# Contribution of an Electro-Vortex Flow to Primary, Secondary, and Tertiary Electric Current Distribution in an Electrolyte

E. Karimi-Sibaki, <sup>1</sup> A. Kharicha,<sup>1,z</sup> M. Wu,<sup>2</sup> A. Ludwig,<sup>2</sup> and J. Bohacek<sup>2</sup>

 <sup>1</sup> Christian-Doppler Laboratory for Metallurgical Applications of Magnetohydrodynamics, Montanuniversitaet of Leoben, A-8700 Leoben, Austria
 <sup>2</sup> Chair of Simulation and Modeling of Metallurgical Processes, Montanuniversitaet of Leoben, A-8700 Leoben, Austria

Three different approaches, known as primary, secondary, and tertiary current distributions, are employed to calculate the electric current distribution throughout an electrochemical system. Ohm's law is used for the primary and secondary, whereas Nernst-Planck equations for the tertiary. The electrochemical system. Ohm's law is used for the primary and secondary, whereas Nernst-Planck equations for the tertiary. The electrovers flow and concentration fields of ions are solved only in the electrolyte, air, electrode, and graphite crucible), while the electro-vortex flow and concentration fields of ions are solved only in the electrolyte. The model accounts for the faradaic reaction of the formation of  $Fe^{2+}$  at the anode and the discharge of  $Fe^{2+}$  and  $Ca^{2+}$  at the cathodic crucible. The electric double layer (EDL) is modeled considering the generalized Frumkin-Butler-Volmer (gFBV) formula. The dissimilarity in the calculated concentration of  $Fe^{2+}$  between secondary and tertiary current distributions decreases with the increase of the applied voltage. A strong stirring of the electrolyte by (exclusive) Lorentz force cannot guarantee uniform concentration for all ions. As the applied voltage increases the migration may locally surpass the advection flux, leading to accumulation of ions near the anode/cathode. All current distributions coefficients for all ions, despite the non-uniform distribution of electrical conductivity in the tertiary current distribution. The modeling results enabled us to elucidate the origin of an experimentally observed phenomenon, i.e., the formation of FeO under the tip of electrode.

Manuscript submitted April 30, 2018; revised manuscript received August 27, 2018. Published September 7, 2018.

Electro-vortex flows are frequently observed in the conducting fluids, such as an electrolyte or a molten metal.<sup>1</sup> Most often, a small electrode is placed at the surface of the conducting fluid. Meanwhile, a non-uniform electric current flows through the system. The electric current spreads radially outwards near the electrode-conducting fluid interface. The interaction between the electric current and the self-induced magnetic field creates a rotational electromagnetic (Lorentz) force. Thereby, a vortical flow, which is known as electro-vortex flow, develops as the (irrotational) pressure force cannot compensate for the (rotational) Lorentz force.<sup>2,3</sup>

The electro-vortex flow of the conducting fluid significantly influences the efficiency of numerous electro-metallurgical processes involving electromagnetic stirring<sup>4</sup> as well as extraction and refining of metals.<sup>5</sup> Copper magneto-electrolysis<sup>6</sup> and aluminum smelting<sup>7</sup> are well-known processes to extract metals. Furthermore, electric arc furnace (EAF),<sup>8</sup> vacuum arc remelting (VAR),<sup>9</sup> and electroslag remelting (ESR)<sup>10</sup> processes are extensively used to refine alloys. The core of the ESR process is the CaF<sub>2</sub>-based electrolyte, which is typically composed of CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and FeO. The electrolyte serves to remove sulfur and non-metallic inclusions from the alloy and provide heat through Joule heating into the ESR process. Several alloy/electrolyte elements, such as Fe, Ti, S, O, and Ca, can participate in electrochemical (faradaic) reactions that occur at the electrolyte-metal interface.<sup>11,12</sup> These reactions occur to achieve further purification and refining of the alloy.

Apparently, the distribution of electric current density throughout the electrolyte remarkably affects the rate of Faradic reactions, electromagnetic field, concentration of ions, and flow fields. Therefore, a precise prediction of the distribution of electric current density is a pivotal step toward modeling of electro-metallurgical processes. Conventionally, three classes of electric current distribution are identified: primary, secondary, and tertiary. The electrode kinetics and composition variations in the electrolyte are ignored in primary current distribution, whereby the electrical resistance is determined using Ohm's law.<sup>6,7,13</sup> In a similar manner, the secondary current distribution ignores composition-dependent effects, and the electrolyte is assumed to obey Ohm's law. However, effects of faradaic reactions (electrode kinetics) on the distribution of electric current density are considered.<sup>14,15</sup> The tertiary current distribution takes into account both electrode kinetics and the non-uniformity of the concentration field. The electrolyte behaves in accordance with Nernst-Planck equations subject to the approximation of electro-neutrality.<sup>16</sup>

In this study, a typical molten electrolyte for the ESR process made of CaF<sub>2</sub> (%wt 98)-CaO (% wt 2) is studied. The electromagnetic field is calculated in the entire system, including an electrode made of pure iron, molten electrolyte, air, and graphite crucible (see Fig. 1). Primary, secondary, and tertiary current distributions for the electrolyte are calculated. The interplay between the flow in the molten electrolyte and electromagnetic field is taken into account. Furthermore, the concentration field in the electrolyte is evaluated. The governing equations are solved using the Finite Volume Method (FVM), which has the following key features.<sup>17</sup> FVM is extensively used to accurately model the flow. Mass conservations of all ions are automatically satisfied. In addition, there is no restriction on the total number of ions involved (reacting or non-reacting). In the present study, the electrode is anodic, and ferrous ion (Fe2+) is injected to the electrolyte at electrode-electrolyte interface. Additionally, Fe<sup>2+</sup> and Ca<sup>2+</sup> are discharged at the interface between the cathodic crucible and molten electrolyte. A multi-regression analysis is performed to extract activation and concentration overpotentials at the anodic interface using generalized Frumkin-Butler-Volmer (gFBV) formula.<sup>18,19</sup> These parameters are required as input data for calculations of secondary and tertiary current distributions. Here, the influence of the operational parameter, such as applied voltage on transport phenomena (e.g., flow and electromagnetic field), is also discussed. The ultimate goal is to obtain a fundamental understanding of the contribution of the electro-vortex flow on transport/reaction of ions. Based on the modeling results, we propose an explanation for a phenomenon, namely, the formation of a thick layer of FeO under the electrode tip, which was observed in situ in the DC operated ESR-like process.12

## Modeling

All symbols used in this paper are described in the List of Symbols. For the sake of simplicity, the following key assumptions are made:

 All molecules of the molten electrolyte at the elevated temperature of the process (1803 K) split into ions. Thus, the electrolyte is assumed to be fully dissociated,

$$CaF_2 \rightarrow Ca^{2+} + 2F^-$$
[1]

```
<sup>z</sup>E-mail: Abdellah.kharicha@unileoben.ac.at
```

 $\mbox{CaO} \rightarrow \mbox{Ca}^{2+} + \mbox{O}^{2-} \eqno(2)$ 



Figure 1. Configuration of the computational domain and boundaries are illustrated. Given names for boundaries are described. Of note, given names for boundaries (abbreviations) are used to describe boundary conditions in Table I.

 (ii) The following faradaic reactions are considered in our calculations (secondary and tertiary) at the anode (+) and cathode (-),

(At anode): 
$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 [3]

(At cathode): 
$$Fe^{2+} + 2e^- \rightarrow Fe$$
 [4]

(At cathode): 
$$Ca^{2+} + 2e^- \rightarrow Ca$$
 [5]

In our calculations for the secondary current distribution, we exclusively consider the ferrous ion  $(Fe^{2+})$  as the electro-active ion. In terms of mathematical modeling, a positive mass flux of  $Fe^{2+}$  is applied at the anodic electrode-electrolyte interface where  $Fe^{2+}$  is injected into the electrolyte (Eq. 3). Subsequently,  $Fe^{2+}$  is removed from the electrolyte at the cathodic crucible-electrolyte interface as described in Eq. 4.

Of note, the concentration fields of all types of ions (reacting and non-reacting) influence the tertiary current distribution. As such, mass conservations of all involving ions must be satisfied. The electric current is delivered between anode/cathode and electrolyte by means of faradaic reactions involving Fe<sup>2+</sup> (Eqs. 3–4). On the other hand, no Fe<sup>2+</sup> is initially present in the electrolyte. Thus, another ion (here Ca<sup>2+</sup>) must react at the cathodic interface (Eq. 5) to ensure that the electric current flows through the entire system. As time proceeds, sufficient amounts of Fe<sup>2+</sup> can reach the cathode where they participate in faradaic reactions (Eq. 4). Both Fe<sup>2+</sup> and Ca<sup>2+</sup> compete for electrons at the cathodic crucible-electrolyte interface. Fe<sup>2+</sup> exhibits a higher priority to gain electrons as it has a higher standard reduction potential.<sup>20</sup> We ignore the neutral iron (Fe) and neutral calcium (Ca) in our calculations.

(iii) The potential drop at the anodic electrode-electrolyte interface due to the formation of electric double layer (EDL) is implicitly modeled as further described in section Estimation of activation overpotential. In the present study, the mass transfer phenomena at the cathodic crucible-electrolyte interface are of no interest. Therefore, influences of faradaic reactions and the formation of the EDL at the cathode on the electric potential field and concentration fields of ions are not taken into account. The active area of the cathodic crucible is much larger than that of the anodic electrode (by a factor of twenty) so that a significantly smaller amount of electric current density flows through the cathode compared to that of the anode. Therefore, the activation/concentration overpotentials are expected to be much smaller (assumed negligible) at the cathode compared to that at the anode. Here, we assume that the electro-active ferrous ion (Fe<sup>2+</sup>) unlimitedly reacts at the cathode surface where the value of the concentration of Fe<sup>2+</sup> is set to zero.

- (iv) The condition of bulk electro-neutrality of the electrolyte holds in all calculations, including primary, secondary, and tertiary current distributions. Mathematically, this condition is expressed as follows:  $\sum z_i c_i = 0, i = Ca^{2+}, Fe^{2+}, F^-, O^{2-}$ .
- (v) Formation of oxyfluorides, complexation of metal ions, and any other chemical reactions, such as generation/recombination reactions that may occur in the molten  $CaF_2$ -based electrolyte, are not included in the model.<sup>21</sup>
- (vi) To best of our knowledge, diffusion coefficients of involving ions (Ca<sup>2+</sup>, Fe<sup>2+</sup>, F<sup>-</sup>, and O<sup>2-</sup>) for the given molten electrolyte are unknown. A large uncertainty on reported values of coefficients for CaF<sub>2</sub>-based electrolytes exists given that several parameters, such as temperature, pressure, electrolyte composition, radius and valency of diffusing ions, can affect diffusion coefficients.<sup>21</sup> In the present study, an identical value  $(5 \times 10^{-9} \text{ m}^2.\text{s}^{-1})$  is assumed for the diffusion coefficients of all ions.
- (vii) To calculate the electric current distribution, we assumed that the current is only carried by the movement of ions. Thus, any plausible electronic conduction through the molten electrolyte is ignored.<sup>22</sup>
- (viii) The isothermal flow in the electrolyte is exclusively driven by the electromagnetic (Lorentz) force. It has to be pointed out that spatial variations in the species concentration fields throughout the molten electrolyte attributes a non-uniform density of the electrolyte. The latter gives rise to a force which is known as solutal buoyancy. In the present study, a uniform density for the electrolyte is assumed so that the solutal buoyancy is ignored.

As shown in Fig. 1, a 2D axisymmetric computational domain is considered. The induced magnetic field throughout the entire system is dominantly azimuthal. Hence, the process conditions are assumed to be axisymmetric.

*Governing equations.*—*Flow field.*—The continuity (Eq. 6) and momentum (Eq. 7) equations are solved to determine the flow field as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0$$
 [6]

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot (\mu (\nabla \vec{u} + \nabla \vec{u}^T)) + \rho \vec{g} + \vec{F}_L.$$
 [7]

The fluid (electrolyte) is considered to be Newtonian and incompressible. The isothermal flow in the electrolyte is exclusively driven by the electromagnetic (Lorentz) force. The force originates in the interaction between the electric current and its own magnetic field as follows:

$$\vec{F}_L = \vec{j} \times \vec{B}.$$
 [8]

Calculations of the electric current density and magnetic fields are thoroughly described in the next section.

The flow is not calculated in the air zone. The electrolyte-air interface is assumed to remain stationary. A free-slip boundary condition is applied at the free surface of electrolyte with the given name of (ElecAE) as shown in Fig. 1. The no-slip flow condition is considered for other boundaries of electrolyte, including anode electrolyte-side (AnE) and cathode electrolyte-side (CaE).

*Magnetic field.*—The electromagnetic field is calculated in the entire domain using the A- $\varphi$  formulation,<sup>23,24</sup> where  $\varphi$  is the electric scalar potential and  $\vec{A}$  denotes the magnetic vector potential. Mathematically, the magnetic field is defined by the curl of the magnetic vector potential,

$$\nabla \times \vec{A} = \vec{B}.$$
 [9]

A direct voltage (DC current) is applied to the system. Thus, the magnetostatic  $\vec{A}$  satisfies the following equation:

$$\nabla \times \left(\frac{1}{\mu_0} \nabla \times \vec{A}\right) = \vec{j}.$$
 [10]

To achieve a unique solution for Eq. 10, the coulomb gauge  $(\nabla \cdot \vec{A} = 0)$  is employed.<sup>25</sup> In addition, a constant magnetic permeability ( $\mu_0$ ) is assumed in the entire domain.

A value of zero is applied for radial and axial components of  $\vec{A}$  at crucible side (SC) and crucible bottom (BC) boundaries. The flux of  $\vec{A}$  is zero at the electrode top (TM), air top (TA), and crucible top (TC). Furthermore, continuity of the magnetic field is applied at all interior boundaries.

*Electric current density field.*—The conservation equation of electric current density is given as

$$\nabla \cdot \vec{j} = 0. \tag{11}$$

A summary of all governing equations pertaining to boundary conditions for primary, secondary, and tertiary current distributions are listed in Table I. The electric current density is dependent on the electric scalar potential and concentration of ions. In the calculation of primary and secondary current distributions, Eq. 11 is reformulated such that Ohm's law is applied. Therefore, a linear relationship exists between the electric current density and the electric field ( $\vec{E} = -\nabla \varphi$ ). As described in Table I, the correlation coefficient is referred to as electrical conductivity ( $\sigma$ ), which relies on the concentration of all ions. Customarily, a uniform concentration field ( $\|\nabla c_i\| \approx 0$ ) is presumed to calculate the electrical conductivity in both primary and secondary current distributions. In the presence of excess of nonreaction ions (supporting electrolyte), the migration flux of the electroactive ion (here Fe2+) is neglected in calculations of secondary current distribution.<sup>20</sup> Migration flux arises from the movement of ions in response to the imposed electric field. As a result, the concentration field for the electro-active ion (here Fe<sup>2+</sup>) is determined by solving the non-steady diffusion-advection equation (Table I). Furthermore, the electrical conductivity is assumed to remain constant regardless of the variation in the concentration field for the electro-active ion.<sup>26</sup>

As reported in Table I, both primary and secondary current distributions share identical boundary conditions for electric potential in all boundaries except at the anodic electrode-electrolyte interface. From a modeling point of view, this interface is a conjugate wall where the influence of the formation of EDL is implicitly modeled. The primary current distribution assumes that faradaic reactions are extremely fast; thus, electrode kinetics are negligible. Correspondingly, the formation of EDL and consequently the potential drop at the anodic interface are ignored ( $\varphi^{AnM} = \varphi^{AnE}$ ). In contrast, the potential drop due to faradaic reactions at the anodic interface, which is known as activation overpotential, is considered in secondary current distribution. The fluxes of electric potential ( $\approx$  electric current density) on both sides of the conjugate wall (anodic interface) are equal to each other, whereas the electric potential magnitudes are unequal. The relationship between activation overpotential and electric current density is further described in section Estimation of activation overpotential. Eventually, the amount of current density determines the flux of electro-active  $Fe^{2+}$  at the anodic interface.



Figure 2. Schematic representation of electric double layer (EDL) is presented. Electric potential and concentration of ions are plotted schematically across the entire EDL.

In contrast to primary and secondary current distributions, the electrolyte defies Ohm's law in the calculation of tertiary current distributions. The effects of the transport/reaction of each individual ion (reacting or non-reacting) on the electrical behavior of the electrolyte are considered. Eq. 11 is solved, and the electric current density is governed by fluxes of ions as described in Table I. Additionally, the total flux, including advection, diffusion, and migration, for each ion must be conserved. The imposition of electro-neutrality provides a simplification. The concentration field for one non-reacting ion, which is typically the supporting electrolyte with the opposite charge number (here  $F^-$ ), is obtained using distributions of concentrations of other involving ions.<sup>16</sup>

Secondary and tertiary current distributions share equivalent boundary conditions to calculate electric potential. Of note, the total potential reduction across the EDL, including activation and concentration overpotential, must be considered at the anodic interface in the calculation of tertiary current distributions. This information is further described in section Estimation of activation overpotential. The total mass flux (advection+ diffusion+ migration) of non-reacting ions is zero at all boundaries as described in Table I. A positive mass flux related to the electric current density is applied for Fe<sup>2+</sup> at the anodic interface. The concentration of Fe<sup>2+</sup> is set to zero at the cathodic interface where the flux of Ca<sup>2+</sup> is dependent on the flux of Fe<sup>2+</sup> and the magnitude of electric current density. The latter was fully elucidated in assumption (ii).

*Estimation of activation overpotential.*—At the interface between the metal and electrolyte, an electric double layer (EDL) forms as schematically illustrated in Fig. 2. The charged electrode surface attracts ions of the opposite charge (counter-ions). As a result, the concentration of counter-ions increases compared with co-ions in an area near the charged surface known as the EDL. The EDL is composed of Table I. Governing equations and related boundary conditions are listed for primary (I), secondary (II), and tertiary (III) current distributions. Given names for boundaries (abbreviations) are described in Fig. 1.

Governing equations	Boundary conditions
(I) Primary current distribution	$\varphi^{TM} = V_{app},$ $\varphi^{TC} = 0$
$\nabla \cdot (-\sigma \nabla \varphi) = 0,$	$\varphi^{CaC} = \varphi^{CaE},$
$\sigma = F^2 \sum \frac{D_i}{RT} z_i^{\ 2} c_i,$	Flec A A Flec A F
$\ \vec{\nabla}c_i\  \approx 0.$	$\varphi^{Dictrim} = \varphi^{Dictrim},$
(II) Secondary current distribution	$egin{array}{ll} rac{\partial arphi^{TA}}{\partial n} &= rac{\partial arphi^{BC}}{\partial n} = rac{\partial arphi^{SC}}{\partial n} = 0, \ arphi^{TM} &= arphi^{AnB}. \end{array} \ arphi^{TM} &= V_{app}, \ arphi^{TC} &= 0, \end{array}$
$\nabla \cdot (-\sigma \nabla \phi) = 0$	$\varphi^{CaC} = \varphi^{CaE},$
$2 - D_{1} - 2$	$\varphi^{ElecAA} = \varphi^{ElecAE},$
$\sigma = F^2 \sum_i \frac{D_i}{RT} z_i^{-2} c_i,$	$\frac{\partial \varphi^{TA}}{\partial \varphi} = \frac{\partial \varphi^{BC}}{\partial \varphi} = \frac{\partial \varphi^{SC}}{\partial \varphi} = 0.$
$\ ec{ abla}c_i\ pprox 0.$	dn dn dn dn
$\frac{\partial c_{Fe^{2+}}}{\partial t} = -\nabla \cdot (uc_{Fe^{2+}} - D_{Fe^{2+}} \nabla c_{Fe^{2+}})$	$j^{AnE} = -j^{AnM} = j_0 \exp(-\frac{\eta_{AcL}}{b_{AcL}}),$ $\eta_{Act.} = \varphi^{AnE} - \varphi^{AnM},$ $\frac{\partial c^{ElecAE}}{Fe^{2+}} = 0,$ $c^{CaE}_{Fe^{2+}} = 0,$ $D_{Fe^{2+}} \frac{\partial c^{AnE}_{Fe^{2+}}}{\partial n} = +\frac{j^{AnE}}{z_{Fe^{2+}}F}.$
(III) Tertiary current distribution	$\varphi^{TM} = V_{app},$
$N_i = uc_i - D_i \nabla c_i - \frac{c_i \nu_i r}{RT} c_i \nabla \varphi,$ $i = C a^{2+} E a^{2+} E^{-} Q^{2-}$	$\varphi^{TC} = 0,$
$i = Ca^{-1}, Fe^{-1}, F^{-1}, O^{-1}$	$\varphi^{CaC} = \varphi^{CaE},$
$\nabla \cdot [F \sum z_i N_i] = 0,$	$\varphi^{ElecAA} = \varphi^{ElecAE},$
$ \begin{aligned} &\frac{\partial c_{ca2+}}{\partial t} = -\nabla \cdot N_{Ca^{2+}}, \\ &\frac{\partial c_{Fa^{2+}}}{\partial t} = -\nabla \cdot N_{Fe^{2+}}, \\ &\frac{\partial c_{Q^{2-}}}{\partial t} = -\nabla \cdot N_{Q^{2-}}, \end{aligned} $	$\frac{\partial \varphi^{TA}}{\partial n} = \frac{\partial \varphi^{BC}}{\partial n} = \frac{\partial \varphi^{SC}}{\partial n} = 0,$ $j^{AnE} = -j^{AnM} = j_0 \exp(-\frac{\eta_{Tot}}{b_{Tot}}),$ $\eta_{Tot.} = \varphi^{AnE} - \varphi^{AnM},$ $N^{ElecAE} = N^{ElecAE} - N^{ElecAE} = 0$
$z_{F^-}c_{F^-} = -(z_{Ca^{2+}}c_{Ca^{2+}} + z_{Fe^{2+}}c_{Fe^{2+}} + z_{O^{2-}}c_{O^{2-}})$	$\begin{split} N_{Ca^{2+}} &= N_{O^{2-}} = N_{Fe^{2+}} = 0, \\ N_{Ca^{2+}}^{AnE} &= N_{O^{2-}}^{AnE} = 0, \\ z_{Fe^{2+}} F N_{Fe^{2+}}^{AnE} &= j^{AnE}, \\ N_{O^{2-}}^{CaE} &= 0, \\ c_{Fe^{2+}}^{CaE} &= 0, \\ z_{Fe^{2+}} F N_{Fe^{2+}}^{CaE} + z_{Ca^{2+}} F N_{Ca^{2+}}^{CaE} &= j^{CaE} \end{split}$

the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), and the diffusive layer. IHP passes through the "specifically adsorbed ions" that are in direct contact with the electrode. The solvated ions have a distance of closest approach to the charged surface known as OHP. Both layers between IHP and OHP are immobile due to the presence of strong electrical forces.<sup>19,20</sup> In contrast, the diffusive layer is mobile where a net charge density exists. The thickness of diffusive layer is known as Debye screening length ( $\lambda_D \sim 100$  nm). The electric potential decreases in a linear manner through the immobile portion of the EDL, including IHP and OHP near the anodic charged surface. The electric potential at the plane of OHP is known as zeta-potential.<sup>20</sup> The concentration of counter-ions diminishes exponentially across the diffusive layer according to the Poisson-Boltzmann equation.<sup>18-20</sup> Given that the faradaic reaction occurs at the charged surface (more precisely IHP), the relationship between the rate of reaction, current density, and the state of electro-neutral bulk is described by the generalized Frumkin-Butler-Volmer formula (gFBV):19

$$j = j_0^t e^{\left[\frac{(\alpha n - z_0)F}{RT}(\zeta - \varphi)\right]} \left[ e^{\left[\frac{(1 - \alpha)Fn}{RT}(V_{ext} - \varphi)\right]} - e^{\left[\frac{-\alpha Fn}{RT}(V_{ext} - \varphi)\right]} \right].$$
[12]

In Eq. 12, the exchange current density  $(j_0^t)$  is dependent on the forward/backward reaction rate, concentrations of ions at equilibrium,

and temperature.<sup>20</sup> The electric current density is exponentially related to the potential drop across the diffusive layer  $(\zeta - \varphi)$  and the potential drop through the entire double layer  $(V_{ext} - \varphi)$ . Let us assume that the potential drop across the diffuse layer is a fraction (between 0 and 1) of the total potential drop across the entire EDL:

$$\zeta - \varphi = \gamma (V_{ext} - \varphi).$$
[13]

The potential drop across the compact layer (IHP and OHP) is known as activation overpotential ( $\eta_{Act.}$ ), whereas the potential drop through the diffuse layer is the concentration overpotential ( $\eta_{Conc.}$ ). Therefore, Eq. 13 can be expressed as follows:

$$\eta_{Conc.} = \gamma(\eta_{Conc.} + \eta_{Act.}).$$
[14]

Traditionally, the voltage drop (or capacitance) across the compact layer is compared with the entire EDL.<sup>27</sup> For that purpose, the ad hoc ratio  $\gamma$  (bounded between 0 and 1) is effectively employed. In the limit of a large ratio ( $\gamma \rightarrow 1$ ), which is called the Gouy-Chapman limit, the potential drop across the compact layer is negligible ( $\eta_{Conc.} >> \eta_{Act.}$ ). In contrast, in the limit of a small ratio ( $\gamma \rightarrow 0$ ), which is called Helmholtz limit, the voltage drop through the compact layer is dominant ( $\eta_{Conc.} << \eta_{Act.}$ ). The large voltage drop across the compact layer helps to impel the deposition reaction. As a result, neither the concentration field of the reacting ion nor the imposed

Parameter



**Figure 3.** The overpotential is plotted against the amount of imposed current density: (a) the magnitudes of  $\gamma$  (between 0 and 1) and  $j_0^t$  (10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup>) are changed to fit experimental data regarding to the total overpotential. Some curves are labeled with the magnitude of exchange current density ( $j_0^t$ ); (b) Equation of Tafel approximation is used to fit experimental data for total overpotential and estimated data for activation overpotential.

electric field requires being enormous to carry high current densities through the electrochemical cell.<sup>28</sup> The total potential drop due to formation of EDL is given as follows:

$$\eta_{Tot.} = \eta_{Conc.} + \eta_{Act.}.$$
[15]

Considering Eqs. 13, 14 and 15, the gFBV (Eq. 12) can be written using the total overpotential as follows:

$$j = j_0^t e^{\left[\frac{(\alpha - z_0)F_{\gamma}\eta_{Tot.}}{RT}\right]} \left[ e^{\left[\frac{(1 - \alpha)F_{\eta}\eta_{Tot.}}{RT}\right]} - e^{\left[\frac{-\alpha F_{\eta}\eta_{Tot.}}{RT}\right]} \right]$$
[16]

The galvanostatic pulsing technique was utilized to measure the total overpotential ( $\eta_{Tot.}$ ) as a function of the imposed electric current density at the anodic interface.<sup>12</sup> Experimental measurements can be used to establish the relationship between the current density and total overpotential. A simple multi-regression analysis helps us to estimate unknown parameters, including  $j_0^t$  and  $\gamma$  in Eq. 16.  $\gamma$  is bounded between zero and one, whereas the variation range for the exchange current density ( $j_0^t$ ) can be large, e.g.10<sup>3</sup> to 10<sup>5</sup> for CaF<sub>2</sub>-FeO electrolyte at 1723 K.<sup>29,30</sup> As shown in Fig. 3a, both  $\gamma$  (~ 0–1) and  $j_0^t$  (~10<sup>2</sup>-10<sup>5</sup> A.m<sup>-2</sup>) are changed in a wide range to obtain the Table II. Parameters used in our calculations.

1 drumeter	
$\mu_0/H \cdot m^{-1}$	$4\pi  imes 10^{-7}$
$R/J \cdot K^{-1} \cdot mol^{-1}$	8.314546
$g/m \cdot s^{-2}$	9.81
T/K	1803
$F/A \cdot s \cdot mol^{-1}$	96485
$V_{app} / V$	0.1 and 0.5 V
$\sigma_{Electrode}/S.m^{-1}$	$8 \times 10^5$
$\sigma_{Crucible}/S.m^{-1}$	$2 \times 10^{5}$
$\sigma_{Air}/S.m^{-1}$	$10^{-10}$
$\sigma/S.m^{-1}$	Calculated
$\rho/kg \cdot m^{-3}$	2550
$\mu/kg \cdot m^{-1} \cdot s^{-1}$	0.005
α	0.5
$i_0^t/A \cdot m^{-2}$	4000
$i_0/A \cdot m^{-2}$	1000
$b_{Act.}/V$	0.002
$b_{Tot.}/V$	0.0435
$c_{Ca^{2+}}/mol \cdot m^{-3}$	32920
$c_{F^-}/mol \cdot m^{-3}$	64020
$c_{Fa^{2+}}/mol \cdot m^{-3}$	Calculated
$c_{O^{2-}}/mol \cdot m^{-3}$	910
$D_{C_{-2}}/m^2 \cdot s^{-1}$	$5 \times 10^{-9}$
$D_{F^{-}}/m^2 \cdot s^{-1}$	$5 \times 10^{-9}$
$D_{F_{r}^{2+}}/m^{2} \cdot s^{-1}$	$5 \times 10^{-9}$
$D_{0} - 2/m^2 \cdot s^{-1}$	$5 \times 10^{-9}$
- 0 - 1 ··· 2	2
ZC-2+	+2
$Z_{F}$	-1
$Z_{Fa2}$ +	+2
$Z_{O2}^{2-}$	-2

best fit. Correspondingly, a value of 0.99 is estimated for  $\gamma$ , indicating that the concentration overpotential is dominant across the EDL (Eq. 14). In other words, the activation overpotential has a small contribution (only 1%) to the total potential drop through the EDL. Previous calculations and experimental measurements also suggested that the activation overpotential is significantly lower than the concentration overpotential for CaF<sub>2</sub>- based electrolytes.<sup>29,31</sup>

Experimental measurements ( $\eta_{Tot.}$ ) are directly used in the calculation of tertiary current distribution.<sup>12</sup> However, the magnitude of activation overpotential is required to model the potential jump at the anodic interface for secondary (II) current distribution as reported in Table I. Considering the best-fitted value (0.99) for  $\gamma$ , we estimate that the magnitude of the activation overpotential is approximately 1% of the total overpotential ( $\eta_{Act.} = 0.01 \eta_{Tot.}$ ).

For the sake of simplicity and in terms of mathematical modeling, the electric current density is most often adequately related to the magnitude of overpotential through the Tafel approximation:<sup>15</sup>

Secondary (II): 
$$j = \pm j_0 e^{\left[-\frac{\eta_{Act.}}{b_{Act.}}\right]}$$
 [17]

Tertiary (III): 
$$j = \pm j_0 e^{\left\lfloor -\frac{iT_{OL}}{b_{T_{OL}}}\right\rfloor}$$
 [18]

As shown in Fig. 3b, the fitted curves for activation and total overpotentials are obtained. All parameters used in our calculations, including fitting parameters, such as  $j_0, b_{Act.}$ , and  $b_{Tot.}$  are listed in Table II. In Eqs. 17 and 18, the electric current density is positive at the anode (+) and negative at the cathode (-).

It has to be pointed out that values of  $j_0^t$  or  $j_0$  reported in Table II do not conceptually represent exchange current density. As previously mentioned, the exchange current density, which appears in the classical Butler-Volmer formula or gFBV, is dependent on several factors, such as the rate of forward/backward faradaic reactions, concentrations of ions at equilibrium, the nature of the electrode, and

Downloaded on 2018-09-07 to IP 192.236.36.29 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms\_use) unless CC License in place (see abstract).

temperature.<sup>19,20,27,32</sup> Here, ad hoc parameters, such as  $j_0$ ,  $b_{Act.}$ , and  $b_{Tot.}$ , are employed to ensure that the relationship between the electric current density and overpotential is respected.

Simulation setup.—Mitchell et al.<sup>12</sup> conducted several experiments using the galvanostatic pulsing technique to measure the magnitude of overpotential that arises from concentration polarization at the interface between the metal and CaF<sub>2</sub>-based electrolytes. The metallic electrode was pure iron, whereas the counter-electrode was a molybdenum-lined graphite crucible. The experiment was performed under isothermal condition ( $\sim 1803 \pm 5$  K). Details of the experiment are described in Ref. 12. In this paper, the numerical model is configured according to this experiment. The iron electrode has a diameter of 7.3 mm, which is immersed into the electrolyte. The immersion depth of the electrode, including the lateral wall and the electrode tip, is 10 mm. The inner diameter of the crucible, which contains the molten electrolyte, is 35 mm with a height of 33 mm. The 2D axisymmetric configuration of the system is presented in Fig. 1.

A very fine mesh (ca. 0.2 million volume elements) was generated. The smallest mesh is ca. 30  $\mu$ m near the electrode. A successive ratio of 5% is considered to increase the mesh size smoothly/incrementally away from the electrode toward the bulk of electrolyte. All modeling equations are implemented using the commercial software FLUENT-ANSYS v. 14.5, which operates using the well-established finite volume method (FVM). The first-order implicit method is applied for temporal discretization of governing equations.<sup>17</sup> The spatial discretization is acquired by the third-order MUSCL scheme in which variable grid sizes and strong advection/migration flux are accurately handled.<sup>33</sup> The pseudo-transient computation technique was deployed to perform transient calculations.<sup>34,35</sup> Accordingly, the transient terms (temporal derivatives) for all governing equations were retained.<sup>17</sup> Mathematically, the pseudo-transient approach is a homotopy that embeds the steady state problem in a space-time setting.<sup>17,34</sup> Capturing the transient behavior (temporal accuracy) of the system is not the objective so that the temporal accuracy is sacrificed in favor of rapid convergence to the steady state.<sup>34</sup> This technique is utilized to achieve the steady state solution for complex problems involving highly nonlinear equations when the initial iterate is far from the final solution. The steady-state results were subject to further evaluation.

## Results

A series of simulations was performed to explore effects of different current distributions (i.e., primary, secondary, and tertiary) on transport phenomena in the electrolyte. Furthermore, the response of the system to the applied DC voltage (0.1 or 0.5 V) was investigated. A summary of results is presented in Fig. 4 and Fig. 5. The magnetic field in the entire domain for primary (I), secondary (II), and tertiary (III) current distributions at low applied voltage (0.1 V) is illustrated in Fig. 4a. The magnetic field is strong near the lateral wall of electrode in all cases. The intensity decreases gradually away from the electrode toward the bottom of the crucible. Correspondingly, the highest amount of electric current density flows near the electrode as illustrated in 4b. The magnitude of electric current density is relatively low near the bottom of crucible. The magnitude and direction of the Lorentz force is shown in 4c. The electro-vortex flow is presented in Fig. 4d. The direction of flow is identical in all cases (I, II, and III); however, the local magnitude of velocity is dissimilar. The flow is exclusively driven by a Lorentz force that is subsequently dependent on the electromagnetic field (Eq. 8). Accordingly, the highest velocity is observed near the electrode where both the magnetic field and electric current density are very strong. The distinctions in the calculated magnetic, electric current and velocity fields are negligible comparing primary (I) and secondary (II) current distributions. On the other hand, the calculated field structures are approximately one order of magnitude smaller in tertiary (III) current distributions compared with primary (I) and secondary (III) current distributions. As shown in 4e, a comparison is made between secondary (II) and tertiary (III) current distributions regarding to the concentration field of the

electro-active Fe<sup>2+</sup>. Given the strong predicted electro-vortex flow in secondary (II) current distributions, iso-lines of the concentration of Fe<sup>2+</sup> are pushed toward the axis under the shadow of electrode. Furthermore, the predicted concentration of Fe<sup>2+</sup> in secondary (II) current distribution is notably increased compared with tertiary (III) current distributions near the electrode. As described in Table I, the migration flux, which drives Fe<sup>2+</sup> to move toward the cathodic crucible, is ignored in secondary (II) current distributions. Accordingly, a greater amount of Fe<sup>2+</sup> can linger under the shadow of the electrode. The calculated field structures at large applied voltage (0.5 V) are illustrated in Fig. 5. The global behavior of the magnetic, electric current density, Lorentz force, and flow fields are qualitatively similar to those previously discussed for the system operating under the low applied voltage. However, the electromagnetic field and consequently the flow intensify at the large applied voltage. As shown in Fig. 5e, a liquid jet enriched in Fe<sup>2+</sup> is predicted under the shadow of electrolyte by both secondary (II) and tertiary (III) current distributions. A comparison is made between Fig. 4e and Fig. 5e to explore the influence of applied voltage on the calculated concentration field of Fe<sup>2+</sup> by secondary (II) and tertiary (III) current distributions. Evidently, the secondary (II) current distribution more precisely emulates the tertiary (III) current distribution to predict the concentration field of Fe<sup>2+</sup> as the applied voltage increases.

The calculated concentration fields for all ions (Ca<sup>2+</sup>, F<sup>-</sup>, Fe<sup>2+</sup>, and O<sup>2-</sup>) using a tertiary current distribution under different applied voltages are illustrated in Fig. 6. As anticipated, anions ( $F^-$  and  $O^{2-}$ ) move toward the anode, and the cation  $(Ca^{2+})$  accumulates adjacent to the cathode. The migration flux occurs in a direction opposite to the advection flux for anions; hence, they compete against each other. In contrast, migration and advection follow the same route, thus assisting in the transport of cations (Ca<sup>2+</sup> and Fe<sup>2+</sup>) toward the cathodic crucible. As shown in Fig. 6a, the distribution of  $Ca^{2+}$ is non-uniform along the crucible wall at a large applied voltage. The concentration of Ca<sup>2+</sup> is relatively low at the cathodic crucible near the free surface of the electrolyte where the electric current density is high. In the absence of sufficient  $Fe^{2+}$ , the electric current is delivered from the electrolyte to the cathode by the faradaic reaction of  $Ca^{2+}$ . As a result,  $Ca^{2+}$  is not uniformly consumed at the surface of the cathode where the distribution of electric current density is nonuniform. As shown in Fig. 6c, the concentration of Fe<sup>2+</sup> is remarkably high near/at the anodic electrode-electrolyte interface where the Fe<sup>2-</sup> is continuously injected into the electrolyte. In contrast, a region of low Fe<sup>2+</sup> concentration appears along the crucible where intense removal of ferrous ion occurs. Despite the opposition between the advection and migration, a significant amount of anions can accumulate under the tip of anodic electrode. This finding implies that the migration flux surpasses the advection flux of anions near the tip of electrode where a strong electric field/electric current density exists. Furthermore, the severe recirculation of flow in the bulk of electrolyte notably influences the concentration fields of all ions especially near the vortex core. The concentration fields for all involving ions remain non-uniform although a significant amount of current density (order of  $10^5 \text{ A.m}^{-2}$ ) flows through the well-mixed electrolyte ( $u \sim 2 \text{ mm.s}^{-1}$ ). In other words, the presence of an intense electro-vortex flow cannot guarantee a uniform concentration field for ions. Therefore, the traditional key assumption, namely, negligible concentration gradients in the bulk of a strongly stirred electrolyte ( $\|\vec{\nabla}c_i\| \approx 0$ ) to perform primary/secondary current calculations, is questionable.

### Discussion

Generally, numerous parameters, such as applied voltage, temperature, activation/concentration overpotential, and concentration and diffusion coefficient of involved ions, can influence the electrical behavior of the electrolyte. As illustrated in Fig. 7a, the electrical conductivity of the electrolyte remains globally uniform in the calculation of primary (I) and secondary (II) current distributions. The equation of charge conservation (Table I) in a tertiary (III) current distribution



**Figure 4.** Field structures are illustrated for the system operating under the low applied voltage ( $V_{app} = 0.1$  V). Each contour is labeled based on the current distribution: primary (I), secondary (II), and tertiary (III). Equisized vectors are presented to indicate directions; (a) Magnetic field, (b) electric current density field, (c) Lorentz force field, (d) flow field, and (e) concentration field of the electro-active ferrous (Fe<sup>2+</sup>) ion; iso-lines of concentration are inserted. A logarithmic scale is used in all figures.

is expressed as follows:

$$\nabla \cdot \left[ F \sum_{i} z_{i} N_{i} \right] = 0, \qquad [19]$$

where

$$N_i = uc_i - D_i \nabla c_i - \frac{z_i D_i F}{RT} c_i \nabla \varphi, i = Ca^{2+}, Fe^{2+}, F^-, O^{2-}.$$
[20]

Combining Eqs. 19 and 20 with regard to the electro-neutrality conditions (assumption (iv)) leads to the following equation of charge conservation:

$$\nabla \cdot \left[ \sum_{i} z_i D_i \nabla c_i + \sum_{i} \frac{z_i^2 D_i F}{RT} c_i \nabla \varphi \right] = 0.$$
 [21]

The electric current generates the gradients of concentrations of all type of ions throughout the electrolyte. Hence, the term  $(\nabla \cdot [\sum z_i D_i \nabla c_i])$  called diffusive electric current describes the

Downloaded on 2018-09-07 to IP 192.236.36.29 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms\_use) unless CC License in place (see abstract).



**Figure 5.** Field structures are illustrated for the system operating under the high applied voltage ( $V_{app} = 0.5$  V). Each contour is labeled based on the current distribution: primary (I), secondary (II), and tertiary (III). Equisized vectors are presented to indicate directions; (a) Magnetic field, (b) electric current density field, (c) Lorentz force field, (d) flow field, and (e) concentration field of the electro-active ferrous (Fe<sup>2+</sup>) ion; iso-lines of concentration are inserted. A logarithmic scale is used in all figures.

contribution of diffusion to the electric current density. Considering electro-neutrality (assumption (iv)), the diffusive electric current can be equal to zero only when the diffusion coefficients of all involved ions are equal (assumption (vi)). Even in this particular case, Eq. 21 cannot be reduced to the Laplace equation because the concentration of ions and consequently the electrical conductivity depend on coordinates. As shown in Fig. 7a, the non-uniform distribution of the electrical conductivity throughout the electrolyte is impacted by the operational parameter (e.g., applied voltage) in tertiary (III) current distributions.

The influence of the formation of electric double layer (EDL) adjacent to the anodic electrode on the electric potential field under different applied voltage is illustrated in Figs. 7b–7c. The electric potential field along the axis of both the electrode and electrolyte is plotted for different current distributions. The formation of EDL is included in secondary and tertiary current distributions, which results in a potential jump at the anodic interface as shown in Fig. 7b. Expectedly, the potential jump is always higher for the tertiary current distribution compared with the secondary current distribution regardless of the applied voltage. The potential jump is relatively small for the secondary (II) current distribution as the activation overpotential has an insignificant contribution ( $\sim 1\%$ ) to the total potential drop across the EDL. The potential jump at the interface is more pronounced in tertiary (III) current distributions that account for both activation and concentration overpotentials. With the increase in applied voltage, the ratio of the magnitude of the potential jump across the EDL to the total applied voltage decreases. This finding indicates that the impact of the formation of EDL on the global electric field is reduced with the increase in the applied voltage. Fig. 7c illustrates the variation in electric current density along the surface of electrode, including the lateral wall and tip, for different current distributions. The maximum current density is obtained near the slag-free surface. The choice of current



**Figure 6.** The calculated concentration fields of all involved ions in the electrolyte using tertiary current (III) at (left contour) low applied voltage ( $V_{app} = 0.1 V$ ) and (right contour) high applied voltage ( $V_{app} = 0.5 V$ ) are compared: (a) concentration field of  $Ca^{2+}$ , (b) concentration field of  $F^-$ , (c) concentration field of Fe<sup>2+</sup> (logarithmic scale), (d) concentration field of  $O^{2-}$ . In all contour, iso-lines of concentration are also inserted.

distribution influences the distribution of electric current density along the surface of electrode. The tertiary (III) current distribution predicts a relatively uniform electric current density along the entire electrode surface. With the increase of applied voltage, the dissimilarity among (I), (II), and (III) in the predicted distribution of electric current density decreases. In addition, the electric potential field is plotted along the surface of the electrode including the lateral wall and tip, for tertiary (III) current distributions in Fig. 7c. The field remains unchanged on the electrode side (more precisely the interface between the metal and IHP). The difference in the magnitude of electric potential between the electrode and electrolyte side is equivalent to the total overpotential across the EDL. Unlike the electrode side, the electric potential varies along the electrolyte side (more precisely the interface between the diffusive layer of EDL and the bulk of electrolyte). The amplitude of this variation becomes larger with the increase in applied voltage.

Mitchell et al.<sup>12</sup> reported the formation of a thick layer of iron oxide (FeO) under the tip of electrode (not the lateral wall) during the experiment. FeO formation requires the presence of an excessive amount

of O<sup>2-</sup> near the anodic electrode where an enormous amount of Fe<sup>2+</sup> is injected into the electrolyte. As previously described, the strong advection flux opposes the migration flux for anions (e.g., O<sup>2-</sup>) near the electrode. Therefore, a significant amount of O<sup>2-</sup> must be washed away from the electrode surface by the flow. To propose a possible explanation for the aforementioned phenomenon, magnitudes of advection flux,  $\|\vec{u}_{C0^2}\|$ , diffusion flux,  $\|D_{0^2} - \nabla c_{0^2}\|$ , and migration flux,  $\|\frac{D_{0^2}}{RT}Fz_{0^2} - c_{0^2} - \nabla \phi\|$ , for  $O^{2-}$  along the surface of electrode and axis of electrolyte are plotted as shown in Fig. 7d. The advection and migration exhibit relatively similar strength near the lateral wall. However, the migration defeats the advection in the region near the tip of electrode where the electric field (current density) is large. The magnitude of velocity is notably small in the vicinity of electrode tip as illustrated in Fig. 7d. Therefore, a massive amount of O<sup>2-</sup> can reach the tip of electrode to participate in a chemical reaction with Fe<sup>2+</sup>. The aforementioned finding can explain the in situ observation of the formation of a thick FeO layer under the tip of electrode.<sup>12</sup> As previously mentioned in assumption (viii), the solutal buoyancy is not included in our calculations. The latter can influence the velocity field



**Figure 7.** (a) Calculated electrical conductivity based on primary (I), secondary (II), and tertiary (III) are compared as follows: (left) I or II, (middle) III at low applied voltage ( $V_{app} = 0.1$  V), (right) III at high applied voltage ( $V_{app} = 0.5$  V); In (b), (c), and (d), a number of parameters are plotted across some boundaries that are bolded and marked using a green box. (b) The electric potential is plotted across the axis of electrode and axis of electrolyte at different applied voltages ( $V_{app} = 0.1$  and 0.5 V); (c) normalized distribution of electric current density along the surface of electrode at  $V_{app} = 0.1$  is plotted across the lateral wall and tip of the electrode (top), normalized distribution of electric current density along the surface of electrode at  $V_{app} = 0.5$  (middle), the electric potential of tertiary (III) is plotted across the lateral wall and tip of the electrode under different applied voltage ( $V_{app} = 0.1$  and 0.5 V) at the electrode side (more precisely the interface between metal and IHP) and electrolyte side (more precisely the interface between the diffusive layer of EDL and the bulk of electrolyte); (d) advection, diffusion, and migration fluxes are plotted along the electrode surface (lateral wall and tip) and the axis of electrolyte. Additionally, the contour of velocity field under the tip of electrode is inserted.

and consequently the advection flux of ions. As such, it is necessary to include the solutal buoyancy in the future model.

Electrical resistance is an important factor to characterize an electrochemical system. The charge carriers (ions) collide with each other as they flow through the bulk of electrolyte, which attributes the bulk electrical resistance of the electrolyte ( $R_B$ ):

$$R_B = \frac{1}{I^2} \int \int \int \vec{j} \cdot \vec{E} \, dV.$$
 [22]

The formation of EDL at the electrode-electrolyte interface exerts an extra electrical resistance to the system known as interfacial electrical resistance  $(R_I)$ :

$$R_I = \frac{1}{I^2} \int \int \eta \ \vec{j} \cdot d\vec{S}.$$
 [23]

In Eq. 23,  $\eta$  is activation overpotential ( $\eta = \eta_{Act.}$ ) considering secondary current distribution, whereas the total overpotential ( $\eta = \eta_{Tot.}$ ) is used in tertiary current distribution. A summary of calculated bulk and interfacial electrical resistances under different applied voltages for primary (I), secondary (II), and tertiary (III) current distributions is described in Table III. The bulk electrical resistance remains unchanged in all cases regardless of variations in the applied voltage or Table III. Calculated imposed current, bulk electrical resistance, interfacial electrical resistance, and total electrical resistance are described for primary, secondary, and tertiary current distributions under different applied voltage.

Electric current distribution	$V_{app}\left(V ight)$	I (A)	$R_{B}\left(\Omega\right)$	$R_{I}\left(\Omega\right)$	$R_{T}\left(\Omega ight)$
Primary (I)	0.1 0.5	2.98 14.98	$0.0326 \\ 0.0323$	0 0	0.0326 0.0323
Secondy (II)	0.1 0.5	2.83 14.92	$0.0326 \\ 0.0326$	$0.0017 \\ 0.0005$	0.0343 0.0331
Tertiary (III)	0.1 0.5	1.028 9.88	0.0328 0.0329	0.064 0.0166	0.096 0.0486

the types of current distribution (I, II, or III). Interestingly, the bulk electrical resistance of electrolyte for tertiary (III) current distribution is insensitive to the non-uniform distribution of electrical conductivity throughout the electrolyte (Fig. 7a). Obviously, no interfacial electrical resistance exists for primary (I) current distribution in which the formation of EDL is ignored. The calculated interfacial electrical resistance is minor for secondary (II) current distribution. The highest amount of total electrical resistance ( $R_T = R_B + R_I$ ) and consequently the lowest magnitude of the imposed current is obtained at low applied voltage for tertiary (III) current distribution. The interfacial electrical resistance remarkably decreases as the applied voltage increases. Conclusively, the inequality in the predicted total electrical resistance among primary, secondary, or tertiary current distributions becomes minimal under the condition of a large applied voltage and small potential drop across the EDL ( $V_{app} \gg \eta_{Tot.}$ ).

Of note, we mathematically verified our presented model to solve the Nernst-Planck equations.<sup>32,35</sup> Additionally, the obtained modeling results were successfully validated against an experiment.<sup>29,31,36</sup> In the present study, we lack experimental data to further validate our model. For that purpose, we require measurements of the local transport parameters, such as velocity or concentration throughout the electrolyte. Generally, experimental analysis and measurements are difficult due to high degree of opacity of materials at the elevated temperature ( $\sim$ 1800 K) of electro-metallurgical processes. Nevertheless, the presented model helps us to improve our knowledge on the effects of the electro-vortex flow, applied voltage, and formation of EDL on transport phenomena (e.g., electromagnetic, concentration and velocity field) in the electrolyte. Eventually, the obtained results can well-explain the origin of an observed phenomenon, namely, the formation of a thick layer of FeO under the tip of electrode, in the experiment.

#### Summary

A 2D axisymmetric model is used to investigate the influence of electro-vortex flow on electrical behavior of the electrolyte composed of CaF<sub>2</sub> (%wt 98)-CaO (% wt 2) at molten state. The electromagnetic field operates in the entire system (CaF2-based electrolyte, air, electrode, and graphite crucible), while the electro-vortex flow and concentration fields of ions act only in the electrolyte. Three different approaches, known as primary, secondary, and tertiary current distributions, are compared. Ohm's law is used for the primary and secondary, whereas Nernst-Planck equations for the tertiary. The faradaic reaction of the formation of Fe<sup>2+</sup> is considered at the anode. The discharge of both Fe<sup>2+</sup> and Ca<sup>2+</sup> is taken into account at the cathode. The model implicitly accounts for the formation of an electric double layer (EDL) at the anode-electrolyte interface. The total overpotential  $(\eta_{Tot.})$  measured in an experiment is considered in tertiary calculations to evaluate the influence of EDL on the electric potential field. The secondary current distribution requires the activation overpotential ( $\eta_{Act.}$ ), which is estimated using the generalized Frumkin-Butler-Volmer (gFBV) formula. Main conclusions are drawn.

Estimation of  $\eta_{Act.}$  reveals that the electrolyte behaves in accordance with Gouy-Chapman model  $as\eta_{Act.} \sim 1\%$  of  $\eta_{Tot.}$  across the EDL.

The overpotential is ignored for primary current distribution. As anticipated,  $\eta_{Tot.}$  is greater for tertiary than that for secondary current distribution. As the overpotential decreases, the amount of electric current density that flows through the electrolyte increases, and the flow subsequently intensifies. Quantitatively, the calculated velocity and electric current density depend on the modeling approach (primary, secondary, or tertiary). Qualitatively, all approaches predict similar direction for velocity and electromagnetic fields.

When applying low voltage (current), the predicted  $Fe^{2+}$  concentration near the anode is significantly different between secondary and tertiary current distributions. By ignoring the  $Fe^{2+}$  migration, the secondary current distribution remarkably overestimates the  $Fe^{2+}$ . Significant amounts of  $Fe^{2+}$  are allowed to accumulate under the anode. With the increase of applied voltage, the discrepancy between both approaches (secondary and tertiary) to predict  $Fe^{2+}$  concentration field decreases.

Ion concentrations (Ca<sup>2+</sup>, F<sup>-</sup>, Fe<sup>2+</sup>, and O<sup>2-</sup>) are calculated in tertiary current distributions. The mixing of electrolyte by (exclusive) Lorentz force cannot ensure uniform ion concentrations. As the applied voltage (strength of Lorentz force) increases, the migration flux increases. The migration may locally exceed the advection flux. Consequently, a massive accumulation of ions may occur near the anode/cathode where the electric field (current density) is strong. The accumulation of ions (Fe<sup>2+</sup>, O<sup>2-</sup>) and subsequent formation of the FeO layer under the anodic electrode is qualitatively in agreement with the experiment.<sup>12</sup> However, it is necessary to include the solutal buoyancy in the future model to improve the quantitative accuracy of the model.

By immersing electrode into the electrolyte, an uneven electric current flows across the lateral wall and electrode tip. The potential drop along the entire surface of the electrode is negligible at the electrode side (more precisely the interface between the metal and IHP), while a noteworthy potential drop occurs at electrolyte side (more precisely the interface between the diffusive layer of EDL and the bulk electrolyte). As the applied voltage increases, the variation in the amplitude of electric potential along the entire surface of electrode becomes more potent.

Electrical resistance in the bulk electrolyte and at the anodeelectrolyte interface which is known as interfacial electrical resistance are calculated. In the absence of a diffusive electric current, equal diffusion coefficient for all involved ions, the electrical resistance in the bulk of the electrolyte becomes identical regardless of variations in the applied voltage or the types of current (i.e., primary, secondary, or tertiary). In this particular case, the bulk electrical resistance for tertiary current distribution seems insensitive to the non-uniform distribution of electrical conductivity in the electrolyte. The highest total electrical resistance, corresponding to the lowest current, is obtained at low applied voltage for tertiary current distributions. As the applied voltage increases, the interfacial resistance significantly decreases. Thus, the inequality among three approaches in the predicted total electrical resistance is appreciably reduced under the conditions of a large applied voltage and small potential drop across the EDL ( $V_{app} \gg \eta_{Tot.}$ ).

Finally, the modeling results enabled us to elucidate the origin of an experimentally observed phenomenon, i.e., the formation of a thick layer of FeO under the tip.

# Acknowledgments

The authors acknowledge financial support from the Austrian Federal Ministry of Economy, Family and Youth and the National Foundation for Research, Technology and Development within the framework of the Christian-Doppler Laboratory for Metallurgical Applications of Magnetohydrodynamics.

# List of Symbols

Calcium ion
Fluoride ion
Ferrous ion
Oxygen ion
Magnetic vector potential/ V s $m^{-1}$
Magnetic field / T
Concentration of each ion / mol m <sup>-3</sup>
Diffusion coefficient of each ion / m <sup>2</sup> s <sup>-1</sup>
Electric field / V $m^{-1}$
Faraday constant / A s mol <sup>-1</sup>
Volumetric Lorentz force / N m <sup>-3</sup>
Gravity constant / m $s^{-2}$
Imposed electrical current/ A
Electric current density / A m <sup>-2</sup>
Exchange current density in Tafel equation / A $m^{-2}$
Exchange current density in gFBV equation / A m <sup>-2</sup>
Number of exchanged electrons
Advection flux / mol $m^{-2} s^{-1}$
Diffusion flux / mol $m^{-2} s^{-1}$
Migration flux / mol $m^{-2} s^{-1}$
Total flux of each ion / mol $m^{-2} s^{-1}$
Pressure/ Pa
Universal gas constant / J $K^{-1}$ mol <sup>-1</sup>
Bulk electrical resistance / $\Omega$
Interfacial electrical resistance / $\Omega$
Total electrical resistance / $\Omega$
Area vector / $m^{-2}$
Time / s
Temperature / K
Velocity vector/ m $s^{-1}$
Applied voltage / V
Electric potential at the surface of electrode / V
Distance / m
Charge number of each ion
Charge number of oxidized species

#### Greek

ρ	Density / kg $m^{-3}$
μ	Viscosity / kg m <sup><math>-1</math></sup> s <sup><math>-1</math></sup>
$\mu_0$	Magnetic permeability / H m <sup>-1</sup>
$\lambda_D$	Debye screening length / m
φ	Electric potential / V
ε <sub>s</sub>	Electric permittivity / F $m^{-1}$
α	Charge transfer coefficient
ζ	Zeta potential / V
$\eta_{Act.}$	Activation overpotential / V
η <sub>Conc.</sub>	Concentration overpotential / V
η <sub>Tot.</sub>	Total overpotential / V
γ	Fraction of electric potentials across electric double
	layer
σ	Electrical conductivity of electrolyte /S m <sup>-1</sup>
σ <sub>Electrode</sub>	Electrical conductivity of electrode /S m <sup>-1</sup>
σ <sub>Crucible</sub>	Electrical conductivity of crucible /S m <sup>-1</sup>
$\sigma_{Air}$	Electrical conductivity of air /S m <sup>-1</sup>
<u> </u>	Derivative along the outward-drawn normal to the

# boundary surface /m<sup>-1</sup>

# ORCID

#### E. Karimi-Sibaki D https://orcid.org/0000-0002-2275-6699

#### References

- 1. V. Bojarevics, J. A. Freibergs, E. I. Shilova, and E. V. Shcherbinin, Electrically induced vortical flows, Kluwer Academic Publisher, 1989, Dordrecht, The Netherlands.
- 2. P. A. Davidson, An introduction to Magnetohydrodynamics, Cambridge University Press, 2001, Cambridge, New York, USA.

- 3. N. Weber, V. Galindo, F. Stefani, T. Weier, and T. Wondrak, "Numerical simulation of the Tayler instability in liquid metals," *New J. Physics*, 15, article 043034 (2013).
  H. K. Moffatt, "Electromagnetic stirring," *Physics of Fluids*, 3, 1336 (1991).
- D. R. Sadoway, "New Opportunities for Metals Extraction and Waste Treatment by 5. Electrochemical Processing in Molten Salts," J. Mater. Res., 10, 487 (1995).
- 6. G. Mutschke, A. Hess, A. Bund, and J. Fröhlich, "On the origin of horizontal counterrotating electrolyte flow during copper magnetoelectrolysis," Electrochimica Acta, 55, 1543 (2010).
- V. Bojarevic and M. V. Romerio, "Long waves instability of liquid metal-electrolyte interface in aluminum electrolysis cells: a generalization of Sele's criterion," Eur. J. Mech./B fluids, 13, 33 (1994).
- 8. O. Kazak, "Modeling of vortex flows in direct current (DC) electric arc furnace with different bottom electrode positions," Metall. Mater. Trans. B, (44), 1243 (2013).
- 9. A. Jardy and D. Ablitzer, "Mathematical modelling of superalloy remelting operations," Materials Science and Technology, 25(2), 163 (2009).
- 10. A. Kharicha, E. Karimi-Sibaki, M. Wu, A. Ludwig, and J. Bohacek, "Review on Modeling and Simulation of Electroslag Remelting," Steel Res. Int., 89, article 1700100 (2018).
- 11. N. Q. Minh and T. B. King, "The contribution of electrochemical reactions to sulfur transfer from electrode to slag in electroslag remelting," Metall. Trans. B, 10, 623 (1979).
- 12. A. Mitchell and G. Beynon, "Electrode polarization in the DC electroslag melting of pure iron," Matall. Trans., 2, 3333 (1971).
- 13. C. Madore, M. Matlosz, and D. Landolt, "Experimental investigation of the primary and secondary current distribution in a rotating cylinder Hull cell," J. Appl. Electrochem., 22, 1155 (1992).
- 14. C. T. J. Low, E. P. L. Roberts, and F. C. Walsh, "Numerical simulation of the current, potential, and concentration distributions along the cathode of a rotating cylinder Hull cell," *Electrochimica Acta*, **52**, 3831 (2007).
- 15. M. Rosales and José L. Nava, "Simulations of Turbulent Flow, Mass Transport, and Tertiary Current Distribution on the Cathode of a Rotating Cylinder Electrode Reactor in Continuous Operation Mode during Silver Deposition," J. Electrochem, Soc., 164. E3345 (2017).
- 16. E. J. F. Dickinson, H. Ekstrom, and E. Fontes, "COMSOL Multiphysics: Finite element software for electrochemical analysis. A mini-review," Electrochem. Commun., 40, 71 (2014).
- 17. H. Versteeg and W. Malalasekera, "An introduction to computational fluid dynamics: the Finite Volume Method, Pearson Education Limited, Essex, 2007.
- 18. L. H. Olesen, H. Bruus, and A. Ajdari, "AC electrokinetic micropumps: the effect of geometrical confinement, faradaic current injection, and nonlinear surface capacitance," Phys. Rev. E, 73, article 056313 (2006).
- 19. P. M. Biesheuvel, M. van Soestbergen, and M. Z. Bazant, "Imposed currents in galvanic cells," Electrochimica Acta, 54, 4857 (2009).
- 20. J. Newman and K. E. Thomas-Alyea, Electrochemical systems, John Wiley & Sons, New Jersey, 2004
- 21. K. C. Mills and B. J. Keene, "Physicochemical properties of molten CaF2 -based slags," Int. Met. Rev., 26, 21 (1981).
- 22. M. Barati and K. S. Coley, "Electrical and electronic conductivity of CaO-SiO2-FeOx slags at various oxygen potentials: Part II. Mechanism and a model of electronic conduction," Metall. Mater. Trans. B, 37, 51 (2006).
- 23. H. Song and N. Ida, "An eddy current constraint formulation for 3D electromagnetic field calculation," IEEE Trans. on Magnetics, 27, 4012 (1991).
- 24. E. Karimi-Sibaki, A. Kharicha, J. Bohacek, M. Wu, and A. Ludwig, "A dynamic mesh-based approach to model melting and shape of an ESR electrode," Metall. Trans. B, 46, 2049 (2015).
- 25. M. D. Semon and J. R. Taylor, "Thoughts on the magnetic vector potential," American *Journal of Physics*, **64**, 1361 (1996). 26. G. B. Ngo Boum and A. Alemany, "Numerical simulations of electrochemical mass
- transfer in electromagnetically forced channel flows," Electrochimica Acta, 44(11), 1749 (1999).
- 27. M. Z. Bazant, K. T. Chu, and B. J. Bayly, "Current-voltage relations for electrochemical thin films," SIAM J. Appl. Math., 65, 1463 (2005).
- 28. K. T. Chu and M. Z. Bazant, "Electrochemical thin films at and above the classical limiting current," SIAM J. Appl. Math., 65, 1485 (2005).
- 29. R. Prange, K. Heusler, and K. Schwerdtfeger, "Charge transfer at Fe/FeO (CaF2) electrodes at 1450°C: exchange current density, electrode capacitance, diffusivity, Metall. Trans. B, 15, 281 (1984).
- 30. J. Douglas Ray, "A study of the interfacial reaction kinetics in the iron-calciumfluoride system at 1450 degrees C (PhD. Thesis), McMaster University, Canada, 1981.
- 31. E. Karimi-Sibaki, A. Kharicha, M. Wu, A. Ludwig, and J. Bohacek, "Toward Modeling of Electrochemical Reactions during Electroslag Remelting (ESR) Process," Steel Research int, 88, article 1700011 (2017).
- 32. E. Karimi-Sibaki, A. Kharicha, M. Wu, A. Ludwig, and J. Bohacek, Modeling electrochemical transport of ions in the molten CaF2-FeO slag operating under a DC voltage, Applied Mathematics and Computation (2018),
- 33. B. Van Leer, "Toward the ultimate conservative difference scheme. V. A second-order sequel to Godunov's method," *J. Comput. Phys.*, **32**, 101 (1979). 34. T. S. Coffey, C. T. Kelley, and D. E. Keyes, "Pseudotransient continuation and
- differential-algebraic equations," SIAM J. Sci. Comput., 25, 553 (2003).
- E. Karimi-Sibaki, A. Kharicha, M. Wu, A. Ludwig, and J. Bohacek, "Confrontation 35. of the ohmic approach with the ionic transport approach for modeling the electrical behavior of an electrolyte," Ionics, 24, 2157 (2018).
- 36. N. Nowack, K. Schwerdtfeger, and D. Krause, "Some observations on current transfer at iron/calcium fluoride electrodes- model experiments for current transfer in the ESR process," Arch. Eisenhüttenwes, 12, 463 (1982).