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Magnetoelectrolysis

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The present state of our understanding of the influence of an imposed magnetic field on electrochemical processes is reviewed. In particular, the effects of combined electric/magnetic fields on electrolyte properties, mass transport, electrode kinetics and the quality of electroplated metals is emphasized.

Nomenclature

$\mathbf{B}$	magnetic flux density vector; B_0 magnitude of the imposed magnetic field
c	concentration
D	electrolyte diffusivity
$\mathbf{E}$	electric field vector; E its magnitude
Gr	Grashof number
Ha	Hartmann number
I	electric current
i	electric current density, i_{LFC} limiting value due to forced convection; i_{LNC} limiting value due to natural (free) convection
$\mathbf{j}$	electric current density vector
k	Boltzmann's constant, 1.3805×10^{-23} ($\mathrm{J\,K^{-1}}$)
ΔP	pressure drop along channel
Re	Reynolds number
R_{H}	Hall constant
Sc	Schmidt number
Sh	Sherwood number
T	temperature
t	transference number
$\mathbf{v}$	velocity vector
W	ionic kinetic energy
z	ionic valency
η	electrolyte concentration
μ	ionic mobility
σ	electrolyte conductivity
$\phi_{\mathbf{B},\mathbf{v}}$	inclination angle between velocity vector and magnetic flux density vector

1. Introduction

The decomposition of a chemical compound (or several chemical compounds) by electric current in the presence of an imposed magnetic field is called magnetoelectrolysis. It is a relatively new branch of electrochemical science but it has grown rapidly in recent years and has shown promise for certain practical applications. Since current understanding of the combined effect of electric and magnetic fields on electrolyte behaviour is far from complete, discussion in this paper will be focussed on four major specific aspects of the electric/magnetic field interactions. There has been considerable progress in the elucidation of the magnetic field effect on electrolyte properties, electrolytic mass transport, and to a smaller extent, on electrode kinetics and (cathodic) deposit quality. The purpose of this paper is to review the 'current state of art' in these four areas and to indicate certain directions of growth where future research would bring, at least in the author's opinion, fruitful and practical results. Given this framework, the review does not intend to provide a lexical catalogue of magnetoelectrolytic processes, nor is it a compendium of the subject matter. Its primary aim is to promote the appreciation of magnetoelectrolysis and to foster further interest in it.

2. The effect of magnetic fields on electrolyte properties

The effect of magnetic fields on electrolyte solutions has intrigued numerous researchers since Faraday's pioneering but inconclusive observations [1]; landmarks of pertinent earlier literature have recently been summarized by Olivier [2]. In this

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section a selected number of magnetically induced phenomena will be discussed.

2.1. *The Hall effect and conductivity in magnetic fields*

In the classical theory of particle electrodynamics non-interacting charges of density q moving with velocity $\mathbf{v}$ in an electric field of density $\mathbf{E}$ and a magnetic field of flux density $\mathbf{B}$ under the influence of force density

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

generate a current density $q\mathbf{v}$. If all charge species are considered under equilibrium conditions, then

$$\mathbf{E} = \mathbf{j}/\sigma - R_{\mathrm{H}}(\mathbf{j} \times \mathbf{B}) \qquad (2)$$

where $\mathbf{j}$ is the total current density, σ the electrolyte conductivity and R_{H} is the Hall constant. The second term in Equation 2 represents the electric field due to the Hall effect introduced by the presence of the magnetic field. In an appropriately designed apparatus, potential differences related to the Hall effect may be measured in principle and R_{H} can be obtained. Early experimental studies of the Hall effect [3–13] suffer from lack of refinement in potential measurement and, in some cases, from failing to distinguish the effect of slight temperature and concentration differences. More recent investigations (e.g. [14–18]) covering various electrolyte solutions report potential differences up to several tens of millivolts in constant imposed electric fields, whereas in alternating fields high precision measurements [19–21] have been able to detect potential differences ranging from a few tens of nanovolts to a few microvolts. The alternative-field technique owes its success to the advent of powerful noise-free pre-amplifiers and to the meticulous elimination of parasitic current flows.

Apart from the challenging experimental conditions of its measurement, the Hall effect has further significance in providing an empirical test for the theories of electrolytic conductance in magnetic fields. If h_+ denotes the ratio of the mobility of the positive charge carrier in the magnetic field to the magnitude of same in the absence of the magnetic field, and h_- denotes the same ratio for the negative charge carrier, (also known as ionic Hall numbers) the Hall constant may be rewritten [22] as

$$R_{\mathrm{H}} = \frac{1}{n|e|}(t_+^2 h_+ - t_-^2 h_-) \qquad (3)$$

where t_+ and t_- are the cationic and anionic transference numbers, respectively, n is the charge density and e is the charge of the electron. Elementary theoretical approaches for the estimation of R_{H} have been based on solid-state charge carrier models [23–25]; in more sophisticated attempts an enhanced mobility in magnetic fields [26], the concept of the activation energy for ionic mobility [27], the extent of ionization [28, 29], the concept of mixed ionic and electronic conduction [30], the theory of irreversible thermodynamics [31, 32], kinetic gas theory [33] and the kinetic theory of slightly ionized plasmas [34] have been employed. Using advanced statistical mechanics, Friedmann [35, 36] introduced a Brownian-motion based model of ionic mobility ('brownon' model) where R_{H} is directly proportional, in a first approximation, to the imposed magnetic field strength and inversely proportional to the coefficient of friction between ions and solvent. Intermolecular interaction was considered by Tran-Cong-Kahn [37] in terms of individual solvent–solvent, solute–solute, and solute–solvent contributions to the total potential energy of ions; starting with this approach and a previous model of Pagès–Nelson [33], Olivier [2] has recently formulated the relationship

$$R_{\mathrm{H}} = \frac{\mu_+^2\Gamma_+ - \mu_-^2\Gamma_-}{F\eta_0(\mu_+ + \mu_-)^2} \qquad (4)$$

where η_0 is the electrolyte concentration in the absence of a magnetic field, F is Faraday's constant and μ is the ionic mobilities in the absence of a magnetic field. The characteristics ionic coefficients, Γ, may be computed as

$$\frac{1}{\Gamma} = erf(R) + \frac{4R}{(\pi)^{1/2}}\epsilon^{-R^2}\left(\frac{1}{2} + \frac{R^2}{3}\right);$$

$$R \equiv \frac{W}{kT} \qquad (5)$$

As shown in Table 1 in the case of selected univalent ions, Γ varies between 1 000 and 10 000 at average room temperature; its temperature dependence is not negligible, e.g., in the case of K^+ ions

*Table 1. Numerical values of parameters in Equation 5 for selected univalent ionic species**

Ionic species	$10^{20} \times W$ (J ion^{-1})	R^2 ($T = 297.66$ K)	Γ
OH^-	4.081	9.733	639.7
H^+	4.428	10.561	1312.4
Rb^+	4.714	11.243	2375.5
Cs^+	4.813	11.480	2924.7
K^+	4.935	11.770	3775.9
I^-	5.069	12.090	5010.2
Br^-	5.112	12.192	5486.4
Na^+	5.339	12.733	8866.3
Li^+	5.353	12.767	9138.8

* Computations are based on Table II.B.5, ref. 2.

$\Gamma \simeq 5486$ at 293.16 K and $\Gamma \simeq 3978$ at 302.16 K. Note that in contrast with the earlier employed energy of activation of conduction, whose numerical values are model-dependent, W is the intrinsic kinetic energy of a given ionic species. This is an important refinement for the current theory of the ionic Hall effect.

While numerical agreement between theoretically predicted and experimentally determined values of R_H is generally reasonable, many fundamental questions remain unanswered. One such question is the relationship between ionic Hall numbers and ionic radius. As indicated by Meton and Gerard [22] for univalent cations h_+ is at a minimum for Cs^+ ions ($r_+ = 0.167$ nm; $h_+ = 0.7$) whereas in the case of univalent anions the numerical value of h_- increases monotonically from $h_- = 0.4$ ($r_- = 0.133$ nm) for F^- ions towards unity. While the statistical-mechanic approach by Friedmann permits a conceptually straightforward estimation of the ionic Hall number in terms of energy relaxation time, the variation of h with ionic radius cannot satisfactorily be explained at present by any mechanistic model. Some new light might be thrown on the phenomenon of the Hall effect by considering electrohydrodynamic contributions [38] which result in an approximately one-third reduction of the Lorentz force acting on an ion. Since both viscosity and the dielectric constant vary appreciably in the immediate neighbourhood of an ion [39], it remains to be seen whether models based on continuum mechanics and the concept of uniform viscosity and dielectric constant will effectively improve our current state of understanding and provide better and simpler estimation formulas of Hall numbers.

The foregoing paragraphs illustrate intrinsic difficulties in estimating electrolyte conductivity in a magnetic field: values computed from experimentally induced potential differences depend on their relative orientation to the imposed electric and magnetic fields and theoretical values depend on the model used in computing R_H. According to earlier measurements in constant electric fields (e.g., [23, 37]) the magnetoelectrolytic conductivity is 0.04–0.2 times the conventional conductivity, whereas measurements in alternating fields (e.g., [22]) indicate magnetoelectrolytic conductivity/conventional conductivity ratios of 10^{-9}–10^{-8} order of magnitude. The conceptually easiest interpretation of this complexity is via plasma theory [34, 40] where the (1,1) and (2,2) diagonal elements of the mobility tensor μ:

$$\mu_{11} = \mu_{22} = \frac{q\tau}{m} \cdot \frac{a}{a^2 + \omega_B^2 \tau^2};$$
$$a \equiv 1 + i\omega\tau,\ i \equiv -1 \qquad (6)$$

account for the Hall effect. Here, τ is the ionic 'plasma' time constant, ω is the frequency of the alternating electric field, ω_B is the ionic cyclotron frequency and m is the ionic mass. Ionic Hall constants computed by means of Equation 6 show remarkable closeness to similar values obtained via Friedmann's complicated brownon theory [35, 36]. Such agreements do not mean that the magnetic field effect on electrolyte conductivity is clearly known; the development of a relatively simple theory explaining *all* experimental findings remains a serious challenge to theoretical electrochemists.

2.2. *Thermal effects*

When d.c. current begins to flow in an electrolytic cell placed in a uniform constant magnetic field, the electrolyte reaches a higher temperature level after a transient period. If the sign of the d.c. current is then changed, a net variation in local temperatures can be measured; these variations whose magnitude can be a fraction of a degree, remain symmetrical as the direction of the current is alternated upon reaching steady state (for each alternation). As shown in the comprehensive studies of Tronel-Peyroz [41–43] and Olivier [2] the general trend of this variation of such temperature differences with current (at a fixed value of **B**) is an initial decrease, followed by a monotonic increase past the attainment of a minimum value. Utilizing a fundamental model based on Boltzmann's classical distribution equations, Olivier [2] interprets observed temperature variations in terms of the kinetic energy of ions and the ionic relaxation time. The discrepancy between temperature differences measured with high precision and computed by the model is ascribed to slight changes in the degree of dissociation of water caused by the magnetic field. Accurate estimation of heats of ion transfer in magnetic fields might be one useful application of this approach.

2.3. *Viscosity and diffusivity*

Relatively little information is currently available on the variation of the viscosity and diffusivity of electrolytes with magnetic field strength. At $\mathbf{B} = 1.2$ T, the relative increase of the viscosity of aqueous KCl solutions with respect to the absence of an imposed magnetic field diminishes as the concentration increases [44]; at $c = 0.01$ mol dm^{-3} the relative increase is about 0.25%, dropping gradually to 0.07% at $c = 3$ mol dm^{-3}, at 25° C. At lower values of **B** the relative increase in viscosity is lower [45]. Similar findings have been reported in the case of certain monovalent halides for diffusivity [45, 48], although the direction of change seems to depend on the nature of the cation. At 25° C and 0.5 tesla the relative increase can be as high as 6% (0.01 mol dm^{-3} KCl) or as low as 0.08% (≈ 1.57 mol dm^{-3} HCl). Although the effect on viscosity has been ascribed [44] to the mechanism of molecular rotation and translation, and the effect of diffusivity to the structure of hydration spheres and ions [45], theoretical models based on irreversible thermodynamics [49, 50] fail to predict relative changes of such magnitude. Indeed, it remains to be seen if sufficiently sensitive experimental techniques will be developed within the forseeable future to measure pertinent elements of the diffusivity tensor postulated by irreversible thermodynamics and plasma theory (e.g., [51]). This is an area where painstaking and meticulous research is needed for advancing significantly the current *niveau* of understanding.

3. The effect of magnetic fields on mass transport

In contrast with the weak influence magnetic fields exert on the physical properties of electrolytes, mass transport rates can be significantly altered in electrolytic processes when magnetic fields are externally imposed on the electric field. Experimental data hitherto obtained on bench-scale and pilot-plant scale metal deposition processes indicate that the magnetic field effect is relatively strongest when mass transport is the controlling mode, i.e., in the neighbourhood of the limiting current plateau. The effect of magnetic field superposition may, therefore, be attributed to chiefly magnetohydrodynamic (MHD) phenomena interacting with the structure of the convective diffusion layer at the electrodes. The mathematical analysis of mass transport must inevitably depend on MHD-oriented models, properly combined with the concepts of free-, forced-, and mixed convection in order to establish at least approximate estimation methods of reasonable accuracy. An absolutely rigorous mathematical treatment relying on fundamental electrochemical, transport-phenomena and MHD principles is prohibited by the large number of unknown variables and the development of approximate techniques is the major (if not only) avenue of mathematical analysis.

The mathematical framework based on pertinent fundamental equations of MHD and convective diffusion theory [52, 53] is summarized in Table 2. The rate of mass transport is proportional to the current density; if a single ionic species is involved in the mass transport process, then its current density

$$i_A = \frac{zF}{1-t_A}(\mathbf{v}c_A - D \operatorname{grad} c_A) \quad (7)$$

determines the rate of mass transport under steady state conditions. The rigorous solution of Equation 7 in terms of the entries in Table 2 being impossible, approximate solutions have been actively sought which consider the relative importance of the MHD effect via three model categories:

1. The magnetic field effect is not strong enough to interact significantly with the convective diffusion structure of the system; the magnetic field superposition may be represented by an 'MHD perturbation' model where the (conventional) convective diffusion equations are modified by small-order contributions from MHD phenomena.

2. The magnetic field effect is sufficiently strong to modify significantly the convective diffusion structure and is considered as a forced-convector generator. The model respresents mixed-mode control of free and forced convection.

3. The magnetic field effect is predominant; convection diffusion is regarded as a small 'perturbing' modification in the sense that the flow regime in the convective diffusion layer is considered to be essentially of MHD origin.

The best example for the first category is free convection at planar electrodes, where the MHD effect is considered as a perturbation of the fully developed free-convection process in the absence of a magnetic field. In the specific case of vertical electrodes where the imposed magnetic field is horizontal and perpendicular to the electrodes, the rate of mass transport is proportional, according to an approximate model [54], based on free-

Table 2. The framework of mathematical analysis of the magnetic field effect on mass transport

Equation of motion	$\frac{D\mathbf{v}}{Dt} + \operatorname{grad} p = \nu \operatorname{divgrad} \mathbf{v} + \frac{\nu}{3} \operatorname{grad} \operatorname{div} \mathbf{v} + \mathrm{F}$
Equation of continuity	$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0$
Ohm's law	$\mathbf{j} = \sigma(\mathbf{E} + \mathbf{v} \times \mathbf{B})$
Ampère's law	$\operatorname{curl} \frac{\mathbf{B}}{\mu} = \mathrm{j}$
Electrical energy equation	$\mathbf{E} \cdot \mathbf{j} = \frac{\mathrm{j}^2}{\sigma} - \mathbf{j} \cdot (\mathbf{v} \times \mathbf{B})$
Vorticity Equation	$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\omega}{\rho}\right) - \frac{\omega}{\rho} \cdot \operatorname{grad} \mathbf{v} = \frac{1}{\rho} \operatorname{curl}\left(\frac{\mathbf{j} \times \mathbf{B}}{\rho}\right)$
Force density	$F = \rho \mathrm{g} + \sigma \mathrm{E} \times \mathbf{B} - \sigma \lvert \mathbf{B}^2 \rvert \mathbf{v} + \sigma \lvert \mathbf{B} \rvert \lvert \mathbf{v} \rvert \cos \phi_{\mathbf{B},\mathbf{v}} \mathbf{B}$
Magnetic Continuity Equation	$\operatorname{div} \mathbf{B} = 0$
Kirchhoff's (first) law	$\operatorname{div} \mathrm{j} = 0$
Convective diffusion equation (minor ionic species in excess supporting electrolyte)	$\frac{\partial c_i}{\partial t} + \mathbf{v} \cdot \operatorname{grad} c_i = D_i \operatorname{div} \operatorname{grad} c_i$

convective diffusion theory [55], to the one-fourth power of the imposed magnetic field strength. The model agrees closely with experimental transport rates up to $B \simeq 1$ T [56]. Using disc electrodes and axial magnetic fields in an experimental cylindrical cell Blum [57] has demonstrated a linear relationship between mass transport rates and $(B)^{1/2}$ up to $B = 1$ T; in the $1 < B < 1.25$ T range experimental scatter indicates a 0.38–0.5 exponent. The experimental results are in good agreement up to $B \simeq 1$ T with his theoretical model [58] based on potential theory modified with respect to MHD interaction. When the magnetic field is vertical and parallel to vertical plate electrodes, the strongly enhancing effect of magnetic field superposition [59, 60] cannot be predicted by a simple MHD perturbation approach. The vorticity generation model [52, 61] where the MHD perturbation is applied to the vorticity equation (see Table 2) offers only a semi-quantitative interpretation of the experimental observations. However, experimental observations at strongly turbulent conditions can be successfully modelled in certain highly symmetric geometries, as shown [62, 63, 64] in the instance of concentric cylindrical cells and parallel-plate cells in series where the magnetically induced azimuthal flow is described via open-channel flow theory modified by an MHD perturbation approach.

The second category is represented primarily by configurations where the magnetic field superposition generates significantly larger currents than those existing without a magnetic field; the (usually non-uniform) magnetic field effect manifests itself via a relatively strong forced convection component imposed upon free convection due to d.c. electrolysis. The overall process is then considered as a mixed model of free and forced convection. One can define *a priori* indeterminate interaction parameter, m, via the relationship [64]

$$\frac{i_{\mathrm{L}}}{i_{\mathrm{LNC}}} = \left[1 + \left(\frac{i_{\mathrm{LFC}}}{i_{\mathrm{LNC}}}\right)^{1/m}\right]^{m} \tag{8}$$

The purely free-convective and forced-convective contributions to the limiting current may be estimated by appropriate relationships available in the literature and m can be found via experimentally observed values of i_{L} using $i_{\mathrm{L}}/i_{\mathrm{LNC}}$ versus $i_{\mathrm{LFC}}/i_{\mathrm{LNC}}$ plots. Typically, m may vary between 1/3 and 3/4, $m = 0$ corresponds to purely forced- and $m = 1$ to purely free convection. A similar interaction-parameter analysis in heat transfer has also been proposed [65].

As in conventional electrolysis, regression analysis of experimental data in the mixed mode is an important means of establishing mass transport relationships, usually in a dimensionless form. The magnetic field effect is represented by the dimensionless Hartmann number defined as

$$Ha \equiv aB_0 \frac{\sigma^{1/2}}{\eta^{1/2}} \tag{9}$$

where a is the half-length of the cell coordinate normal to the magnetic field; it may be regarded as the ratio of magnetically induced stress to the hydrodynamic shear stress. In aqueous electrolytes $Ha < 10$. At low Reynolds numbers ($2.5 < Re < 500$) and low Hartmann numbers ($0.01 < Ha < 2.08$) a transverse magnetic field enhances mass transport rates in a rectangular cell with vertical electrodes according to the relationship [66]

$$f_{\mathrm{m}} \equiv Sh_{\mathrm{m}}/Sh_0 = 1 + \tfrac{11}{69}\, Gr^{1/4} Sc^{-1/4} Re^{-1/3} Ha \tag{10}$$

fitted to an 80 × 5 regression matrix containing experimental data, at an average relative error of 7.7%. The linear relationship between f_{m} and Ha agrees reasonably well with Blum's extended Karman-Pohlhausen model [58] of boundary layer flow on a permeable planar surface which predicts an $Sh_{\mathrm{m}} \propto Ha^{1/3}$ interdependence within the experimental Ha-range, except at very low Hartmann numbers. In contrast to transverse fields, when the electric and magnetic fields are parallel the magnetic field has a retarding effect on mass transport; in the case of flow past horizontal electrodes to which both fields are perpendicular [67],

$$Sh_{\mathrm{m}} \propto \phi_{\mathrm{m}}^{1/3} Re_{\mathrm{L}}^{1/2} Sc^{1/3} \tag{11}$$

where the ϕ_{m} coefficient is a decreasing linear function of B^2, in the $4 < B < 685$ mT range. Equation 11 is apparently a transitional case fitting between limiting laws [68]

$$Sh_{\mathrm{m}} \propto Ha^{1/3} Re_{\mathrm{L}}^{1/3} Sc^{1/3} \quad \text{large } Ha \tag{12a}$$

$$Sh_{\mathrm{m}} \propto Re_{\mathrm{L}}^{1/2} Sc^{1/2} \quad \text{small } Ha \tag{12b}$$

derived from a boundary layer model for longitudinal MHD flow past a flat plate. MHD boundary layer theory has been shown to be reasonably successful [58] in interpreting experimental data on flow around cylinders [69].

The third category contains essentially instances where MHD channel flow models are adequate to describe mass transport. These models are based on laminar flow theory of conducting viscous liquids between parallel walls with a transverse magnetic field, known as the classical Hartmann problem [70, 71]. The velocity profile in fully developed flow may be written as [70]

$$V = \bar{V}\,\frac{Ha\left[\cosh(Ha) - \cosh\left(Ha\dfrac{x}{a}\right)\right]}{Ha\cosh(Ha) - \sinh(Ha)} \qquad (13)$$

where $\bar{V}$ is the mean velocity:

$$\bar{V} = \frac{\Delta P}{\sigma B^2}\cdot\frac{Ha\left[\cosh(Ha) - \sinh(Ha)\right]}{\sinh(Ha)} \qquad (14)$$

The maximum velocity at the centre of the channel becomes asymptotically proportional to B^{-2} as $H \to \infty$; hence, in a strong magnetic field the velocity profile flattens out in the channel but its gradient at the wall is considerably larger than in its absence. The combination of Hartmann flow theory and convective diffusion theory [58] predicts closely experimental mass transport rates in forced-flow electrolysis between parallel plates [69]; at $Ha \simeq 12$ enhancement in mass transport rates, relative to $Ha = 0$, is about 11% (ferro-ferricyanide system). A simpler but less powerful approximation [72] based on the same principles predicts larger improvements for the cathodic deposition of copper at lower values of Ha.

While classification in the three categories discussed above facilitiates the study of the magnetic field effect on mass transport in electrolytes, it by no means follows that all mass transport phenomena observed in magnetic fields can be interpreted in this manner. As shown in the case of magnetoelectrolysis using inclined electrodes [53], a correct interpretation of the complex magnetic field effect requires a rather sophisticated analysis which uses the principle of asymptotic superposition of flow models pertinent to horizontal and vertical configurations. Similarly, when low frequency sine-wave or square-wave potential fields are employed for electrolysis [73–76] the nature of the interaction between frequency and magnetic field strength cannot be explained in an adequate manner in terms of the fundamental theory of convective diffusion and/or magnetohydrodynamics. In fact, direct flow visualization techniques [e.g. 77–79] applied to magnetoelectrolysis indicate clearly intrinsic limitations of mechanistic modelling for a complete understanding of the magnetic field effect on flow regimes and mass transport rates in electrolysis.

4. The effect of magnetic fields on the kinetics of electrode processes

Relatively little is known about this specific effect; Kelly [80] has proposed a modification of conventional Butler-Volmer kinetics in terms of the magnetically induced potential difference and analysed polarization behaviour in an experimental Ti/H_2SO_4 cell on its basis. Similar but less comprehensive results have been published in the instance of iron–amalgam systems [81], the electrolysis of copper salts [82–84] and sodium carbonate electrolytes [85]. Although the interaction of magnetic fields with the catalytic activity of certain ferromagnetic materials [86–88] has been demonstrated in weak magnetic fields, there is no straightforward evidence of such an effect on electrode kinetics. The magnetic field effect on the relative speed of reversible reactions is vanishingly small in weak fields inasmuch as the magnetic correction term in the reaction equilibrium constant [89]:

$$-\ln K = \frac{1}{RT}\sum_{i}\nu_i\left(\mu_i^0 - \frac{\mu_0\chi_i}{2}H^2\right) \qquad (15)$$

is only about 10^{-5} (in Equation 15, ν_i are the stoichiometric coefficients, μ_i^0 the standard chemical potentials, χ_i the magnetic susceptibility of the reaction components, μ_0 the magnetic permeability and H the magnetic field vector magnitude). There is much potential for comprehensive fundamental investigations in this area.

5. The effect of magnetic fields on deposit quality in magnetoelectrolysis

In the electroplating of metals, the quality of the electrolytic deposit is of primary interest. Numerous observations reported in the literature of the magnetic field effect on the surface deposit pattern are contradictory since morphological characteristics of the deposit crystal structure cannot be related in a straightforward manner to the imposed magnetic flux density. There is, nevertheless, ample evidence for the beneficial effect of an imposed uniform magnetic field on surface evenness and firmness [60, 90–92] under carefully chosen experimental conditions. Experiments in a pilot-plant scale magnetoelectrolytic reactor [93], where copper was deposited from acid-free aqueous $CuSO_4$ solutions onto stainless steel cathodes, indicate that the growth orientation of crystals depends on the interrelation between magnetic field strength distribution, temperature, electric current and potential distribution along the electrode surface: Fig. 1 illustrates the variability of the copper deposit on the surface (active area = 50.54 dm^2) in a typical run. In the darker sections where partial oxide formation has taken place, the magnetic field gradient is relatively weak, whereas over the brighter areas where oxide formation is negligible or very little, the gradient is relatively large. (in the experimental apparatus [94, 95] axial gradients up to 0.25 $mT\,cm^{-2}$ can be produced.) Examination of specimens under a scanning electron microscope (SEM) points to a fibrous nature of magnetoelectrolytically deposited copper. The fibres form a screen structure [96] where the initial fibre-deposit is aligned parallel to the magnetic field; this is followed by cross deposits leading to an eventually closely woven deposition pattern.

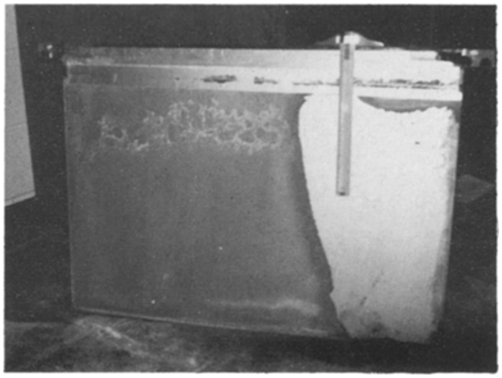

Fig. 1. Copper deposition on a stainless steel cathode in a magnetoelectrolytic reactor operating in a strongly non-uniform (solenoidal) magnetic field [94, 95]. The lighter portion on the right is the steel surface after the screen-type deposit was peeled off.

It is worthwhile to consider briefly recent research concerning the effect of magnetic fields on surface deterioration brought about at current densities in the neighbourhood of the limiting plateau. In oscillatory electric fields, a uniform transverse magnetic field accelerates the appearance and the spread of loose and powdery oxide deposits [74] on an electrode surface, most likely due to a complex interaction with various electrode reactions. Very recent results [97] seem to indicate that the rugosity of the deteriorated surface is closely linked to the strength of the magnetic field; these aspects have not yet been fully analysed. Under extreme conditions, magnetically assisted surface deterioration can be utilized to increase the production rate of powdered metals and/or metal oxides [98]. This accelerating effect may possibly be linked to the enhancement of diffusion-controlled corrosion of metals [99].

6. Some practical aspects and future perspectives

The major practical advantage of electrolysis in magnetic fields is the attainment of large mass transport rates; in the electrolytic deposition of metals this aspect is particularly important since the quality of the cathode deposit will not suffer from large current densities, in appropriate electric/magnetic field configurations. Table 3 illustrates the enhancing effect of magnetic fields on the rate of the deposition of copper from an acidified aqueous electrolyte [59, 64] in uniform magnetic fields. If electrolysis were carried out in the absence of a magnetic field (represented by the second column; B_0 = 4mT is the residual magnetic field in the Walker 5 kVA regulated electromagnet employed), the deposit quality would be poor past a cell voltage drop of about 400 mV. On the other hand, the deposit obtained at *all* values of the cell voltage in the magnetic fields shown is of good quality; in this cell copper can be deposited at three times the rate corresponding to the limiting current plateau in the residual field in a reasonably weak magnetic field of 540 mT. Mass transport enhancements of similar magnitude can be achieved in even weaker fields if they are *non-uniform* [61, 94, 95]: such fields can be readily generated by winding electric cables around the

Table 3. Magnetoelectrolysis of an aqueous copper sulphate solution in a cylindrical cell using concentric vertical ring electrodes [59, 64]. $Cu^{2+} = 0.1895$ mol dm^{-3}; $H_2SO_4 = 1.56$ mol dm^{-3}. Cathode radius: 1.43 cm. Cathode height: 4.45 cm

Cell voltage drop (mV)	*Cathode current density*, A dm^{-2}				
	$B_0 = 4$ mT	$B_0 = 110$ mT	$B_0 = 200$ mT	$B_0 = 370$ mT	$B_0 = 540$ mT
400	1.000	1.161	1.226	1.276	1.358
500	1.079	1.286	1.374	1.552	1.689
600	1.094	1.315	1.423	1.764	1.963
700	1.109*	1.413	1.868	2.684	3.079

* Limiting current density; the theoretically estimated values are 1.002 A dm^{-2} (sulphate-model) and 1.209 A dm^{-2} (bisulphate-model) when the Newman–Selman procedure is employed [101].

electrolyte cell in a solenoidal pattern. Hence, the current flowing in the electrolyte cell can be used for solenoid excitation and the only additional energy expense is associated with the ohmic drop of the solenoid. This point raises the question of cost-effectiveness.

Considering the specific electric energy utilization, its value, about 1.6 kg kWh^{-1} in the cell of Table 3, and values obtained in magnetically assisted deposition of copper in low frequency pulse electrolysis (about 0.79 kg kWh^{-1}; [76]) compare favourably to 0.34–0.51 reported [100] for conventional copper electrowinning, 0.28–0.46 for laboratory-scale fluidized beds and 0.69 for a laboratory scale flow-through fixed bed cell; it is lower, however, than the 2.27–5.05 kg kWh^{-1} range representing conventional copper electrorefining. In general, the breakeven point for the profitability of a magnetoelectrolytic cell is given by

$$\frac{C_p}{C_e} = \frac{E}{\lambda\gamma} \qquad (16)$$

where C_p is the value of the cathode product per unit mass, C_e is the cost of electricity per unit energy expended, E is the magnitude of the electric field (potential per unit length) perpendicular to the cathode, λ the specific area (area per unit cell volume) and γ the electrochemical equivalent (mass per electricity) of the cathode product. The rate of profit generated per unit time in a magnetoelectrolytic cell with current I:

$$P = \left(\gamma C_p - \frac{Ec_e}{\lambda}\right) I \qquad (17)$$

determines its economic viability. In-depth studies of the economics of magnetoelectrolysis are still lacking.

The study of galvanic corrosion in magnetic fields may also lead to practically important results. It has been shown recently [99] that in relatively weak solenoidal fields the rate of corrosion of copper in acidic dichromate solutions may be doubled (e.g., at 2.4 mT at about 80% increase in the corrosion rate has been observed). Since this increase can be ascribed to magnetic enhancement of mass transport in the anodic boundary layer it is logical to assume that in proper configurations of electric, magnetic and flow fields corrosion may be retarded in a manner similar to electrolysis discussed before (e.g. [67, 80]). A new field, called perhaps 'magnetoelectrolytic prevention of corrosion' may emerge upon intensive research. Many unknown aspects of the magnetic field effect of potential importance require exploration: electroorganic reduction and oxidation, thin-layer electrochemistry, cathodic co-deposition of metals, electrocatalysis, and electrochemical machining are some examples. It is quite possible that the effect of magnetic fields on the human body and behaviour, known at present to a very limited extent, is strongly related to the influence of magnetic fields on body electrolytes: comprehensive studies in this domain will lead to the science of magneto-bioelectrochemistry and related branches. The exciting panorama is only beginning to unfold.

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