Role of Magnetic Forces in Electrochemical Reactions at Microstructures

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The effect of an external magnetic field (up to 0.8 T) on the anodic dissolution of microstructures has been investigated systematically. Copper and silver wires (100 μm in diameter) were embedded in epoxy resin and dissolved potentiostatically while a magnetic field was periodically switched on and off. A special feature of the thus prepared structures is that they show a smooth transition from an inlaid disk to a recessed disk electrode. An increase or a decrease of the limiting current density in the presence of B was found depending on the orientation of the magnetic field and the hydrodynamic conditions in the cell (natural or forced convection). The magnetic forces which are responsible for this are the Lorentz force and the gradient force. We propose a model which discusses the interaction of these forces with the natural and the forced convection to explain the experimental results.

1. Introduction

It has been shown that a magnetic field can enhance mass transport in electrochemical reactions. This effect is called the magnetohydrodynamic (MHD) effect[1,2,3] and is caused by magnetic forces which induce convective movement in the electrolyte.

The probably best investigated magnetic force in electrochemical reactions is the Lorentz force density, f_L, which is given by eq 1

$$\vec{f}_L = \vec{j} \times \vec{B} \tag{1}$$

where j is the current density in A m^{-2} and B is the magnetic flux density in T (tesla). As is obvious from the cross product, this force becomes maximum when j is perpendicular to B.

In addition, there can be forces, f_G, due to the gradients of the magnetic field and of the magnetic susceptibility,[4,5] eq 2

$$\vec{f}_G = \frac{\chi \vec{B}}{\mu_0} \nabla \vec{B} + \frac{B^2}{2\mu_0} \nabla \chi \tag{2}$$

where χ is the dimensionless magnetic susceptibility and μ_0 the permeability of free space ($4\pi \times 10^{-7}$ N A^{-2}).

Gradients of the magnetic flux density, ∇B, can occur due to the experimental setup (e.g., if the external field is inhomogeneous across the electrochemical cell) or if the electrode is made from a ferromagnetic material.

Gradients of the magnetic susceptibility, $\nabla \chi$, can occur as a consequence of concentration gradients in the solution. If solid Cu is dissolved, then there will be a concentration gradient, ∇c, of the paramagnetic Cu^{2+} species in front of the electrode (Nernst diffusion layer) and $\nabla \chi = \chi_m \nabla c$ (χ_m is the molar susceptibility in m^3 mol^{-1}). As this gradient comprises volume elements with different susceptibilities, there will be a force which tends to keep volume elements with a high concentration of cupric ions near the electrode. The existence of such a force can be easily visualized by using a chemical reaction which produces colored species.[6,7]

It has been argued that the concentration gradient paramagnetic force must compete with the force driving the diffusion which should be proportional to ∇c as well.[8] However, this approach seems a little bit too simplistic. The forces f_L, eq 1, and f_G, eq 2, are body forces which induce the convection of the electrolyte. The so-called "diffusion force" acts on an individual species (ions, molecules, etc.) and causes a flux of molecules or ions. Simply speaking, it would make no sense to use this "diffusion force" in the Navier–Stokes equation. Leventis et al. showed that it is important to distinguish between the above-described magnetic volume forces and magnetophoresis ("flux of magnetic dipoles driven by a magnetic field"[9]).

As the magnetic forces f_L and f_G induce convection in the electrolyte, an increase of the limiting current density, j_L, is usually observed. There are semiempirical equations relating j_L and B[10–12] and some hydrodynamic treatments for simple geometries.[13,14] For macroscopic electrodes, a linear dependence of j_L with $B^{1/3}$ is found in most cases;[11,12] whereas for microelectrodes, a proportionality of j_L to B is reported.[15] The reported investigations at microelectrodes were mainly performed with inlaid disk electrodes. However, from a hydrodynamic point of view, recessed microstructures are more interesting. There is, for example, the question if magnetohydrodynamic stirring is possible in such confined geometries.[16] Metal depositions in confined geometries (e.g., vias) are strongly limited by mass transport effects. The void-free filling of these structures is a challenging task which is mainly accomplished by special additives[17] or pulsed electrodeposition.[18] It seems promising to enhance the mass transport in such electrochemical processes by tailored magnetic fields.

For most experimental setups involving an electrochemical reaction which is limited by mass transfer, another body force must be taken into consideration. At long times, especially when the diffusion layer has become quite thick, natural (or free) convection sets in. The driving force for natural convection is the density gradient of the electrolyte which arises from concentration changes in front of the electrode.[19] White et al.

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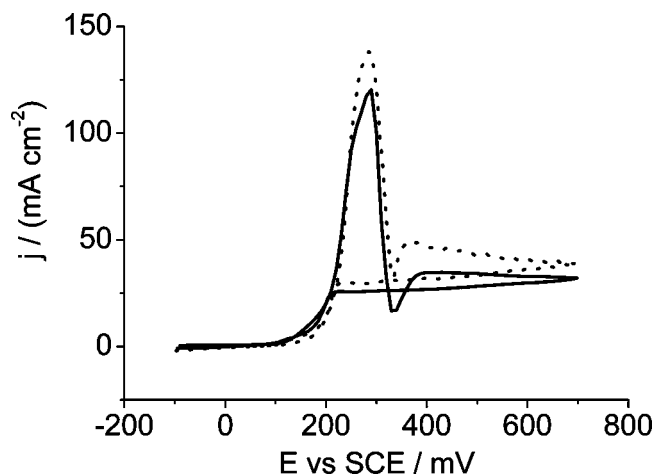
Figure 1. Potentiodynamic polarization curves (10 mV/s) of an array of six copper disk microelectrodes in 1 M H_2SO_4 in orientation I without a magnetic field (—) and for $B = 0.6$ T (⋯).

showed that magnetic forces can nullify the natural convection.[20] Obviously, the forces driving the natural convection are in the same order of magnitude as the magnetic forces. Iwakura et al.[21] studied the interaction of natural convection and Lorentz forces. Their general conclusion was that a current enhancement can be expected when the natural convection and the Lorentz force have the same direction.

The aim of this paper was to study systematically the influence of the geometrical arrangement between the current lines and the magnetic field in electrochemical reactions at inlaid and recessed microstructures. As a special feature of these investigations, the aspect ratio (depth/width) of the recessed structures was adjusted in situ by electrochemical dissolution.

2. Experimental Section

The electrolytes were prepared from p.a. grade chemicals and doubly distilled water. All measurements were performed in a thermostated cell at 298.0 ± 0.1 K.

Arrays (2×3) of six microdisk electrodes were prepared by embedding copper or silver wires (diameter 100 μm) in epoxy resin. After the resin was cured, the resulting blocks were cut and polished yielding two arrays of six microdisk electrodes. The distance between the individual electrodes was 3 mm. For the systematic investigation of the magnetic field effects, the electrode arrays were fixed in a holder with well-defined

distances between the working electrodes (i.e., the microdisks), the counter electrode (a Pt sheet of 12×12 mm^2), and the reference electrode (a saturated calomel electrode, SCE). In addition, a stirring paddle could be mounted close to the working electrode to mimic the conditions of forced convection. The Cu microstructures were anodically dissolved at 500 mV vs SCE. In most experiments, the electrolyte was 1 mol/L sulfuric acid which contained 0.5 mL/L of a fluorocarbon surfactant (FC 140C, 3 M). In some experiments, copper sulfate was added to the sulfuric acid to study the influence of the concentration gradient. For some selected samples, the etch process was monitored with an optical microscope equipment with a micrometer. The depths of the microholes were determined from the distance difference for focusing the top of the sample (i.e., the epoxy) and the bottom of the microhole. The accuracy ($\pm 1\%$) of this method was asserted by measuring the depth from cross sections of the same sample.

The silver wires were dissolved in 1 M HNO_3 at 800 mV vs Ag/AgCl in saturated KCl (including a double junction filled with 1 M $NaNO_3$).

A water-cooled electromagnet (VEB Polytechnik, Phylatex, Chemnitz, Germany) was used to apply magnetic fields up to 0.8 T. The magnetic flux density was adjusted by the current through the coils and was measured with a Hall probe (Lake Shore, model 450). The cylindrical poles (diameter 10 cm) which guide the magnetic flux are made from iron. The electrochemical cell (diameter 2 cm) was positioned in the center of the poles. Over this 2 cm distance, the flux density varied from 700 mT (center) to 705 mT which gives a radial gradient of 2.5 mT cm^{-1}. Given the small diameter of the electrodes (100 μm), the magnetic field can be considered as uniform across the electrode surface.

3. Results and Discussion

To gain some insight into the dissolution process of the copper structures, cyclic voltammetry experiments were performed in the potential range from -100 to 700 mV vs SCE. In the anodic sweep, the current strongly increases at ca. 200 mV, reaches a maximum at ca. 290 mV, and quickly drops down. For $B = 0$ (Figure 1, solid line), the maximum current is ca. 120 mA cm^{-2}, and for $B = 0.6$ T (Figure 1, dotted line), it is 140 mA cm^{-2}. Between 330 and 380 mV a local minimum of the current appears. After that an almost constant current of ca. 34 mA cm^{-2} ($B = 0$ T) or 45 mA cm^{-2} ($B = 0.6$ T) is observed. The
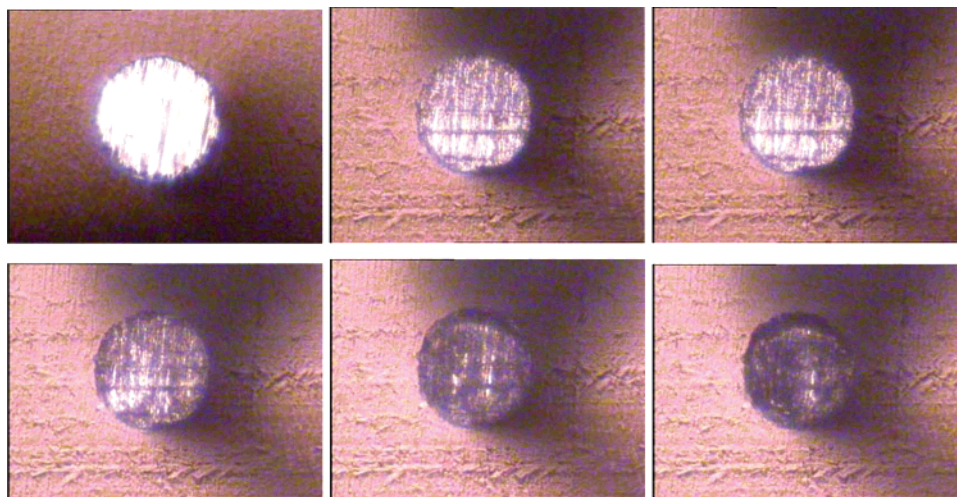

Figure 2. Series of microscopic photographs during the anodic dissolution of a copper disk microelectrode at 500 mV vs SCE in 1 M H_2SO_4. The series covers approximately the first 4 min of the dissolution reaction.

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behavior seen in Figure 1 is indicative for passivation. It is also obvious that the magnetic field reduces the passivation (higher maximum active current density and higher passive current density). In alkaline media, the passivation of Cu occurs via the formation of copper oxides and hydroxides.[22,23] In sulfuric acid, passivating films of $CuSO_4$ are formed by supersaturation.[24] Figure 2 shows a series of images taken with an optical microscope during the anodic dissolution of one copper microdisk (out of six). It is clearly visible that the electrode surface becomes covered with a dark layer, presumably copper sulfate.
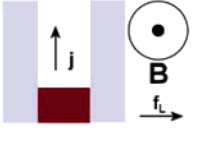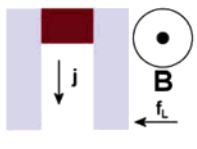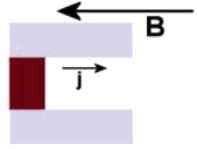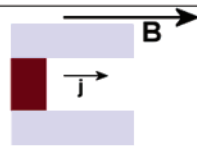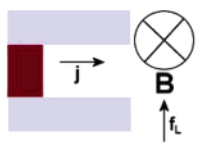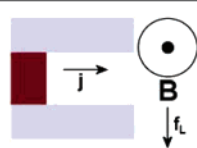
Potentiostatic polarization of the Cu microstructures at 500 mV vs SCE lead to the formation of six microholes whose aspect ratio (depth-to-width) increases with time. It is well-known that the transition from Cu(0) to Cu(II) proceeds via the intermediate Cu(I) and that the step Cu(I) to Cu(II) is slow and thus rate determining.[25] Therefore, during the anodic dissolution of Cu there will be a relatively high concentration of cuprous ions, Cu(I), near the electrode. It has been shown that the rates of the charge-transfer reactions are not affected by a magnetic field.[8,11,16] However, the question arises if there is a magnetic field effect on this relatively thin layer of diamagnetic ions. To shed some light on this question, we calculated the current efficiency of the anodic dissolution of our Cu microstructures with and without a magnetic field. The amount of dissolved Cu was determined by measuring the depth of the microholes after a fixed time with a microscope (see Experimental section). Relating this amount to the passed electrical charge gives the current efficiency of the dissolution reaction. From a series of measurements in orientations I and II, a value of 1.34 ± 0.05 was obtained. Within the limit of error, we did not find an effect of the magnetic field on the current efficiency. Of course, a value above one indicates that cuprous ions are produced and removed from the electrode (by diffusion and convection), but the effect of the magnetic field on this process seems to be small.

When a magnetic field of 0.6 T was periodically applied during the anodic polarization, the current density increased or decreased depending on the orientation of the B field (Table 1). The limiting current density transients at $B = 0$ were extrapolated to the times where $B = 0.6$ T using third-order polynomial functions. Notice, that the thus obtained fitting parameters have no physical meaning. The procedure just provides values for the current density at intermediate times. To quantify the effect of the magnetic field, we define the relative change of the limiting current density, j_{rel}, according to eq 3

$$j_{rel} = \frac{j_L(B) - j_L(B = 0)}{j_L(B = 0)} \qquad (3)$$

Table 1 summarizes the results of a large number of measurements at Cu microstructures. Each orientation depicted in Table 1 was investigated at least five times to ensure the reproducibility of the results. At first glance one might expect an increase of j_L for all configurations where B and j are perpendicular, that is, I, II, V, and VI. If the bulk solution is not stirred, then one finds this expected result except for orientation V. On the other hand, when B and j are parallel (configurations III and IV), there is no Lorentz force and thus no MHD stirring. Therefore, one would expect no effect of B on j_L. However, the data in Table 1 show that j_L decreases for these configurations. If the solution was stirred, then the effect of B was in general smaller than that without forced convection (third column of Table 1). However, one very interesting result was the reversal from enhancement to suppression (configuration

TABLE 1: Influence of a Magnetic Field (0.6 T) on the Anodic Cu Dissolution from a Microstructure in Terms of the Relative Change Limiting Current Density[a]

Arrangement	No Stirring	Stirring
I	+ 5-10%	− 1-3%
II	+ 10-20%	+ 3-5%
III	− 1-3%	− 1%
IV	− 1-3%	− 1%
V	− 5-10%	+ 2-5%
VI	+ 5-10%	+ 5%

[a] The vectors j, B, and f_L indicate the actual direction of the current density, the magnetic flux density, and the Lorentz force, respectively.

I) and from suppression to enhancement (configuration V) under conditions of forced convection. In the following paragraphs, we will discuss the results which are summarized in Table 1 in more detail. The discussion has been grouped into three logical blocks comprising the configurations I/II, III/IV, and V/VI.

3.1. Parallel Arrangement of Current and B Field (orientations III and IV). If B and j are parallel to each other, the only direct force which can appear is the concentration gradient force according to eq 2. For orientations III and IV, a slight decrease of the limiting current density was obtained when B was on (Figure 3). At the beginning of the experiment, the presence of B reduced j_L by ca. 3%. With increasing etch depth, the effect of B went down to 1%. If the bulk electrolyte was stirred, then the effect was the same.

White et al. showed experimentally[20] and numerically[26] that cyclotron flows (flows rotating around the circumference) are generated in the volume element adjacent to inlaid microelectrodes if B and j are parallel. Interestingly, this cyclotron flow seems to reduce the flux of electroactive species toward the electrode surface and thus to decrease the limiting current density. In their experiments with nitrobenzene in acetonitrile,
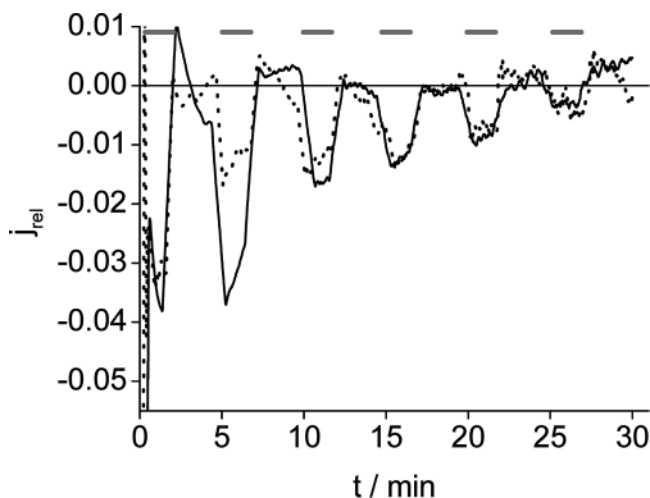
Figure 3. Relative changes of the current density for potentiostatic Cu dissolution at 500 mV vs SCE in 1 mol/L H_2SO_4 under the influence of an oscillating magnetic field ($B = 0.6$ T) for orientations III (−) and IV (···) in unstirred solution. Horizontal gray bars mark the times where B is on.

they observed decreases of the limiting current density by 5% for B fields up to 0.5 T. The occurrence of this rotating flow can be qualitatively explained with the fact that the radial current distribution at a microdisk electrode has components both parallel and perpendicular to the externally applied B field. The components of j which are perpendicular to B will generate a Lorentz force density according to eq 1. Detailed considerations show that the final flow profile is the above-described circular or cyclotron flow.[26] The cyclotron flow interacts with the natural convection and counterbalances it partly. As a consequence, the flux of electroactive species is reduced and the limiting current density is decreased. Uhlemann et al. confirmed the slight decrease of the limiting current density (in their case for the Cu deposition macroscopic electrodes with areas between 0.2 and 1 cm²) at low B fields.[27] They also explained this finding with the cyclotron flow. Our results seen for orientations III and IV (Table 1) could be explained with the effect of the cyclotron flow as well. However, during the experiment, the inlaid electrode becomes a recessed electrode. At the end of the experiments shown in Figure 3, the aspect ratio (depth/width) is approximately one and j_L still decreases when B is switched on. Because of this and because of the results with Ag electrodes (to be discussed below), another mechanism seems to be active. As has been shown by Leventis et al.,[7] the concentration gradient paramagnetic force tries to keep volume elements with high magnetic susceptibility at locations of high concentration (thus, it formally has the opposite direction as diffusion). The net effect should be a slight decrease in the diffusion-limited current density, which is in perfect agreement with the experimental results (Table 1). Stirring the bulk of the electrolyte does not affect this force balance because the forced convection does not enter the cavity.

Note, that according to eq 2 f_G is proportional to B^2 and thus does not depend on the direction of B which is also in agreement with the experimental results.

The results given in Table 1 were obtained in pure sulfuric acid. If the experiments were performed in copper sulfate solution, then the suppressing effect of B on j_L became weaker and disappeared completely in a solution containing 1.3 mol/L Cu (Figure 4A). This is approximately the saturation limit of copper sulfate at room temperature. The result shown in Figure 4A can be explained as follows. In a solution with a cupric ion
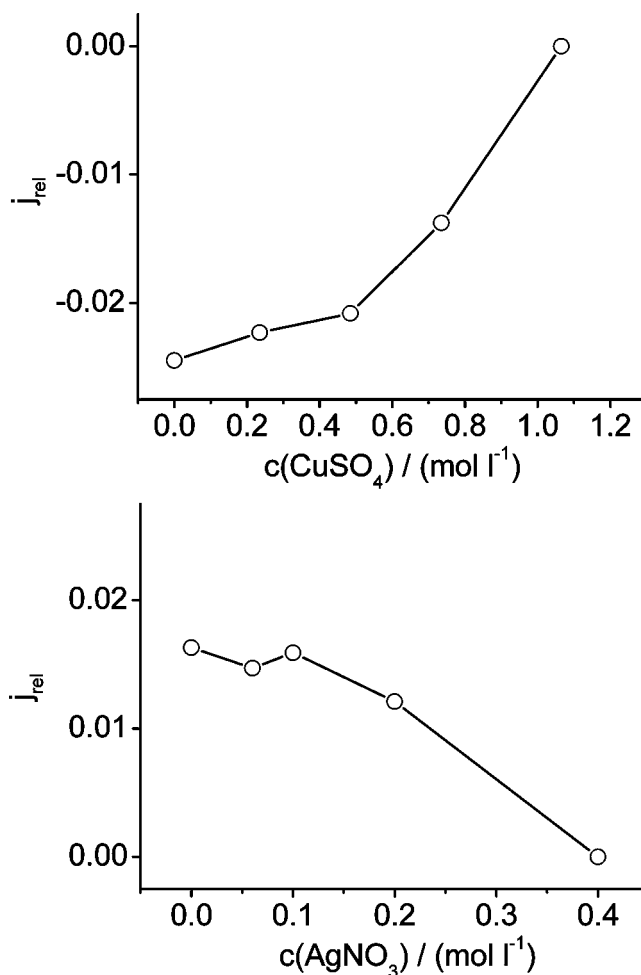

Figure 4. Relative changes of the current density under the influence of a magnetic field (orientation IV) for different concentrations of the electrolyte. The connecting lines are just a guideline for the eye and have no physical meaning: (A) copper dissolution in copper sulfate, $B = 0.6$ T; (B) silver dissolution in silver nitrate, $B = 0.8$ T.

concentration close to saturation, there will be almost no concentration gradients and therefore no concentration gradient force. Thus, magnetic field will not affect the current density.

If copper was replaced by silver (Ag^+ is diamagnetic), then the opposite behavior was found (Figure 4B). Now, the current density increases under the influence of a magnetic field. This finding can be explained with a diamagnetic concentration gradient force which moves volume elements out of the cavity. Although this diamagnetic force is approximately 3 orders of magnitude smaller than the paramagnetic force,[6] it seems to be able to induce convective movement and to affect the limiting current density.

3.2. Perpendicular Arrangement of Current and B Field (orientations I and II). As j and B are perpendicular to each other in these configurations, one can expect a typical MHD effect, that is, an increase of j_L in the presence of B. If the electrolyte is not stirred, one obtains the expected result (Table 1). In configuration I, j_L increased by 5−10% in the presence of B and in configuration II, by ca. 10−20% (Figure 5). Applying the right-hand rule, one sees that the Lorentz force is directed parallel to the electrode surface (inlaid electrode) or toward the side walls of the microhole (recessed electrode). It is difficult to speculate about the resulting flow profile for the latter case without performing numerical simulations. It might consist of microturbulences inside the cavity which could enhance the mass transport out of the structures. In configuration
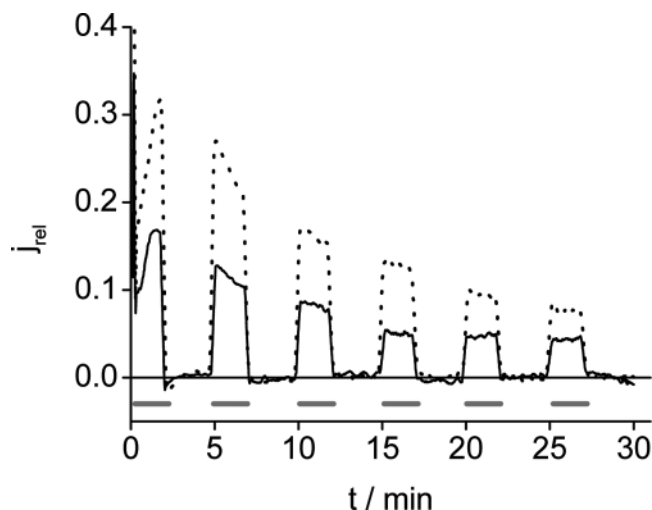
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Figure 5. Relative changes of the current density for potentiostatic Cu dissolution at 500 mV vs SCE in 1 mol/L H_2SO_4 under the influence of an oscillating magnetic field ($B = 0.6$ T) in orientations I ($-$) and II ($\cdots$) in unstirred solution. Horizontal gray bars mark the times where B is on.

II, the electrode faces downward and the dissolution reaction is facilitated by a strong natural convection. Therefore, the absolute values of the current density are higher in this case, and the enhancement by the magnetic field is stronger. If the electrolyte is stirred, then the natural convection is strongly disturbed. This explains the smaller current enhancement for configuration II under conditions of forced convection. For configuration I, a suppression of j_L is observed if the electrolyte is stirred which is again an unexpected result. This suppression can be explained with a retarding force whose origin is again the concentration gradient force (see section 3.1). The tangential streaming profile above the structure leads to an increase in the concentration gradient of the cupric ions (Figure 6). As outlined in section 3.1 in the presence of B, this gradient produces a gradient force which exerts a retarding force on the volume elements containing paramagnetic cupric ions. As a net result, the limiting current density decreases when $B > 0$.

3.3. Perpendicular Arrangement of Current and B Field (orientations V and VI). Configuration VI showed the expected behavior. The magnetic field enhanced the limiting current density. In the unstirred solution, the enhancement was somewhat stronger (5−10%) than that in the stirred solution (2−5%). However, configuration V showed a peculiar result. j_L was suppressed by 5−10% in the magnetic field without stirring. Note, that the suppression in configuration V is in the same order of magnitude as the enhancement in configuration VI. If

the solution was stirred, j_L increased by 5% when B was switched on. This behavior was reproducible as is shown in Figure 7. The solid line shows the current increase (between 15 and 3% depending on the etch depth) whereas the dotted trace shows the effect of switching the stirrer off (after 7 min), on again (after 13 min), and off again (after 17 min) while at the same time the B field was periodically switched on and off (bold, gray lines mark the times where B is on). It can be clearly seen that without stirring B suppresses the current while with stirring B increases the current. To explain this unexpected result, one has to take into consideration the interaction of the natural convection and the flow which is induced by the Lorentz force. Under the conditions of anodic dissolution in configurations V and VI, there will be a downward stream of copper sulfate driven by natural convection (Figure 8, blue arrows marked with v_{NC}). The Lorentz force will be directed upward (orientation V) or downward (orientation VI) depending on the orientation of B. For orientation V, the flow which is induced by f_L has the opposite direction as v_{NC} (Figure 8, left), whereas for orientation VI, both flows have the same direction (Figure 8, right). Thus, for orientation V, the velocity of the downward flow will decrease, and for VI, it will increase (compared to the situation without magnetic field). As the downward flow removes cupric ions from the microstructure, it reduces the polarization of the electrode and therefore increases the current density in a potentiostatic experiment. This is exactly what is observed in the experiment. In orientation V, the current density goes down when B is on because the downward flow in front of the electrode is "slowed down" a bit. In orientation VI, the Lorentz force accelerates the downward flow and j increases in the presence of B. As the aspect ratio of the structure increases, the effect of the downward flow on the removal of cupric ions is less effective (we are moving toward a recessed electrode). Therefore, the magnetic field effect on j becomes weaker.

If the electrolyte is stirred, then the natural convection disappears and both orientations show the same behavior, that is, a slight increase (approximately 5%) of j_L in the presence of B.

4. Summary and Conclusions

Our results show that a magnetic field of ca. 1 T affects the limiting current density, j_L, of the dissolution of copper and silver microstructures (100 μm in diameter) in the order of some percent. Depending on the orientation of B and the magnetic properties of the ions, a suppression or increase of j_L can be observed. It has been shown that the effect of the paramagnetic concentration gradient force is in the same order of magnitude as the Lorentz force. Both forces induce MHD convection which
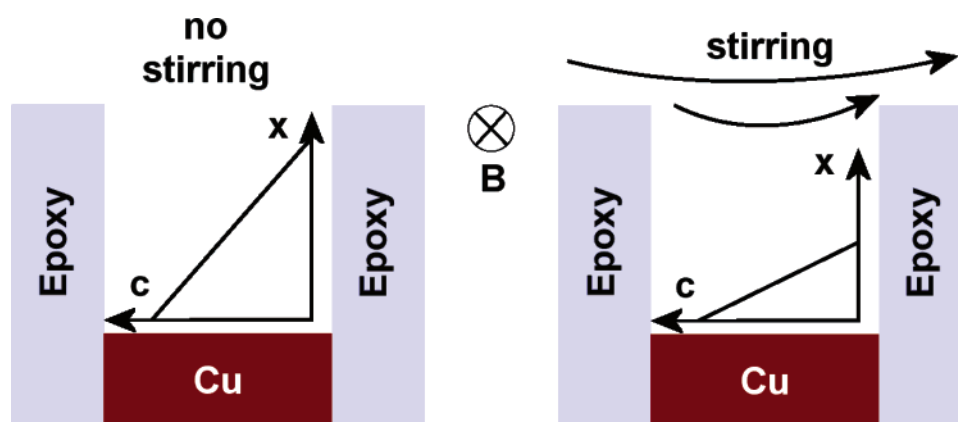

Figure 6. Schematic representation of the increase in the concentration gradient under the influence of forced convection in orientation I.
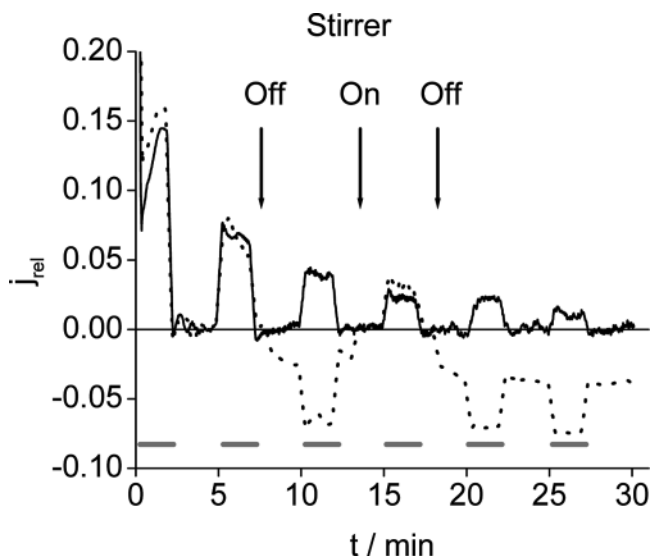
Figure 7. Relative changes of the current density for potentiostatic Cu dissolution at 500 mV vs SCE in 1 mol/L H_2SO_4 under the influence of an oscillating magnetic field ($B = 0.6$ T) in orientation V in a stirred solution ($-$) and for periodic switching off and on of the mechanical stirring ($\cdots$). Arrows mark the switching times of the stirrer. Horizontal gray bars mark the times where B is on.
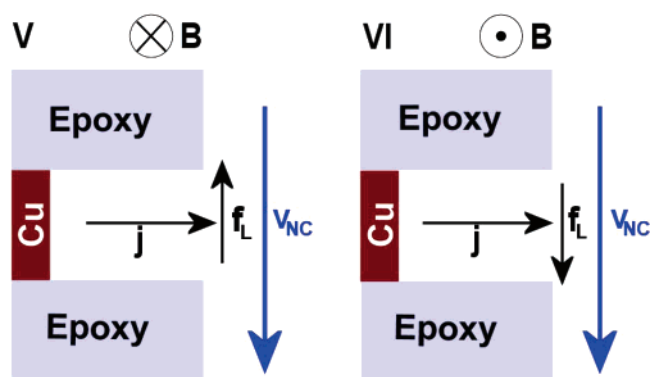

Figure 8. Schematic representation of the interplay between natural convection, v_{NC}, and Lorentz force, f_L, in orientations V and VI.

may interact with the natural convection. For a parallel orientation of B and j, the paramagnetic concentration gradient force leads to a suppression of j_L if paramagnetic species (Cu^{2+}) are produced in the dissolution reaction. For diamagnetic species (Ag^+), the opposite behavior was found. With an increase in aspect ratio of the microstructures (recessed electrodes), the magnetic field effects become weaker which is a clear indication for the hydrodynamic character of these effects.

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