

TECHNICAL NOTE

# Enhanced mass transfer on a rotating disc—electrode surface in coupled electric and magnetic fields

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**Nomenclature**

<i>A</i>	Constant in Equation 8
<i>B</i>	Magnetic field strength
<i>c<sub>0</sub></i>	Electrolyte bulk concentration
<i>D</i>	Electrolyte diffusivity
<i>e<sub>r</sub>, e<sub>θ</sub>, e<sub>z</sub></i>	Directional unit vectors in the cylindrical co-ordinate system
<i>E</i>	d.c. electric field
<i>F</i>	Faraday constant (96 487 C mol <sup>-1</sup> )
<i>F<sub>L</sub></i>	Lorentz force
<i>F(§), G(§), H(§)</i>	Velocity functions in rotating disc theory
<i>i</i>	Current density via d.c. electrolysis
<i>I</i>	Current flow
<i>j</i>	Magnetically induced electric current density
<i>n</i>	Valency
<i>N</i>	Speed of rotating electrode
<i>Pr</i>	Prandtl number
<i>R</i>	Radius of rotating electrode
<i>Re<sub>m</sub></i>	Magnetic Reynolds number
<i>r</i>	Radial space coordinate
<i>v</i>	Velocity
<i>z</i>	Axial co-ordinate
<i>θ</i>	Azimuthal co-ordinate
<i>μ</i>	Magnetic permeability
<i>ν</i>	Kinematic viscosity of electrolyte
<i>§</i>	Dimensionless axial co-ordinate
<i>σ</i>	Electrical conductivity of electrolyte

In a rotating disc-electrode cell, the components of the velocity vector

$$\mathbf{v} = e_r v_r + e_\theta v_\theta + e_z v_z \quad (1)$$

can be computed via Cochran's convective diffusion theory [1] as

$$v_r = rNF(\S); \S = \sqrt{\frac{N}{\nu}} z \quad (2a)$$

$$v_\theta = rNG(\S) \quad (2b)$$

$$v_z = \sqrt{(\nu N)} H(\S) \quad (2c)$$

in the boundary layer adjacent to the disc; furthermore, the concentration distribution in the layer can be computed as

$$\frac{c}{c_0} = \frac{\int_0^Y \epsilon^{-u^3} du}{\int_0^\infty \epsilon^{-u^3} du} = Y\gamma^* \left( \frac{1}{3}, Y^3 \right) \quad (3)$$

$0 \leq \xi < 3.6$

where  $Y \cong \frac{\S Pr^{1/3}}{1.8}$  and  $\gamma^*$  is an incomplete gamma function. The functions *F* and *H* are zero and *G* = 1.0 at  $\S=0$ ; as  $\S$  is increased *F* reaches a maximum at about  $\S \cong 0.9$ , then tends asymptotically toward zero. *H* monotonically increases in the negative sense, while the value of *G* gradually decreases to zero. For calculation of mass transfer of the active species, the limiting current in a constant electrostatic field has been shown to be [2]:

$$i_L = 0.62 nFD^{2/3} \nu^{-1/6} c_0 N^{1/2} \quad (4)$$

Experimental verification of the square-root dependence between limiting current density

and rotation speed was described as early as 1948 [3].

One intriguing question, in view of the recently reported mass transfer enhancement at plane electrodes in magneto-electrolysis [4, 5], is whether the electrolytic current can be increased beyond its limiting value in a constant electrostatic field, by magnetic field superposition. For the sake of analysis, consider an arbitrary magnetic field of components coincident with the velocity components in the boundary layer, i.e.

$$\mathbf{B} = e_r B_r + e_\theta B_\theta + e_z B_z \quad (5)$$

From the theory of magnetohydrodynamics [e.g. 6] the fundamental stability condition:  $\text{div } \mathbf{B} = 0$  implies that

$$\frac{1}{r} \frac{\partial}{\partial r}(r B_r) + \frac{\partial B_\theta}{r \partial \theta} + \frac{\partial B_z}{\partial z} = 0 \quad (6)$$

and, in addition, Ampère's law:  $\text{curl } \mathbf{B} = \mathbf{uj}$  must also be obeyed. It then follows, that mass transfer is augmented under such conditions if the net Lorentz-force contribution to the electric current,  $\sigma \mathbf{v} \times \mathbf{B}$ , at the surface disc is non-zero:

$$e_z(v_r B_\theta - v_\theta B_r) \neq 0 \quad (7)$$

In order to simplify analysis, let us adopt for the moment the usual 'low magnetic Reynolds number' approximation for aqueous electrolytes. This assumption, as shown later, does not restrict the validity of the analysis but it allows the omission of Ampère's law. The simplest field configuration which now satisfies the stability conditions is a radially imposed magnetic field of strength distribution:

$$B_r = \frac{A}{r} \quad (8)$$

and  $B_\theta = B_z = 0$ . The magnetically induced current density can be written as:

$$\mathbf{j}_0 = -e_z \sigma N A \quad (9)$$

where the negative sign indicates flow into the disc electrode. The average magnitude of this contribution is computed from the total flow of the magnetically induced current:

$$\langle j_0 \rangle = \frac{\sigma N}{R^2 \pi} \int_0^{2\pi} \int_0^R (r^2 B_r) dr d\theta = \sigma N A \quad (10)$$

The enhancement factor is the ratio of Equation 10 and Equation 4:

$$\frac{\langle j_0 \rangle}{i_L} = k N^{1/2} A; k \equiv 1.6129 \frac{\sigma v^{1/6}}{n F D^{2/3} c_0} \quad (11)$$

If the low  $\text{Re}_m$  approximation is now abandoned, Ampère's law yields the additional relationship:

$$\mu j_z = \frac{1}{r} \left[ \frac{\partial(r B_\theta)}{\partial r} - \frac{\partial B_r}{\partial \theta} \right] \quad (12)$$

inasmuch as the d.c. electrolytic current flows in the  $z$ -direction. Since  $B_r$  is only  $r$ -dependent in the case being considered, integration of Equation 12 yields:

$$B_\theta = \frac{\text{constant}}{r} + \frac{1}{2} \mu j_z r \quad (13)$$

As  $z \rightarrow 0$ ,  $F(\zeta) \rightarrow 0$  and  $V_r \rightarrow 0$  regardless of the numerical value of  $B_\theta$ ; hence Equation 9 is satisfied and the low  $\text{Re}_m$  approximation is not a necessary, although an acceptable condition for an aqueous electrolyte, for this analysis.

The magnetic field configuration given by Equation 8 can be approximated to a desired degree of accuracy on the disc surface: the surface should consist of thin concentric annular layers of metals or alloys. The magnetic permeability of each metal annulus should be progressively smaller in proportion to its distance from the centre of the disc. Consider, for example, a disc electrode whose surface is constructed as shown in Table 1; the last column in the table contains the magnetic permeabilities pertaining to a magnetic field intensity of  $H_r = 795.8 \text{ A m}^{-1}$ , (10 Oe). The radial distribution of the magnetic field strength along the disc surface may be approximated as  $B_r/\mu_0 H_r = 200/x$ , where  $x$  is the fractional distance from the disc centre (on the basis of areas under the two curves, the inaccuracy of the approximation is 3.5%). If the disc diameter is 5 cm, Equation 8 reads:

$$B_r = \frac{0.01}{r} \quad (14)$$

in SI units ( $r, m$ ;  $B$ , tesla). If the electrolyte is a mixture [4] of copper sulphate ( $0.0463 \text{ mol dm}^{-3}$ ) and sulphuric acid ( $1.502 \text{ mol dm}^{-3}$ ), then  $\sigma = 58 \text{ S m}^{-1}$ ,  $D = 6.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $v = 1.12 \times$

Table 1. Disc electrode surface in the illustrative example

Material of surface layer	Position of surface layer in terms of fractional radius	Fractional width of layer annulus	$\frac{B_r}{\mu_0 H_r} = \frac{\text{Magnetic field strength}}{\text{Magnetizing force}}$ $H_r = 795.8 \text{ A m}^{-1}$ [7]
Supermendur	0.0-1.05	0.15	2,293
Sinimax	0.15-0.30	0.15	1,054
Pure Ni(401)	0.30-0.70	0.40	401
30% Ni-Fe (Alloy 143)	0.70-1.00	0.30	143

$10^{-6} \text{ m}^2 \text{ s}^{-1}$ . Consequently,  $k = 1.4076 \text{ V}^{-1} \text{ m s}^{-1/2}$  (Equation 11) and  $kA = 0.014076 \text{ s}^{1/2}$ . At a rotation speed of  $N = 5 \text{ s}^{-1}$ , the enhancement factor is about 3%; at  $N = 150 \text{ s}^{-1}$ , about 17%. Conversely, one could design a disc electrode surface for a specified enhancement factor, by carrying out a similar calculation in reversed order.

It is worth mentioning that Equation 8 is not the only field configuration which satisfies the fundamental equations of magnetohydrodynamics. Apart from the trivial case of  $B_r = 0$  (no enhancement of mass transfer) one could specify that:

$$r \frac{\partial B_\theta}{\partial \theta} + r \frac{\partial B_z}{\partial r} = f(r) \tag{15}$$

where  $f(r)$  is some indeterminate function. Then,  $B_r$  would have to obey the more general condition:

$$r \frac{\partial B_r}{\partial r} + B_r + f(r) = 0 \tag{16}$$

If  $f(r)$  is stipulated to have the form  $r^n$ ,  $n$  in-

determinate integer, then Equation 16 is solved as:

$$B_r = \frac{K_1}{r} - \frac{K_2}{r} \ln r; n = -1 \tag{17a}$$

$$B_r = \frac{K_1}{r} - \frac{K_2}{n+1} r^n; n \neq -1 \tag{17b}$$

One would still have to solve for  $B_\theta$  and  $B_z$ ; at any rate, the resulting magnetic field strength  $\mathbf{B}$  would be much more complicated than the simple and physically realizable case treated above.

References

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 [6] J. A. Shercliff, 'A Textbook of Magnetohydrodynamics Section 3.8' Pergamon Press (1965).  
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