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Magnetic field effects in electrochemical reactions

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Abstract

The influence of an external magnetic field *B* on the electrochemical behaviour of the systems Cu^{2+}/Cu , Ni^{2+}/Ni , and $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ has been studied. In the case of Cu depositions in an electrochemical cell with a large ratio of the electrode area and the cell volume the increase of the limiting current density with *B* can be explained with the interplay of natural convection and the Lorentz force acting on the resulting flow profile (magneto hydrodynamic or MHD effect). Ni depositions also show an MHD effect as well as a tendency to form more fine grained material in the presence of a magnetic field. The results on the homogeneous redox system $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ at 50 µm diameter micro electrodes are in qualitative agreement with recently proposed relationships to describe the influence of a *B* field on the limiting current density. © 2003 Elsevier Ltd. All rights reserved.

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1. Introduction

If one looks through the literature about magnetic field effects in electrochemical reactions ("magnetoelectrolysis"), the first effect one will probably encounter is the magneto hydrodynamic (MHD) effect. Its origin is the Lorentz force $F_{\rm L}$ acting on moving charges (ions) in a perpendicular magnetic field of flux density B, $F_{\rm L} = i \times B$, where i is the current density. In most cases the MHD effect will lead to an increase of the limiting current density because the thickness of the Nernst layer is reduced by the magnetically stimulated convection. At the first glance it may seem that the law of the conservation of energy is violated, because a static magnetic field cannot transfer the energy, needed to stir the system. The action of B is to induce a force component which is perpendicular to the velocity vector and the B field. However, the absolute value of the momentum of the ion remains constant.

The design of the electrochemical experiment (cell dimensions, size and arrangement of electrodes, etc.) strongly influences the resulting flow profiles [1]. There are empirical relations in the form of Eq. (1) [2–4].

$$i_{\rm L} = i_{\rm L,0} + mB^p \tag{1}$$

where $i_{\rm L}$ and $i_{\rm L,0}$ are the limiting current densities in the presence and the absence of a magnetic field, respectively. The parameters *m* and *p* are empirical constants, with *p* in the range from 0.25 to 1.64.

In a systematic investigation on the influence of the individual parameters Leventis et al. arrived at the semi-empirical Eq. (2) for the limiting current density $i_{\rm L}$ (A cm⁻²) [5,6].

$$i_{\rm L} = 4.31 \times 10^2 \times n^{3/2} F A^{-1/4} B^{1/3} D v^{-1/4} c^{4/3}$$
 (2)

with ν kinematic viscosity (cm² s⁻¹), *D* diffusion coefficient (cm² s⁻¹), *A* area (cm²), *c* concentration (mol cm⁻³) and the numerical constant has units of cm mol^{-1/3} T^{-1/3} s^{-1/4}.

An interesting feature of Eq. (2) is the dependence of the current density on the electrode area and the exponent 3/2 for *n*, the number of transferred electrons, which was explained with a "feedback mechanism according to which a higher *n* causes a higher magnetic current which causes more vigorous hydrodynamic stirring" [6]. However, Eq. (2) can only be true for a certain range of *B* (and for B > 0) because at B = 0 $i_{\rm L}$ would be zero what is definitely not the case.

White et al. were the first to introduce microelectrodes (sometimes also called ultra microelectrodes, UMEs [7]) in the field of magnetoelectrolysis. Their theoretical description yields an expression for the net force on the diffusion layer and qualitatively agrees with their experimental results [8]. Despite the increasing efforts to describe quantitatively the

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influence of the B field on the limiting current density a quantitative description of the MHD effect based on the Navier–Stokes equation is still pending. This is due to the complex mathematics of hydrodynamics.

If the magnetic field is in parallel with the current lines, $F_{\rm L} = 0$. Nevertheless, there are reports of an influence of the B field on the current characteristics of the cell under these conditions [9–12]. In the case of large magnetic fields (up to 9.4 T) White et al. could show that the increase of $i_{\rm L}$ is due to local gradients of the B field causing paramagnetic forces [13]. The origin of these gradients can be either gradients of the external field itself or gradients of the magnetic susceptibility in the solution. During an electrochemical reaction the magnetic susceptibility χ of the Nernst layer can become different from the bulk value, because it is depleted from the electro-active species. The gradient of χ , which is proportional to the concentration gradient, can induce convection by pulling paramagnetic ions into the direction of higher B or by pushing diamagnetic ions out of the B field [9,14–16]. According to the authors of refs. [17,18] the paramagnetic forces as well as the Lorentz forces should be 6-7 orders of magnitude smaller than the diffusional forces arising from typical concentration gradients. Therefore, the question arises how such small forces can influence $i_{\rm L}$ to a measurable extent.

The question whether the electron transfer kinetics are influenced by a *B* field is still discussed controversively in literature [2,19,20]. It seems that these effects are small in moderate *B* fields and will be paralleled in most cases by paramagnetic and Lorentz force effects. Therefore, well reproducible electrochemical systems with high exchange current densities are needed as model systems for systematic investigations on the *B* field influence on electrode kinetics.

This paper summarises some results from the authors' lab contributing to the above mentioned questions. One aim was to investigate the B field effect in cells with a large ratio of the electrode area A and the cell volume V (A/V ratio). In such cases the experimental findings cannot be explained by extrapolating the results from mini- and microelectrodes because the magnetic forces will set the whole electrolyte into motion. Furthermore, the question if there is a B field effect on the structure of an electrodeposited ferromagnetic metal should be studied. Finally, many investigations on heterogeneous redox couples are done on the ferri/ferro cyanide system, which is known to reveal some problems with reversibility. Most non-aqueous systems, which are also often used as model systems for systematic investigations on the B field influence are experimentally more demanding. Therefore, the usability of the aqueous heterogeneous redox system $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ should be explored.

2. Experimental

All experiments were performed in the homogeneous field of a water-cooled electromagnet (VEB Polytechnik,

Phylatex, Karl-Marx-Stadt). The magnetic flux density B was measured with a Hall probe (Lake Shore, model 450). Note, that in the following, the expressions parallel and perpendicular refer to the orientation of the B field relative to the electric current lines in the electrochemical cell.

All solutions were prepared from ultra pure water and analytical grade chemicals. As the electromagnet produces a lot of heat careful control of the temperature was crucial in all experiments. Therefore all electrochemical cells were equipped with a thermostating jacket which was fed from a water thermostate (25.0 ± 0.1 °C, Neslab RTE-110).

The electrochemical experiments were performed with a Jaissle IMP 88PC-R potentiostat, controlled by the ECMWin Software (IPS Schrems, Germany). All potentials are referred to a saturated (KCl) calomel electrode (SCE, Meinsberg Sensortechnik, Meinsberg, Germany).

Copper depositions were studied from 10 mM CuSO₄, 0.1 M Na₂SO₄ at pH 2. A PMMA cuvette (10 mm × 10 mm × 45 mm) was used as the electrochemical cell containing two Cu sheets (width 9 mm, thickness 0.5 mm) as working electrode (WE) and counter electrode (CE), respectively. The CE and WE were placed parallel to each other at two opposite walls. For the WE two vertical dimensions were investigated: $A_1 = 12$ mm and $A_2 = 40$ mm, the CE had the larger height A₂ in all experiments. Cu deposition was performed for 80 s at -150 mV. After each deposition the WE was polarised at 80 mV for 60 s to start each experiment with a reproducible surface morphology.

Nickel depositions and dissolutions were studied in a cylindrical thermostated glass cell (diameter 28 mm). The Watts type electrolyte contained $0.17 \text{ M NiCl}_2 \cdot 6 \text{H}_2 \text{O}$, 0.77 M NiSO₄·6H₂O, 0.65 M H₃BO₃, 1 mg/ml surfactant Ni719 (Atotech, Berlin, Germany) and was adjusted to pH 4.2 by adding solid NaHCO₃. The electrolyte was purged for 8 min with Ar (99.998%) prior to each experiment. The WE (1.5 mm diameter Pt mini-disc electrode sealed in a glass tube) was polished with abrasive paper (Struers, SiC, P#4000). After each experiment the Ni film was dissolved in 20% HCl. The surface was checked before and after each Ni deposition with an optical microscope (Reichert, Austria). The CE (Pt foil, ca. $10 \text{ mm} \times 10 \text{ mm}$) was placed at the bottom of the cell. Thus, the magnetic field was always perpendicular to the current lines.

The effect of a perpendicular *B* field on a homogeneous redox couple was studied on the system $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ in the same cuvettes as the Cu experiments. The electrolyte contained 0.1 M NaCl, 2 mM K₂[IrCl₆] (Aldrich). Lab-made 50 μ m diameter Pt microelectrodes sealed in glass tubes were used [21]. The CE was a Pt sheet. Five cycles between 300 and 1100 mV were recorded at a scan rate of 10 mV/s. Sweeps started at 700 mV into the cathodic direction.

Table 1 Relative increase of the limiting current density of the Cu reduction for different orientations of the *B* field (details see Figs. 2 and 3) and different sizes $(A_2 > A_1)$ of the working electrode (WE)

Orientation	Relative current increase at 1 T (%) (area of WE A1)	Relative current increase at 1 T (%) (area of WE A2)
Fig. 2a	30	37
Fig. 2c	26	23
Fig. 3a	49	75
Fig. 3d	31	18

3. Results and discussion

3.1. Copper depositions

The limiting current density of Cu deposition showed a strong dependence on the orientation of the magnetic field. As a measure for the influence of the magnetic field the relative increase of the limiting current density $(i_{\rm B} - i_{\rm B=0})/i_{\rm B=0}$ (measured at the end of the reduction step, see Section 2) is taken. We can expect a MHD effect for a perpendicular orientation of the B field relative to the current lines. Thus, as the cell is rotated in the B field in steps of 90°, one would expect two arrangements with a strong influence of the B field (perpendicular) and two orientations with a negligible effect (parallel). Interestingly, we found a distinct B field effect in every position. Furthermore, the magnitude of the effect was different for each of the four positions (Table 1). Measurements at intermediate magnetic flux densities showed an almost linear behaviour of the relative current increase on B (shown in Fig. 1 for the parallel orientations). For a perpendicular magnetic field the increase of the limiting current density was strongest in the orientation outlined in Fig. 2a, i.e. the B field pointing away from the observer. If the cell is rotated by 180° (B now points towards to observer, Fig. 2c), the effect is considerably smaller.



Fig. 1. Relative current increase of the limiting current density of Cu deposition (0.1 M Na₂SO₄, 10 mM CuSO₄, pH 2) at -150 mV (SCE) in a parallel *B* field. Lines are drawn just as a guideline for the eye. *A*₁ and *A*₂ refer to the size of the WE (*A*₂ > *A*₁, see text). (\bigcirc) WE *A*₂, orientation as in Fig. 3a, (\square) WE *A*₁, orientation as in Fig. 3d, (\bigtriangledown) WE *A*₂, orientation as in Fig. 3d, (\bigtriangledown) WE *A*₂, orientation as in Fig. 3d, (\bigtriangledown) WE *A*₂, orientation as in Fig. 3d, (\bigtriangledown) WE *A*₂, orientation as in Fig. 3d.



Fig. 2. Schematic representation of the interplay of the natural convection and the MHD effect (B field perpendicular to the current lines).

For a parallel *B* field of 1 T with the orientation outlined in Fig. 3a the current increase was 75%. Rotating the cell by 180° resulted in a current increase of 18% (Table 1). This is a somewhat unexpected behaviour, because at a first glance one would not expect a Lorentz force (and thus no MHD effect) for neither of these two configurations.

As Eq. (2) was deduced from experiments with minielectrodes it will not be applicable to the situation here. The A/V ratio of the cell used here is in the range from 0.2 to 1 cm^{-1} (see Section 2) and thus relatively large compared to experiments with mini- and microelectrodes, where A/Vis typically well below 10^{-3} cm^{-1} . Preliminary experiments using laser Doppler anemometry showed that the magnetic



Fig. 3. Schematic representation of the interplay of the natural convection and the MHD effect (B field parallel to the current lines).

field induced convection in the whole cell [22]. Therefore, to understand the above results at least qualitatively one must take into consideration the flow profile in whole cell and especially the role of natural convection. Natural convection occurs in unstirred solutions as a consequence of density gradients (Figs. 2 and 3, $\rho_{\text{bulk}} > \rho_{\text{N}}$) which arise because the solution in front of the electrode (Nernst layer, density $\rho_{\rm N}$) is depleted from the electro-active species. As a consequence volume elements with a higher density are pushed from the bulk and move upwards in front of the electrode. The result is a convective flow in the Nernst layer pointing upwards. In Figs. 2 and 3 this flow is indicated with the force vectors $F_{\rm C}(y)$. The magnitude of the force increases in the upward direction (positive y-axis), as the density of the volume elements decreases on their way up (depletion of electro-active species). Thus, under the condition of natural convection the current has a component in the y-direction. A perpendicular B field will now induce a Lorentz force with two components, F_{L} and $F_{C,L}$. The component $F_{\rm L}$ is due to the deposition current *i* pointing towards the electrode. Its direction will be in the negative (down, Fig. 2a) or positive (up, Fig. 2c) y-direction, depending on the orientation of B (right hand rule). Furthermore, there will be a component $F_{C,L}$ coming from the Lorentz force acting on the convectional flow. This component will be directed towards (Fig. 2b) or away from (Fig. 2d) the electrode.

The model outlined above can explain the results for a perpendicular *B* field shown in Table 1. For the configuration Fig. 2a $F_{C,L}$ has the same direction as the deposition current and will thus lead to a enhanced transport of electro-active species towards the electrode. For the configuration Fig. 2c $F_{C,L}$ points away from the electrode and should reduce the limiting current density. Increasing the vertical dimension of the WE from A_1 to A_2 increases F_C and the resulting effects on i_L . Thus i_L increases by 7% in the configuration Fig. 2a when going from A_1 to A_2 whereas i_L decreases by 3% in the configuration Fig. 2c (Table 1).

In the case of a parallel *B* field (Fig. 3) the interaction of natural convection and the Lorentz force leads to a rotational flow in front of the electrode [8,13]. Reversing the direction of the B field changes the sense of rotation (Fig. 3c and f) and one would expect the same current increase for both configurations. It has been proposed that the current increase in parallel configurations comes from the a gradient of the magnetic susceptibility (see Section 1). The magnetic susceptibility χ of the Nernst layer will be lower than in the bulk because it is depleted from the paramagnetic ion Cu^{2+} . This gradient of χ leads to paramagnetic forces and can explain the influence of parallel B fields in general. However, it cannot explain the difference between the configuration Fig. 3a and c, because the χ gradient effects are proportional to B^2 and thus independent on the direction of B [9]. Thus, the detailed mechanism of the current increase in the parallel B field remains an open question.

Table 2

Relative increase of the limiting current density and the amounts of fine
and coarse grained material during Ni depositions as a function of the
applied magnetic field

<i>B</i> (T)	Current increase (%)	Relative amount of fine grained material (%)	Relative amount of coarse grained material (%)
0	_	64	36
0.5	10	73	27
1	21	77	23

4. Nickel depositions and strippings

For all Ni experiments the following sequence of potentiostatic steps was used: 30 s at $E_1 = -550 \text{ mV}$, 70 s at $E_2 =$ -1300 mV, 80 s at $E_3 = 200 \text{ mV}$, 150 s at $E_4 = 1000 \text{ mV}$. At E_1 only oxygen reduction occurs. At E_2 the limiting current density for the Ni deposition was reached after 70 s. The stripping potentials E_3 and E_4 were chosen according to a paper of Dahms and Schumacher [23]. They found that dissolution of dendrites and fine grained material occurs at E_3 whereas at E_4 the coarse grained material dissolves. Thus, the two step stripping procedure should allow to quantify the amounts of coarse and fine grained material, respectively. Under the influence of a perpendicular magnetic field the cathodic limiting current density increased (see Table 2). This can be explained with a MHD effect, as discussed above, and is in agreement with literature [24]. As the nickel deposition current is accompanied by a hydrogen reduction current we will not discuss the current increase quantitatively. The focus of the Ni experiments is on structural effects.

In the presence of a B field the first stripping peak decreased, whereas the second increased (Fig. 4). Integration of the stripping peaks revealed a reduction of the mean grain size with increasing B field (Table 2). It was reported by several authors, that the surface roughness of Ni deposits decreases if an external B field is applied during



Fig. 4. Current transients for the deposition and the stripping of Ni films at a Pt mini electrode in a Watts electrolyte (details see text). (--) B = 0 T, (--) B = 1.0 T.

electrodeposition [25–27]. However, care must be taken when comparing our results with these results, because there must be no direct relation between surface morphology and grain size. Nevertheless, our results show that there is a clear dependence of the structure of the electrodeposited nickel and the external *B* field. A first tentative explanation can be based on the theory of electrodeposition, which states that the crystal size of many metals decreases as the deposition rate increases [28]. Thus, the *B* field effect on the morphology of electrodeposits would be induced indirectly by paramagnetic and Lorentz forces. A similar result has been found in the case of nickel deposits from a Watts bath containing 2-butyne-1,4-diol as an organic inhibitor [3].

5. Homogeneous redox reactions

The system $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ is often used as a model system to study the influence of *B* fields on homogeneous redox reactions. However, our experiments with this system suffered from a poor reproducibility (results not shown). The reason for this seems to be the formation of insoluble precipitates (prussian blue), leading to a poisoning of the electrode [29]. The redox couple $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ in aqueous solution is described as a reversible system with a long term stability of several weeks [30].

UMEs were used because they show higher limiting current densities than macroscopic electrodes and thus a larger Tafel region. Furthermore, a steady-state is reached within seconds and natural convection plays a minor role.

The cyclic voltammogram recorded at a UMEs with a diameter of 50 μ m showed the typical shape for a hemispherical diffusion profile (Fig. 5, dashed line). In the presence of a perpendicular magnetic field, both the cathodic and the anodic limiting current density increased (Fig. 5, solid line) which is a typical consequence of the MHD effect. As the



Fig. 5. Cyclic voltammogram (10 mV/s) of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ redox couple at a 50 μ m diameter micro electrode. 0.1 M NaCl, 2 mM K₂[IrCl₆], (--) B = 0 T, (--) B = 0 T, (--) B = 0 T.



Fig. 6. Relative increase of the limiting current densities of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ redox couple at a two similar 50 µm diameter micro electrodes (0.1 M NaCl, 2 mM K₂[IrCl₆]). (\Box) Electrode 1, (\bigcirc) electrode 2. $A_1 \approx 1.4A_2$.

electrolyte contained only the oxidised species, $[IrCl_6]^{2-}$ the following discussion will focus on the reduction wave. The power laws suggested by Eqs. (1) and (2) were tested by plotting $i_{\rm L}$ - $i_{\rm L,0}$ versus $B^{1/3}$ for two similar UMEs (Fig. 6). The absolute values of the limiting currents indicated that the ratio of the areas of the two UMEs was ca. 1.4. The slopes of the regression lines are $(5.7\pm0.9) \times 10^{-5}$ A cm⁻² T^{-1/3}, and $(8\pm2)\times10^{-5}$ A cm⁻² T^{-1/3} for the somewhat smaller UME. The larger slope for the smaller UME is in accordance with Eq. (2) which implies higher values of $i_{\rm L}$ with decreasing area. Using $A = 1.96 \times 10^{-5} \text{ cm}^2$, $D = 6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 0.01 \,\mathrm{cm}^2 \,\mathrm{s}^{-1}$, and $c = 2 \times 10^{-6} \,\mathrm{mol} \,\mathrm{cm}^{-3}$ one obtains a theoretical value of 3×10^{-4} A cm⁻² T^{-1/3} (Eq. (2)) which is one order of magnitude larger than the experimental values. The reason for this deviation is not clear at the moment. However, it must be borne in mind that Eq. (2) was obtained by fitting experimental data from a variety of electrochemical systems to an empirical power law. Furthermore, the area of the working electrode was in the range of mm² (millielectrodes) and as a consequence the diffusion profiles were planar. The diffusion profiles of the UMEs employed here will be mainly hemispherical (at least after some seconds) [31]. As a consequence the diffusion limited current will have components parallel to B field and the net Lorentz force density should be smaller. Again it must be stated that a profound theoretical treatment of the MHD effect must be based on a set of coupled differential equations, Fick's second law of diffusion and a modified form of the Navier-Stokes equation taking into account magnetic field effects [5].

From Tafel plots (not shown) the exchange current density of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ redox couple in 2 mM solution was estimated to 0.1 mA cm⁻² which is ca. 15% of the limiting current density. Therefore, if one uses small overpotentials this system seems to be a promising candidate for a systematic investigation of the influence of a *B* field on the charge transfer kinetics.

6. Summary and conclusions

The increase of the limiting current density for Cu depositions from a cell with large A/V ratios in the presence of a perpendicular magnetic field has been explained by the interplay of natural convection and the Lorentz forces acting on the resulting flow profiles. A strong influence of a parallel magnetic field has been found, the mechanism still being unclear. Future work will aim at the experimental determination of the flow profiles in the cell.

In the case of Ni depositions from a Watts potentiostatic stripping transients indicate an influence on the grain size of the deposits, with a tendency to form more fine grained material in the presence of the B field. These structural effects of the B fields have been explained with an MHD effect, too.

Experiments at UME's with the homogeneous redox system $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ show qualitative agreement with recent semi-empirical relationships describing the dependence of i_L on *B*. The deviations have been explained with the differences in the diffusion profiles at the UMEs and the millielectrodes for which the relationships were developed.

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