{\text{ass}} \)

The copper sulfate dissociation reaction has a significant role in supplying the electrode surfaces with Cu(II) ions. The effects of the CuSO₄ dissociation rate can, therefore, be directly observed in the electrode current density during the cathodic sweep. In Fig. 10 the 10-fold decrease of \( k_{\text{diss}} \) and, thereby, also \( k_{\text{ass}} \) is seen as a diminished current density during the period in which the WE surface overpotential is negative (i.e. when \( t > 9 \) s). Similarly, increasing the dissociation/association reaction rate manifests as increased current density during the cathodic sweep. No significant effect on the anodic sweep is observed.

4.3.3. Effect of Cu(II) activity nonlinearity, \( \gamma_{\text{ETB}} \)

The \( \gamma_{\text{ETB}} \) parameter determines the nonlinearity of the ratio between \( c_{\text{Cu(II)}} \) and \( a_{\text{Cu(II)}} \) and the parameter has shown to have a significant effect on the cathodic side behavior of the WE current density, i.e. when the electrode surface is close to being depleted of Cu species. Fig. 11 illustrates below how altering the \( \gamma_{\text{Cu(II)}} \) parameter affects the \( i-t \) curve on the WE boundary.

Increasing the \( \gamma_{\text{Cu(II)}} \) parameter makes the activity–concentration dependence of the Cu(II) species more linear. This leads to the WE current density being more strongly diminished by the decreasing Cu(II) concentration also at relatively high Cu(II) concentrations during the cathodic sweep. The opposite occurs when decreasing the \( \gamma_{\text{Cu(II)}} \) parameter.

4.4. Model validity under different experiment conditions

In order to evaluate the model under varying practical conditions, the model was simulated with the physical parameters corresponding to the various CV experiment conditions. Specifically, CV sweeps were simulated with the total CuSO₄ concentration at 1, 0.5 and 0.1 mol dm\(^{-3}\) and the sweep rate set to 100, 75 and 50 mV s\(^{-1}\).

4.4.1. Varying CuSO₄ concentration

When comparing the model under varying total CuSO₄ concentration, an interesting observation is that when all the reaction rate
constants of (2) are multiplied with a factor \((c_{\text{CuSO}_4}^{\text{ref}}/c_{\text{CuSO}_4}^{\text{tot}})^{\text{Cu(II)}}\), where \(c_{\text{CuSO}_4}^{\text{ref}} = 0.5\) M, the model behaves better than what it does without this modification. The effects of this modification are illustrated in Fig. 12, where the measured WE current density as well as two model-estimated current densities at the mentioned three \(\text{CuSO}_4\) concentrations are shown. The solid curves correspond to the model where the described modification is made and the dash-dot curves show the model behavior without the mentioned modification.

The explanation for this phenomenon is not trivial at first, but considering that multiplying all the \(k_d,s\) coefficients with a constant essentially corresponds to scaling the system exchange current density (or exchange reaction rate), the modification becomes physically understandable. The results of the modification also emphasize the nature of the modeled activities (which are multiplied with the \(k_d,s\)) as being concentration values scaled to a chosen reference point. It may be considered that the model is initially calibrated to the reference case and with the aforementioned modification then scaled to the varied cases.

### 4.4.2. Varying sweep rate

The CV experiment sweep rate can be varied in order to emphasize mass transfer effects and check model validity on behalf of the mass transfer parameters, in this case the diffusivities and to some extent also the D/A reaction rate. Fig. 13 shows the model-estimated WE current density compared with the measured data when the sweep rate is varied from 100 to 75 and 50 mV s\(^{-1}\).

The model error already visible at the last part of the cathodic sweep can be observed to increase as the sweep rate is decreased and the mass transfer effects become stronger. Importantly, the model does estimate a lower peak current density at slower sweep rates but not as much lower as would be expected upon the data. This model error may be attributed to using constant diffusion coefficients and the errors in reaction rates of the D/A reaction.

### 4.5. Comments

It should be noted that the way \(\text{Cu(I)}\) activity is implemented in this model does affect the magnitude of reaction rate coefficients. Whereas typically the coefficients in the reaction rate terms including the \(\text{Cu(I)}\) species are reported to be several orders of magnitude higher [4] than those in reactions of the \(\text{Cu(II)}\) species, in this paper the difference is reduced because both activities are scaled close to unity. Still, the characteristic behavior is clearly observable, reaction (2b) is significantly faster than reaction (2a) as seen in Fig. 6.

Another observation that should be made on the model parameters is that the \(\text{CuSO}_4\) dissociation/association reaction rate is notably high. This means that although the reaction balance is not completely on either side, the reaction reaches its equilibrium rapidly. This may be related to the mass transfer of copper species because the \(\text{CuSO}_4\) species, being non-ionic (although hydrated), might be considered to diffuse faster than the ionic \(\text{Cu(I)}, \text{Cu(II)}\) or sulfate species, which experience a stronger drag effect due to their electric charge. This indirectly increases also the mass transfer of copper in the electrolyte compared to what it would be if mass transfer were to occur only via diffusion of the ions.

The model misses some important physical phenomena known to affect the electrolysis process, e.g., the dynamic double-layer effects and double-layer capacitance. These are left out due to the relatively slow range of dynamics sought to be captured with the model, if the model was to be applied in pulsed current plating applications, dynamic double-layer effects should be included. Further, a re-calibration of the model parameters should be done with electrolytes containing a supporting electrolyte before the model is applicable to practical process modeling. Also the lumped model used to estimate cell ohmic loss is very rough and should be determined more precisely.

### 5. Conclusions

A copper-copper electrolysis cell model including the copper RedOx step reactions, copper disproportionation and the \(\text{CuSO}_4\) dissociation reaction was constructed. Simple expressions for ionic species’ activity and constant diffusivities were used. Dynamic double-layer effects or double-layer capacitance are not included in the model and are subjects for further model development. The model was verified against a set of data obtained by cyclic voltammetry and the applied model parameters as well as initial values for variables were reported. The model sensitivity to a number of parameters was examined and the model was found to behave in a concise manner, enabling model adaption to other similar systems. The model estimate of electrode current density was found...
to fit the reference CV data well except for the backward part of the cathodic sweep. The cell model estimate for cell potential in two examined cell configurations was also found to be fair. The model operation was examined when the total CuSO₄ concentration and sweep rate of CV sweep was varied and the model output was compared to data measured from the corresponding CV experiments. It was found that the model which is parametrized to function at a certain total CuSO₄ concentration may be modified to operate better at other CuSO₄ concentrations by only scaling all the charge transfer reactions rate constants with a single multiplier.

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References