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

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### Abstract:

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

# **1. 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 order of magnitude estimations of the forces involved, the Lorentz force  $\mathbf{f}_{\mathbf{L}}$  and the magnetic gradient force  $\mathbf{f}_{\mathbf{m}}$ , it was shown 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<sup>2+</sup> (no other magnetic ions are involved), local convection driven by the curl of the magnetic gradient force can explain the structuring effect observed.

In the following, experiments of the deposition of diamagnetic ions were performed as well, and cases where inert magnetic ions are additionally present in the electrolyte, were also considered, mentioning a set of different possible mechanisms [3]. In [4], two different explanations are given when obtaining either structured or inversely structured metal deposits.

Already at the PAMIR 2009 conference, a consistant and unique explanation of all experimental results of deposition in small-scale magnetic gradient fields was proposed by the present authors. 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 [5]. Recently, this reasoning was proven numerically [6]. Below, we present details of numerical simulations performed on this topic, covering the cases of deposition of paramagnetic and of diamagnetic ions.

#### 2. Presentation of the problem

The magnetic gradient force for a number i of species of magnetic ions beside the diamagnetic water molecules can be written as

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

Contrary to the reasoning in [4,7] it can be argued that the ("magnetic") pressure of that force cannot force convection in the deposition setups considered. Instead of this potential part, the rotational part of the force is responsible for the effect. Consider, for example two species of magnetic ions. The curl of the force in this case reads

$$\nabla \times \mathbf{f_m} = \frac{1}{2\mu_0} (\chi_1^{mol} \nabla c_1 + \chi_2^{mol} \nabla c_2) \times (\nabla B^2) \quad .$$
<sup>(2)</sup>

As can be seen, the diamagnetic property of the water molecules does not play any role. Furthermore, inert magnetic ions may have a strong influence on the magnetic gradient force. When depositing from supporting electrolytes that contain a strongly paramagnetic but electrochemically inert cation (e.g.,  $Mn^{2+}$ ,  $Dy^{3+}$ ), changes of concentration of this inert ion become important. Due to electroneutrality, its concentration usually increases at the cathode where its flux must vanish [8]. In case of depositing  $Cu^{2+}$  from an electrolyte that consists of, e.g.,  $c_{Cu2+} \ll c_{Mn2+} \approx c_{SO42-}$  it can be shown that  $\nabla c_{Cu2+} / \nabla c_{Mn2+} \approx -2$ .

For depositing paramagnetic  $Cu^{2+}$  (species 1) in a simple case without other magnetic cations in excess it is known that the curl of the force drives a flow which is resulting in local convection towards the magnet, thereby enriching the concentration boundary layer and thus enhancing mass transfer [2]. If, on the other hand, the supporting electrolyte contains strongly paramagnetic ions, species 2 is dominating the curl since, e.g.,  $\chi_{para}^{mol} / \chi_{Cu2+}^{mol} > -10$  for Mn<sup>2+</sup>, Dy<sup>3+</sup>. Therefore, the curl changes 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 inside the concentration boundary layer towards the magnet where it leaves the electrode. As a result, mass transfer is expected to decrease. The same is valid for the deposition of diamagnetic ions (e.g.,  $\text{Bi}^{3+}$ ,  $\text{Zn}^{2+}$ ), for which  $|\chi_{dia}^{mol}| << \chi_{Cu2+}^{mol}$ . In order to prove this reasoning, numerical simulations have been performed in a vertical cylindrical cell of 8 mm diameter and 10 mm height. At the center of the cathode on top, a cylindrical NdFeB magnet (diameter 1 mm, height 3 mm, distance 70 µm) was placed, which is magnetized in the axial direction. The electrolyte consists of 0.01 M CuSO<sub>4</sub> and 0.1 M MnSO<sub>4</sub>. A potentiostatic deposition at a cell voltage of 0.2 V (copper electrodes) was simulated for a duration of 300 s, leading to diffusion-limited mass transfer. More details will be published elsewhere. Fig. 1 (top part) shows the  $Cu^{2+}$  concentration and the velocity of the electrolyte near the magnetically pure  $Cu^{2+}$  case (left) and the case with magnetic  $Mn^{2+}$ ions (right) at t = 10 s. Depositing  $Bi^{3+}$  in the presence of  $Mn^{2+}$  ions (not shown) looks very similar to the latter case. Clearly, the characteristic convection patterns expected from the above analysis are found which qualitatively persist during ongoing deposition. The evolution of the deposit thickness is shown below and corresponds to the experimental findings in Refs. [3, 4]. Recent measurements in Ref. [9] support the proposed convection model.



Figure 1: Top: Concentration of  $Cu^{2+}$  and normalized velocity vectors at t = 10 s in the domain part below the magnet (black bar on top: radial extent). Left: Cu-case ( $u_{max} = 0.03$  mm/s), right: Cu-Mn case ( $u_{max} = 0.05$  mm/s). Bottom: Corresponding temporal evolution of the thickness of the copper layer [6].

## **3.** Conclusions

The structuring effect in small-scale magnetic gradient fields can be consistently explained by local convection forced by the rotational part of the magnetic gradient force. Numerical simulations clearly support this reasoning.

### 4. References

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