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Shorter Communication

Lorentz force influence on momentum and mass transfer in natural convection copper electrolysis

Tom Weier*, Jürgen Hüller, Gunter Gerbeth, Frank-Peter Weiss

Forschungszentrum Rossendorf, P.O. Box 51 01 19, 01314 Dresden, Germany

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Abstract

The influence of Lorentz forces generated by faradaic currents and magnetic fields from permanent magnets on the momentum and mass transfer in natural convection copper electrolysis is discussed. Flow field measurements and visualizations of the concentration distribution are given and related to measured mean current densities. Flow structure as well as mass transfer depend strongly on the direction of the Lorentz force relative to that of natural convection.

Keywords: Electrochemistry; Fluid mechanics; Mass transfer; Momentum transfer; Magnetic field; Convection control

1. Introduction

The influence of magnetic fields on electrochemical reactions has been the subject of many investigations. For a recent comprehensive review see Fahidy (1999). Besides the controversely discussed magnetic field effects on material properties and electrode reaction kinetics, the influence of the Lorentz force on momentum and mass transfer is a major and well-recognized effect. Despite this, attempts to link direct flow measurements to observed mass transfer modifications are somewhat scarce. As well, scaling laws to estimate possible gains in space-time-yield for real processes under limiting current conditions are not yet available. This short communication does not aim to bridge these gaps completely, but attempts to demonstrate the multitude of flow configurations attainable by the application of simple permanent magnets to an electrochemical cell.

An electromagnetic body force, the Lorentz force, results from the vector product of current density $\boldsymbol{j}$ and magnetic induction $\boldsymbol{B}$

$$\boldsymbol{F} = \boldsymbol{j} \times \boldsymbol{B}. \tag{1}$$

Under the conditions of common electrochemical processes, the current density is determined solely by the faradaic current to a very good approximation. In our case the current density

$$\boldsymbol{j} = \sigma(\boldsymbol{E} + \boldsymbol{u} \times \boldsymbol{B}) - nN_F D\nabla c \tag{2}$$

with $\boldsymbol{E}$ denoting the electric field and σ the electrical conductivity, contains the term $(\boldsymbol{u} \times \boldsymbol{B})$ accounting for potential differences caused by the motion in a magnetic field. However, the currents thus induced are very small in magnetic fields of moderate strength ($\sim 1\,\mathrm{T}$) compared to the faradaic current. The Lorentz force acts as a momentum source for the flow in the cell. The rightmost term in Eq. (2) accounts for the charge transport by diffusion in concentration gradients ∇c of the electroactive species. D denotes the diffusion coefficient of the electroactive species, n its charge number and N_F the Faraday constant. Charge transport by diffusion becomes important in case of concentration gradients which typically evolve at electrodes and may lead to a limitation of the current by mass transfer. Details on the derivation are given in Newman (1991) while Olivas et al. (2004)

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* Corresponding author. Tel.: +49-351-260-2226; fax: +49-351-260-2007.

E-mail address: T.Weier@fz-rossendorf.de (T. Weier).

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discuss this subject related to Lorentz force effects in electroplating.

As the current density is an inherent feature of electrochemical processes, only a suitable magnetic field has to be added to generate a Lorentz force. In economic terms, no running costs are added to the process, provided the magnetic field originates from permanent magnets. This is a more comfortable situation than that faced, e.g., in electromagnetic flow control for naval applications where the electrical currents have to be added (see Weier et al., 2003).

2. Experimental setup

A small electrolytic cell with inner dimensions as given in Fig. 1 was made from PMMA. The side walls forming the electrodes consist of 0.5 mm thick copper plates. These copper plates are reinforced with PMMA frames which allow at the same time to fix permanent magnets behind the electrodes. Neodymium–iron–boron (NdFeB) permanent magnets 30 mm × 10 mm wide in *x* and *y*-direction and 6 mm extension in *z*, i.e. the magnetization direction, are used to provide a static magnetic field mainly oriented in *z*-direction. Its measured decay with increasing distance from the electrode surface is given in the right part of Fig. 1. In all experiments, the lower edge of the magnets coincided with the lower edge of the cell. From Eq. (1) it follows that a current density in *y*-direction and a magnetic induction in *z*-direction will generate a Lorentz force with an *x*-component F_L only. The direction of this Lorentz force (upwards or downwards) depends on the electrical current and the orientation of the magnet as sketched in the left part of Fig. 1.

The chemical reaction under investigation was $Cu^{2+} + 2e^- \rightleftharpoons Cu$. Three different concentrations of $CuSO_4$ (0.1, 0.2 and 0.375 mol/l) in an aqueous 1.5 mol/l H_2SO_4 solution have been used during the experiments. Copper electrodeposition at the working electrode was carried out via an EG&G Instruments Princeton Applied Research Potentiostat Model Versastat. For all concentrations, linear sweep voltammograms have been recorded to determine electrode potentials for limiting current conditions. A working electrode potential of −400 mV versus Pt_{RE} has been found sufficient to guarantee limiting current conditions for copper deposition under all concentrations and field configurations used. The experiments were performed at room temperature. Chronoamperometry was applied to compare different Lorentz force configurations. A Pt wire quasi reference electrode has been used in order to minimize disturbances of the flow.

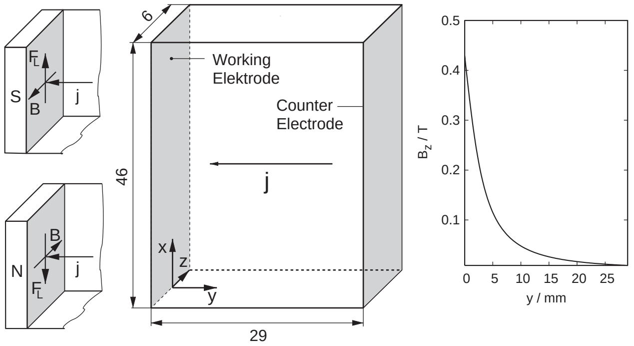

Fig. 1. Sketch of the electrolytic cell and the field configurations near the electrode (left). Decay of B_z with the distance from the electrode (right).

Qualitative information on the concentration distribution in the cell was obtained by a shadowgraph technique. It visualises the second spatial derivative of the density. Velocity fields in the *x*–*y*-plane were measured using a simple digital particle image velocimetry (DPIV).

3. Results and discussion

Fig. 2 shows the response of the cell current for a 0.1 M $CuSO_4$ solution to a potential step from the rest potential to −400 mV versus Pt_{RE} at the working electrode. The copper deposition caused by the potential change leads to a decrease of the Cu^{2+} concentration near the working electrode. This diminishes the density of the near-wall solution and leads to an upwards (positive *x*-direction) directed natural convection. Correspondingly, copper dissolves at the counterelectrode, leading to a denser solution and a downwards directed natural convection there. After a certain time, steady-state limiting current conditions are reached. Without the permanent magnet, this is the case ca. 50 s after the potential step with $j_{\mathrm{lim}} = 42.4\,\mathrm{Am}^{-2}$.

Under action of a downwards directed Lorentz force a steady state is reached after approximately the same time, but low frequency current fluctuations are still present. The limiting current density is increased to $j_{\mathrm{lim}} \approx 53.4\,\mathrm{Am}^{-2}$ due to the additional convection caused by the momentum input. Turning the permanent magnet by 180° around the *x*-axis leads to an upwards directed Lorentz force near the electrode. Under these conditions, the current density passes through a local minimum at $t \approx 25, \ldots, 60\,\mathrm{s}$ with $j_{\mathrm{lim}} \approx 62.8\,\mathrm{Am}^{-2}$ and reaches a steady state only after 130 s with $j_{\mathrm{lim}} \approx 69.4\,\mathrm{Am}^{-2}$. The minimum in the current density corresponds to a minimum of the measured *x*-component of the mean velocity ($\bar{u}$) in the near-electrode region. The values of $\bar{u}$ were obtained by averaging over five points in *y*-direction ($y = 2.7, \ldots, 5.5\,\mathrm{mm}$), and are plotted versus the electrode height in Fig. 2 (right). Note that the DPIV measurements do not cover the whole cell height. The largest velocities are found at the beginning of the measurement since the diffusion layer just starts to develop and current densities are much larger than under mass transport limitation. Therefore the Lorentz force has their highest magnitude for $t = 0$. With increasing diffusion layer thickness, current densities decrease and so does the Lorentz force, thus convection slows down ($t = 50\,\mathrm{s}$). However, steady-state current densities are slightly higher inducing again larger velocities ($t = 150\,\mathrm{s}$).

Fig. 3 shows shadowgraph images for three different $CuSO_4$ concentrations and a downwards directed Lorentz