MAGNETOHYDRODYNAMICS Vol. 51 (2015), No. 2, pp. 369–374

NUMERICAL SIMULATION OF THE MASS TRANSFER OF MAGNETIC SPECIES AT ELECTRODES EXPOSED TO SMALL-SCALE GRADIENTS OF THE MAGNETIC FIELD

G. Mutschke[1,2], *K. Tschulik*[3,4], *M. Uhlemann*[3], *J. Fröhlich*[2]

[1] *Helmholtz-Zentrum Dresden–Rossendorf, Institute of Fluid Dynamics,*
Bautzner Landstr. 400, 01328 Dresden, Germany
[2] *Technische Universität Dresden, Institute of Fluid Mechanics,*
01062 Dresden, Germany
[3] *Leibniz Institute for Solid State and Materials Research IFW Dresden,*
Helmholtzstrasse 20, 01069 Dresden, Germany
[4] *currently at: Oxford University, Dept. Chemistry, Oxford OX1 3QZ, United Kingdom*

The mechanisms responsible for the spatially inhomogeneous thickness of metal layers obtained by electrochemical deposition in magnetic gradient fields at small scale are being discussed controversially in the literature. The paper presents the results of numerical simulations which support the reasoning that local convection at the electrode driven by the rotational part of the magnetic gradient force is responsible for the effects observed. The deposition of paramagnetic and diamagnetic ions is discussed, and the influence of electrically inert magnetic ions present in the electrolyte is enlighted.

Introduction. In the recent past, there has been a broad discussion in the community about the mechanisms responsible for the spatially inhomogeneous deposition of magnetic ions obtained in magnetic gradient fields. A variety of experimental studies reported on structured and inversely structured deposits in the milli- and micrometer range, thereby resembling the spatial distribution of the magnetic field at the electrode. For an up-to-date review, we refer to [1]. By an order of magnitude estimation of the forces involved (the Lorentz force $\mathbf{f}_\mathrm{L}$and the magnetic gradient force $\mathbf{f}_\mathrm{m}$), it was shown early that the magnetic gradient force clearly dominates the Lorentz force if the length scale of the magnetic gradient is of the order of millimeter or below [2]. In the same reference it was shown that in case of simple deposition from paramagnetic ions like Cu^{2+}(no other magnetic ions are involved), local convection driven by the rotational part of the magnetic gradient force could explain the structuring effect observed.

In the following, the experiments were extended to the deposition of diamagnetic ions and to the deposition from electrolytes in which inert magnetic cations are present (which do not take part in the deposition process). As an example, an inversely structured deposit is obtained when diamagnetic ions are deposited from an electrolyte which contains strongly paramagnetic ions (inert) in excess. A set of different possible mechanisms is given in [3]. In [4, 7], for more experimental configurations different explanations are given when obtaining either structured or inversely structured metal deposits.

Already at the PAMIR2011 conference, a consistent and unique explanation of all experimental results of deposition in small-scale magnetic gradient fields was proposed by the present authors [5]. A careful analysis of the influence of electrically inert magnetic ions added to the electrolyte allows to argue that the action of the resulting local convection at the electrode can deliver a consistent explanation. Recently, this reasoning has been proven numerically [6]. Below, we present details of the numerical simulations performed on this topic, covering the cases of deposition of paramagnetic and diamagnetic ions. Depending on the electrolyte composition, the influence of electrically inert magnetic ions is enlighted.

1. Presentation of the problem. The magnetic gradient force density in an aqueous electrolyte with N species of magnetic ions can be written as

$$\mathbf{f}_\mathrm{m} = \frac{1}{2\mu_0}\chi_\mathrm{sol}\,\nabla B^2, \qquad \chi_\mathrm{sol} = \chi_{\mathrm{H_2O}} + \sum_{i=1}^{N}\chi_i^\mathrm{mol}c_i. \tag{1}$$

Here $\chi_{\mathrm{H_2O}}$, χ_i^mol, χ_sol, c_i and μ_0 denote the magnetic susceptibility of the diamagnetic water molecules, the molar susceptibility of species i, the magnetic susceptibility of the solution, the concentration of species i and the magnetic permeability of vacuum, respectively. B refers to the applied magnetic field only, which is a reasonable approximation here [5]. Contrary to the reasoning in [4, 7], it can be argued that the irrotational part of the magnetic gradient force (e.g., the magnetic pressure) cannot force convection in the deposition setups considered. Instead, only the rotational part of the force is responsible for the effect observed. Consider, e.g., an electrolyte that consists of two species of magnetic ions. The rotational part of the magnetic gradient force then reads

$$\nabla\times\mathbf{f}_\mathrm{m} = \frac{1}{2\mu_0}\left[\chi_1^\mathrm{mol}\nabla c_1 + \chi_2^\mathrm{mol}\nabla c_2\right]\times\left(\nabla B^2\right). \tag{2}$$

As a uniform concentration of the water molecules can be assumed, there is no influence of their diamagnetic nature on the rotational part of the force. Furthermore, inert magnetic ions may influence the magnetic gradient force if their concentration is not uniform. This becomes very important when depositing from supporting electrolytes that contain a strongly paramagnetic but electrochemically inert cation (e.g., $\mathrm{Mn^{2+}}$, $\mathrm{Dy^{3+}}$). Due to electroneutrality, the concentration of the inert cation usually increases at the cathode, where its flux must vanish [8]. In case of copper deposition from an electrolyte that in the bulk consists of, e.g., $c_{\mathrm{Cu^{2+}}} << c_{\mathrm{Mn^{2+}}} \approx c_{\mathrm{SO_4^{2-}}}$, it can be shown that

$$\frac{\nabla c_{\mathrm{Cu^{2+}}}}{\nabla c_{\mathrm{Mn^{2+}}}} \approx -2. \tag{3}$$

For the reduction of paramagnetic $\mathrm{Cu^{2+}}$(species 1) in a simple case of an electrolyte without other magnetic ions, it is known that the rotational part of the force drives a flow which results in a local convection towards the magnet, thereby enriching the concentration boundary layer and thus enhancing the mass transfer [2]. If, on the other hand, the electrolyte contains other, strongly paramagnetic cations in excess, species 2 is dominating the curl since, e.g.,

$$\frac{\chi_\mathrm{para}^\mathrm{mol}}{\chi_{\mathrm{Cu^{2+}}}^\mathrm{mol}} > 10 \tag{4}$$

for $\mathrm{Mn^{2+}}$, $\mathrm{Dy^{3+}}$. For the ratio of the square-bracket-part of the curl (2) one obtains

$$\frac{\left[\chi_{\mathrm{Cu^{2+}}}^\mathrm{mol}\nabla c_{\mathrm{Cu^{2+}}} + \chi_{\mathrm{Mn^{2+}}}^\mathrm{mol}\nabla c_{\mathrm{Mn^{2+}}}\right]}{\left[\chi_{\mathrm{Cu^{2+}}}^\mathrm{mol}\nabla c_{\mathrm{Cu^{2+}}}\right]} \approx -5. \tag{5}$$

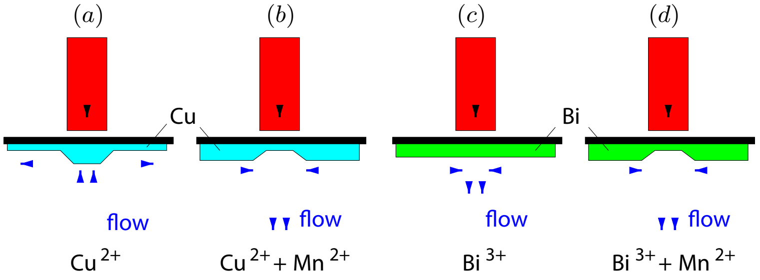

Fig. 1. Sketch of the local convection and the deposition pattern obtained when depositing Cu and Bi from simple electrolytes (*a*), (*c*) and from electrolytes containing strongly paramagnetic inert Mn^{2+}-ions in excess (*b*), (*d*). The magnet which is magnetized in the vertical direction is shown in red. Below the cathode (black), the deposits are shown in light blue (Cu) and light green (Bi), respectively.

Therefore, the curl changes the sign and the direction of convection is inverted compared to the case of simple copper deposition. Thus, a local flow is forced, which brings the depleted electrolyte of the concentration boundary layer towards the magnet, where it leaves the electrode region. As a result, the mass transfer is expected to decrease. The same is valid for the deposition from electrolytes that contain diamagnetic cations (e.g., Bi^{3+}, Zn^{2+}) and strongly paramagnetic cations (inert) in excess, for which $|\chi_{\mathrm{dia}}^{\mathrm{mol}}| << \chi_{\mathrm{Cu}^{2+}}^{\mathrm{mol}}$.

Summarizing the above arguments, the structured deposition of paramagnetic or diamagnetic cations can be divided into four groups, which are schematically described in Fig. 1.

2. Simulation setup. In order to prove our reasoning, numerical simulations have been performed in a vertical cylindrical cell of 8 mm diameter and 10 mm height. For simplicity, only a single magnetic element is considered. On top, closely behind the center of the cathode, a cylindrical NdFeB magnet (diameter 1 mm, height 3 mm, distance 70 μm) is placed, which is magnetized in the axial direction. As the Lorentz force does not need to be taken into account, this setup allows for an axisymmetric simulation in the (r, z)-plane (see Fig. 2). As mass transfer causes density changes, the buoyancy force force is considered in the

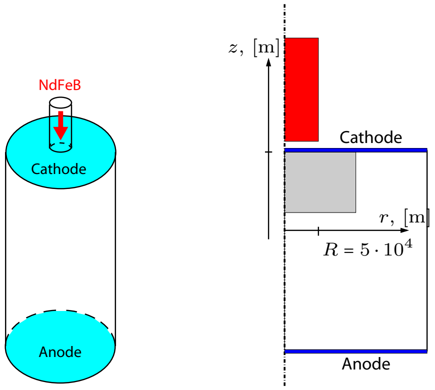

Fig. 2. Left: a cylindrical cell with a NdFeB magnet of cylindrical shape which is magnetized in the axial direction and placed closely behind the center of the cathode. Right: the computational (r, z)-plane of the cell. A region near the magnet (red) is marked in grey (depicted later in Fig. 3).

simulations which reads in the Boussinesq approximation

$$\mathbf{f}_G = \rho_0 \mathbf{g} \sum_i \beta_i (c_i - c_i^0). \tag{6}$$

Here, ρ_0, $\mathbf{g}$, β_i and c_i^0 denote the bulk density of the electrolyte, the vector of gravitational acceleration, and the volume expansion coefficient and the bulk concentration of species i, respectively. The magnetic gradient force is implemented according to Eq. (1), thereby not a priori excluding the influence of the irrotational part of the force [4, 7, 11]. The electrolyte in the cell consists of 0.01 M $CuSO_4$ and 0.1 M $MnSO_4$ and, for simplicity, complete dissociation in Cu^{2+}, $Mn^{2+}$and SO_4^{2-} ions is assumed. The set of equations to be solved consists of the Navier–Stokes equation with the two force terms mentioned, the incompressibility constraint and a Nernst–Planck equation for each ion species. Besides, electroneutrality is assumed in the electrolyte. In order to model different cations to be deposited (Cu^{2+}, Bi^{3+}) in different supporting electrolyte configurations (see Fig. 1) and to ease comparison, in the following, only the magnetic susceptibilities of the involved magnetic species are adjusted, whereas all other material parameters are kept constant. The kinetics of the copper reaction at the electrode is implemented as a Butler–Volmer relation. More details, also on related material and kinetics parameters, can be found in [10]. A potentiostatic deposition at a cell voltage of 0.2 V (copper electrodes) was simulated for a duration of 300 s, leading to a diffusion-limited mass transfer.

The simulations were performed by using the finite element software package COMSOL V. 4.2. The calculation of the magnetic field of the permanent magnet was done as a preprocessing step in a much larger domain in order to avoid any

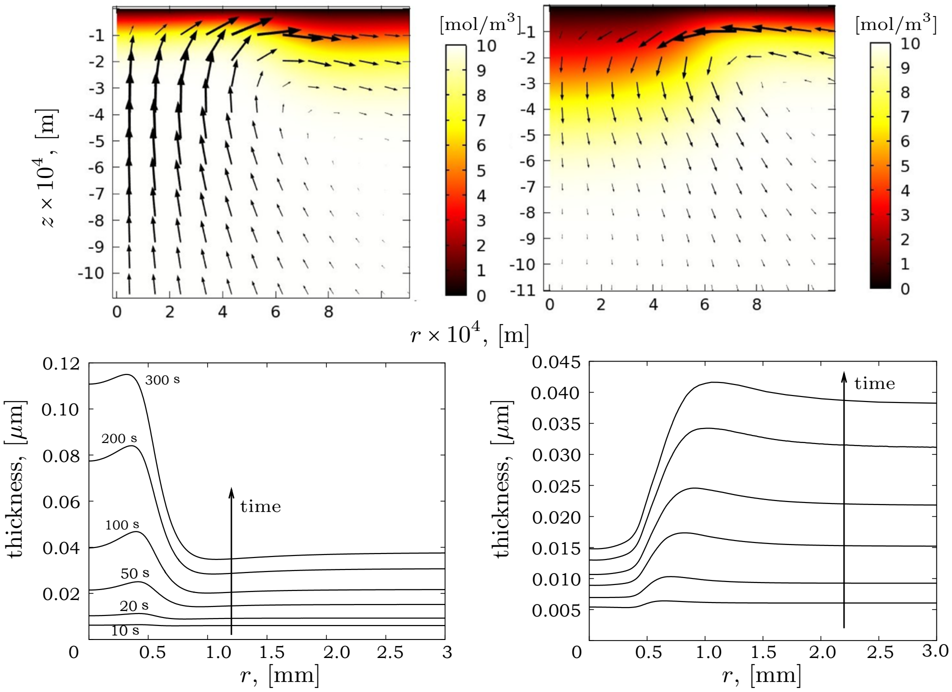

Fig. 3. Top: concentration of $Cu^{2+}$and normalized velocity vectors ($u_{\max} \approx 0.03$ mm/s) at t=20 s in the domain part below the magnet (radius 5 mm). Left: Cu-case, right: Cu-Mn case. Bottom: corresponding temporal evolution of the thickness of the copper layer [6].

influence from imposing boundary conditions at a finite distance from the magnet. The unstructured triangular computational grid was chosen carefully to resolve for the steep field gradients near the rim of the magnet and to ensure accuracy especially in the electrode region near the magnet. Validation showed that grids of approximately 150.000 elements with smallest elements of $3\,\mu$m were sufficient.

3. Results. Fig. 3 (top) shows the Cu^{2+} concentration and the velocity of the electrolyte near the magnet for the magnetically simple Cu^{2+} case (left) and for the case with magnetic Mn^{2+} ions (right) at t=20 s. Clearly, the characteristic convection patterns expected from the above analysis sketched in Figs. 2*a*,*b* were found which qualitatively persisted during ongoing deposition. Although not shown, the case of depositing Bi from electrolytes, where Mn^{2+} ions are present in excess (case (*d*)), looks very similar to the latter case (*b*), as the influence of the Mn^{2+} ions is dominating in both situations. For case (*c*), when depositing Bi^{3+} in the simple configuration without further magnetic metal ions, only rather weak convection patterns were found. This leads to an only tiny inverse structuring effect which has not yet been measured experimentally. The evolution of the deposit thickness for cases (*a*) and (*b*) is shown below and corresponds nicely to the experimental findings in [3, 4].

4. Conclusions. The results of the numerical simulations performed clearly support the reasoning that the structuring effect in small-scale magnetic gradient fields can be consistently explained by local convection which is forced by the rotational part of the magnetic gradient force. Recent measurements in [9] give additional support to the proposed convection model. The influence of electrically inert paramagnetic ions of a supporting electrolyte can be utilized for enhancing the structuring effect during the deposition of diamagnetic ions.

Acknowledgements. We gratefully acknowledge financial support from Deutsche Forschungsgemeinschaft (DFG) through the Collaborative Research Centre 609.

REFERENCES

[1] M. Uhlemann, K. Tschulik, A. Gebert *et al.* *Eur. Phys. J. Spec. Top.,* vol. 220 (2013), pp. 287–302.

[2] G. Mutschke, K. Tschulik, T. Weier, M. Uhlemann, A. Bund, J. Fröhlich. *Electrochim. Acta,* vol. 55 (2010), pp. 9060–9066.

[3] K. Tschulik, X. Yang, G. Mutschke *et al.* *Electrochem. Comm.,* vol. 13 (2011), p. 946.

[4] P. Dunne, L. Mazza, and J.M.D. Coey. Phys. Rev. Lett., 107 (2011) 024501. P. Dunne, R.'Soucaille, K. Ackland, J.M.D. Coey. *Appl. Phys. Lett.,* vol. 111 (2012), p. 07B915.

[5] G. Mutschke, K. Tschulik, T. Weier *et al.* *Magnetohydrodynamics,* vol. 48 (2012), no. 2, pp. 299–304.

[6] G. Mutschke, G.K. Tschulik, M. Uhlemann, A. Bund, J. Fröhlich. *Phys. Rev. Lett.,* vol. 109 (2012), p. 229401.

[7] L.M.A. Monzon, J.M.D. Coey. *Electrochem. Comm.,* vol. 42 (2014), p. 42–45.

[8] C. Wagner. J. Electrochem. Soc., vol. 95 (1949), p. 161.

[9] K. Tschulik, C. Cierpka, G. Mutschke, A. Gebert, L. Schultz, M. Uhlemann. *Anal. Chem.,* vol. 84 (2012), p. 2328.

[10] D. Koschichow, G. Mutschke, X. Yang, A.Bund, and J. Fröhlich. *Russ. J. Electrochem.,* vol. 48 (2012), p. 682–691.

[11] A. Sugiyama, S. Morisaki, R. Aogaki. *Jpn. J. Appl. Phys.,* vol. 42 (2003), p. 5322.

Received 29.01.2015