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Applications of magnetoelectrolysis

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A broad overview of research on the effects of imposed magnetic fields on electrolytic processes is given. As well as modelling of mass transfer in magnetoelectrolytic cells, the effect of magnetic fields on reaction kinetics is discussed. Interactions of an imposed magnetic field with cathodic crystallization and anodic dissolution behaviour of metals are also treated. These topics are described from a practical point of view.

Nomenclature

a_1, a_2	regression parameters (–)
$\boldsymbol{B}$	magnetic field flux density vector (T)
c	concentration ($\mathrm{mol\,m^{-3}}$)
c_∞	bulk concentration ($\mathrm{mol\,m^{-3}}$)
D	diffusion coefficient ($\mathrm{m^2\,s^{-1}}$)
d_e	diameter of rotating disc electrode (m)
$\boldsymbol{E}$	electric field strength vector ($\mathrm{V\,m^{-1}}$)
$\boldsymbol{E}_i$	induced electric field strength vector ($\mathrm{V\,m^{-1}}$)
$\boldsymbol{E}_s$	electrostatic field strength vector ($\mathrm{V\,m^{-1}}$)
$\boldsymbol{F}$	force vector (N)
F	Faraday constant ($\mathrm{C\,mol^{-1}}$)
$\boldsymbol{H}$	magnetic field strength vector ($\mathrm{A\,m^{-1}}$)
i	current density ($\mathrm{A\,m^{-2}}$)
i_L	limiting current density ($\mathrm{A\,m^{-2}}$)
i_L^0	limiting current density without applied magnetic field ($\mathrm{A\,m^{-2}}$)
I	current (A)
I_L	limiting current (A)
$\boldsymbol{j}$	current density vector ($\mathrm{A\,m^{-2}}$)
K	reaction equilibrium constant
k	reaction velocity constant
k_b	Boltzmann constant ($\mathrm{J\,K^{-1}}$)
m_1, m_2	regression parameters (–)
n	charge transfer number (–)
q	charge on a particle (C)
R	gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	temperature (K)
t	time (s)
V	electrostatic potential (V)
$\boldsymbol{v}$	particle velocity vector ($\mathrm{m\,s^{-1}}$)

Greek symbols

α	transfer coefficient (–)
γ	velocity gradient ($\mathrm{s^{-1}}$)
Δ_{MS}	potential difference between metal phase and point just inside electrolyte phase (OHP) (V)
δ	diffusion layer thickness (m)
δ_0	hydrodynamic boundary layer thickness without applied magnetic field (m)
ρ	density ($\mathrm{kg\,m^{-3}}$)
σ	electrolyte conductivity ($\Omega^{-1}\,\mathrm{m^{-1}}$)
μ	magnetic permeability ($\mathrm{V\,s\,A^{-1}\,m^{-1}}$)
ν	kinematic viscosity ($\mathrm{m^2\,s^{-1}}$)
ω	vorticity

1. Introduction

The practical relevance of the application of magnetic fields in electrochemical processes is potentially large. Improved mass transfer in cells, better deposit quality and control of corrosion are just some of the effects that can be promoted. In addition, magnetic fields are powerful scientific tools in, for instance, reaction kinetics and metal deposition or dissolution studies. A review paper by Fahidy [1] appeared in 1983 and since then research has continued and progressed in the field, while its scope is broadening. This review summarizes results obtained on magnetoelectrolytic processes and emphasizes practically relevant aspects in four main areas of interest: mass transport, reaction kinetics, cathodic metal deposition and anodic metal dissolution.

2. Mass transport effects

2.1. *Magnetohydrodynamic phenomena*

Magnetohydrodynamic phenomena arise from the interaction of velocity fields with electromagnetic fields. The total force on a charged particle (electron, ion) moving in an electromagnetic field is the Lorentz force [2]:

$$\boldsymbol{F} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) \qquad (1)$$

where $\boldsymbol{E}$ is the sum of the electric and electrostatic fields $\boldsymbol{E}_i + \boldsymbol{E}_s$. Since the Lorentz force is capable of producing movement of charged particles such as ions, a magnetic field applied during electrolysis gives rise to convection of the electrolyte. This magnetohydrodynamic effect not only influences mass transfer, but also reaction kinetics and deposit quality. Orientating and attracting ions can only be achieved by using large $\boldsymbol{B}$-gradient fields, because these communicate a potential energy larger than the ionic thermal kinetic energy ($k_bT \approx 0.025\,\text{eV}$ at room temperature) [3].

In magnetohydrodynamics, the vector and scalar $\boldsymbol{v}$ and $\boldsymbol{B}$ fields are the most important variables; $\boldsymbol{j}$ and $\boldsymbol{E}$ can be deduced from these. Fundamental equations in magnetohydrodynamics are as follows [2]:

$$\boldsymbol{j} = \sigma(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) \tag{2}$$

$$\text{curl}\,\frac{\boldsymbol{B}}{\mu} = \boldsymbol{j} \tag{3}$$

$$-\frac{\partial \rho}{\partial t} = \text{div}\,(\rho \boldsymbol{v}) \tag{4}$$

$$\rho\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v}\cdot\text{grad})\boldsymbol{v} + \text{grad}\,p = \boldsymbol{j} \times \boldsymbol{B} + \rho\nu\nabla^2\boldsymbol{v} + \rho\boldsymbol{F} \tag{5}$$

$$\boldsymbol{E}\cdot\boldsymbol{j} = \frac{\boldsymbol{j}^2}{\sigma} - \boldsymbol{j}\cdot(\boldsymbol{v} \times \boldsymbol{B}) \tag{6}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\omega}{\rho}\right) - \frac{\omega}{\rho}\cdot\text{grad}\,\boldsymbol{v} = \frac{1}{\rho}\text{curl}\left(\frac{\boldsymbol{j}\times\boldsymbol{B}}{\rho}\right) \tag{7}$$

$$\boldsymbol{j} \times \boldsymbol{B} = (\boldsymbol{B}\cdot\text{grad})\frac{\boldsymbol{B}}{\mu} - \text{grad}\frac{\boldsymbol{B}^2}{2\mu} \tag{8}$$

Given sufficient boundary conditions, a rigorous magnetoelectrolytic mass transport model based on the above magnetohydrodynamic equations may in theory be solved. In practice, however, simplified models [1, 4] and empirical relations have been deduced.

2.2. *Empirical results on magnetoelectrolytic mass transport*

The effect of applying a magnetic field during electrolysis is strongest when mass transport is the controlling mode (limiting current conditions), because of interactions of the field with the convective diffusion layer at the electrodes. Using laser interferometry techniques, this effect can be made visible [5]. The relative strength of this effect is strongly dependent on the mutual positions of the electrodes and the direction of the magnetic and gravity fields. In certain configurations (magnetic and electric fields parallel), mass transport can even be retarded [6].

Quraishi *et al.* [7] described the magnetic field effects on natural convective mass transport with regards to the position (inclination) of circular disc electrodes. The magnetic field was directed parallel to the gravity field. It was clear that mass transport was enhanced more when the electrodes were slightly inclined to the horizontal, than to the vertical plane. Ismail *et al.* [8] studied inclined plate electrodes in a solenoidal field and found an optimal inclination angle of 14° to the vertical.

When the magnetic field is not strong enough to interact significantly with the structure of the convective diffusion layer the magnetic field superposition may be represented as a 'MHD-perturbation' model, where the conventional convective diffusion equations are modified by small order contributions from MHD phenomena [1]. For the specific case of a vertical electrode in a weak or moderate (up to 1 tesla) magnetic field being horizontal and perpendicular to the electrode, the rate of mass transport is proportional (based on free convective diffusion theory) to $B^{1/4}$ [9, 10].

When the magnetic field is vertical and parallel to vertical plate electrodes, the strongly enhancing effect of magnetic field superposition cannot be predicted by a simple 'MHD-perturbation' model [11]. For this case, and low and moderate fields (up to 0.685 T), Fahidy [4] made an attempt to model the magnetic field effect. Analysing experimental data on copper deposition, where limiting current density increased from 20 to 25.6 A m^{-2} on increasing a magnetic field from 0 to 0.685 T, he proposed the interrelationship between limiting current density, i_L, and magnetic field flux density, $\boldsymbol{B}$, for electrodes consisting of nonmagnetic material and where $\boldsymbol{B}$ is parallel to the cathode surface to be

$$i_L = i_L^0 + a_1 B^{m_1} \tag{9}$$

where i_L^0 is the limiting current density without applied magnetic field. Using this equation, for copper deposition: $i_L = 20\,\text{A m}^{-2}$, $a_1 = 10.916$ and $m_1 = 1.6435$ was determined. By comparing the experimental data on limiting current densities and magnetic field strength with various mass transfer models, Fahidy estimated the magnitude of the corresponding diffusion layer thickness δ, and proposed the following equation:

$$\delta = \delta^0 - a_2 B^{m_2} \tag{10}$$

where δ^0 is the hydrodynamic boundary layer thickness without applied magnetic field.

Chopart *et al.* [12] showed for copper magnetoelectrolysis that a magnetic field induces a magnetohydrodynamic velocity gradient, γ, at a rotating disc electrode, which corresponds to

$$I_1 = 0.678 F D^{2/3} c_\infty d^{5/3} \gamma^{1/3} \tag{11}$$

Aaboubi *et al.* [13] showed that:

$$\gamma = kBc_\infty \tag{12}$$

Thus, the limiting current I_L is proportional to $B^{1/3}c_\infty^{4/3}$.

The beneficial effect of coupled electric/magnetic fields is more manifest in multiple electrode cells where enhancement in mass transport can be much larger relative to single pair electrode cells. In experiments in a multiple electrode cell by Mohanta *et al.* [14], a rigorous quantitative analysis of mass transport phenomena was hindered by the absence of limiting current conditions at even weak magnetic fields. Cathodic current densities at room temperature ranged 3–4 times higher than the advisable limit for current densities in industrial copper-refining practice at high temperature. The use of nonuniform magnetic fields, such as solenoidal fields, which can be created by winding current carrying wires around the electrolysis cell, can increase mass transport to an even greater extent [8, 11, 15]. Experimental results [15] show that comparable relative mass transport rates can be achieved in nonuniform fields whose average strength is about one tenth of the uniform field strength otherwise required.

A remark should be made regarding the empirical relationships mentioned. Fahidy [16] demonstrated the statistical indeterminacy of mass transfer dependence on magnetic flux density $\boldsymbol{B}$. Various statistically justified B-exponent dependencies can be obtained when correlating the same set of experimental magnetic flux density/mass transfer data. Correct distinctive modelling requires data measured over a large B-value interval.

Finally, adverse effects of magnetohydrodynamically induced convection have also been reported. Electromagnetic fields present in large aluminium reduction cells can cause unwanted motion of the molten salt electrolyte [17].

2.3. *Magnetoelectrolytic codeposition of metals and inert particles*

Composite materials can be produced by codeposition techniques: inert particles, for instance, may be embedded in a cathodically depositing metal matrix. Dash [18] describes the use of a magnetic field to produce codeposits, e.g. Cu/Al_2O_3. The combination of magnetohydrodynamic forces working on both electrolyte ions and Al_2O_3-particles due to their surface charge, make it possible to codeposit particles which cannot be deposited using conventional techniques. This change in codeposition behaviour can however also be attributed to a magnetically induced change in the structure of the adsorbed ionic layer on the particles [19].

In two Japanese patents, a new method for composite electrodeposition is claimed [20, 21]. Inert particles were first coated with a ferromagnetic material (e.g. WC or Al_2O_3 coated electrolessly with nickel) and consequently codeposited in an electrolytic cell applying a nonuniform magnetic field. Codeposition can be controlled by regulating the magnetic field strength.

3. Kinetic effects

The effects of a magnetic field applied during polymerization [22], photochemical [23], isotopic enrichment [24] and heterogeneous catalytic [25] reactions have been investigated to some extent. Very recently, the magnetic field effect on organic chiral reactions has received much attention [26]. It has been concluded that the electronic structure of reaction molecules and intermediates is determining for the interaction with the field. Changes in reaction entropy have been observed.

Only a few papers deal with the effect of a magnetic field on the kinetics of electrochemical electron transfer reactions at electrode surfaces. Kinetic effects can be modelled by defining a magnetically induced potential difference [27–29]. Kelly [28] uses Butler–Volmer kinetics to describe this, and has analysed the total anodic and cathodic polarization in a cell consisting of two titanium electrodes in a flowing H_2SO_4-electrolyte. The effect of the induced potential difference on current density can be written as (for a purely activation controlled reduction reaction):

$$i = kFc_\infty \exp\left(\frac{-\alpha nF\Delta_{MS}}{RT}\right) \tag{13}$$

where Δ_{MS} = potential difference between metal phase and a point just inside the electrolyte phase (OHP). Consequently, when Δ_{MS} at the electrode/flowing electrolyte interface is changed, the rate of electron transfer is changed. This effect was most elegantly applied by Iwakura *et al.* [30], who developed a cell rotating in a field created by a permanent magnet. The induced potential difference between cathode and anode caused electrochemical reactions to proceed. In this way, direct conversion of mechanical energy to chemical energy is possible, using e.g. wind energy as a power source for rotating the cell.

Transfer coefficients can be determined more accurately applying a magnetic field, because of an increase in the potential range where Tafel's rule is obeyed, due to magnetohydrodynamic effects. In the $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu$ system, transfer coefficients α are not modified when a magnetic field is applied [12, 31]. Olivier *et al.* [32] and Ismail *et al.* [33] also studied copper deposition, and both suggested a kinetic effect when applying a magnetic field, but did not make an attempt to quantify it. Fricoteaux *et al.* [31] showed, by using radiotracers, that a magnetic field induces no detectable modification of the exchange current at the Cu^{2+}/Cu-interface. According to this study, the variation in the exchange current obtained by electrochemical methods is due to modifications of the structural state of the deposit. Chiba *et al.* [34] and Yamashita *et al.* [35] found that a magnetic field had no effect on the rate-determining step in copper deposition, but did increase the charge-transfer current and the efficiency of the deposition process. In contrast, the rate-determining step of *p*-benzoquinone reduction in acetonitrile shifts from mass to electron transfer when a strong magnetic field is applied [36]. The shift is promoted by the low viscosity of the solvent.

Chiba *et al.* [37] observed an increase in zinc deposition efficiency applying a magnetic field; this effect is believed to be due to a decrease of the hydration number of Zn-ions on increasing field strength, which decreases the deposition reaction activation energy thus resulting in an increasing reaction velocity.

Danilyuk *et al.* [38] proposed a model for reaction kinetic effects while applying a magnetic field during copper, nickel and tin deposition, which may account for the contradictory literature on this phenomenon. Danilyuk *et al.* observed that, in the regions of mixed (mass transport and charge transfer) and pure charge transfer kinetics, the magnetic field at a fixed current density generates oscillations in the cathode potential. Depending on the value of the field strength, the electrodeposition process is either inhibited or accelerated. Danilyuk *et al.* proposed this phenomenon as arising from quantum mechanical type interactions of the magnetic field on the conversion of the spin states of the three particles that interact in chemisorption at the cathode surface: an hydrated ion, an adsorption centre and an unpaired conduction electron. Similar current oscillations in regions of mixed control have been observed during potentiostatic anodic dissolution of copper (Section 5).

4. Cathodic deposit morphology effects

Applying a magnetic field during electroplating changes the crystallization behaviour of the metal from the electrolyte. Under carefully chosen conditions the following effects can be promoted: (i) a more uniform deposit morphology (microscopic as well as macroscopic) [27, 31, 33, 39, 40–43], (ii) inhibition of dendrite growth [37, 44], (iii) change in macrostress of the deposit [45], (iv) increased hardness of the deposit [29, 41, 46], (v) a more uniform current distribution [47, 48], (vi) increased corrosion resistance [28, 29] and (vii) composition shift in alloy plating [46].

The influence of magnetic fields on crystallization behaviour appears most strongly at low current densities, where it can be considered that the influence of the magnetic field is larger than that of the electric field. Chiba *et al.* used X-ray analysis to prove this for nickel [41]. In contradiction, Yang [49] observed that the presence of a magnetic field of 0.54 T, either parallel or perpendicular to the cathode, had no effect on the types of crystal orientation in Fe, Ni and Co deposits. However, Yang did observe macroscopic effects: when the field was perpendicular to the cathode, the surface of the deposit became very rough and covered with projections protruding in the direction of the field. The morphology of Cu–Ni alloy was studied by Chiba *et al.* [41], using scanning electron microscopy (SEM). The presence of a magnetic field enhanced the preferred growth direction, indicating a cored or cereal-type structure, i.e. Cu-rich and Ni-rich strata in the solid solution matrix. Contradictory observations on crystal growth may be explained using Danilyuk's theory [38]: certain values of the magnetic field influence the deposition reaction markedly, others do not have any influence.

O'Brien and Santhanam [39] reported remarkably uniform zinc deposits in the cathode over anode position in the electrolysis of $ZnSO_4$, while pulsing the current in a magnetic field. Growth of dendrites when depositing zinc from alkaline zincate baths was inhibited by a magnetic field [37]. There seemed to be only a weak dependence on the type of cathode material and the direction of the field. Chiba *et al.* [44] also reported inhibition of dendrite growth when applying a weak magnetic field (0.12 T) during Pb-deposition.

Copper screens can be deposited on stainless steel cathodes while electrolysing aqueous $CuSO_4$ solutions in a magnetic field [50]. Simultaneous hydronium-ion discharge and subsequent hydrogen gas evolution on the cathode surface are primarily responsible for the particular phenomenon of a screen-type deposit structure, whose characteristics are strongly influenced by the magnetic field. Initially, copper is deposited only parallel to the magnetic field. Thereafter cross-deposits appear. Eventually a closely woven deposition structure appears. During the manufacturing of magnetic wire, a thin film of magnetic alloy with uniaxial magnetic anisotropy is obtained by passing a direct current through the fine wire itself, which serves as a cathode during electrodeposition, to form a magnetic field in the direction of the circumference of the strand [27].

5. Anodic effects

Dash [40] was one of the first to determine the beneficial effect of a magnetic field during anodic dissolution of metals. For copper, it was observed that when no magnetic field was applied, preferential thinning of a (partially immersed) anode took place at the air/electrolyte interface. When a magnetic field of 0.9 T was applied, uniform thinning at one side of the anode was observed; when the magnetic field was reversed, thinning took place at the opposite side. In this way, periodic reversal of the field led to uniform dissolution without preferential cracking at the air/electrolyte interface.

The anodic dissolution of copper anodes in acidic electrolytes and in neutral ones to which specific additives, e.g. thiocyanate ions [51], have been added exhibits current oscillations at constant potential conditions. Oscillations are observed in the transition zone between the charge-transfer and fully mass transfer potential regions, and appear after a certain induction period during which the initially deposit-free anode becomes covered with cuprous and cupric oxides. At the onset of oscillations, the surface is fully covered with oxides.

Applying a magnetic field is a powerful tool to study and even stop this oscillatory behaviour. Gu *et al.* [52] showed that during the induction period the rate of copper oxide formation is proportional to $B^{-1/4}$. As a result of the field, the total induction time until oscillations start increases [53]. The oscillations are destabilized due to mass transport or kinetic interactions [54, 55], and a shift to more positive potentials is observed [50]. Under specific conditions, the field can suppress the oscillations completely. Thus, application of a magnetic field can be used to control oxide-based corrosion of copper, and possibly of other metals.

6. Concluding remarks

A magnetic field can be introduced in electrochemical cells as an extra variable that influences many in-cell processes. Mass transfer effects are well understood and practically relevant, yet difficult to model. Interactions of magnetic fields with metal crystallization behaviour also leads to practically interesting results. Studies of electron transfer and, particularly, corrosion in magnetic fields have produced new, and sometimes controversial, insights. Applications can be foreseen. The broad area of magnetoelectrolytic research is still expanding and progressing.

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