Magnetoelectrochemistry

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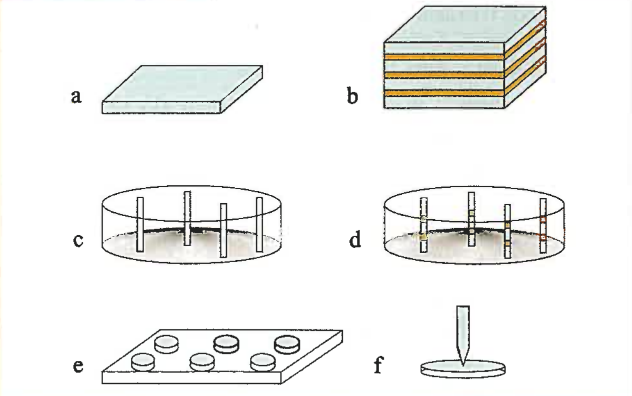
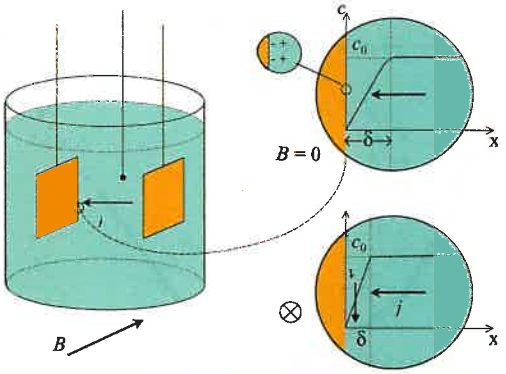
At first sight, magnetism and electrochemistry seem an odd couple. The energies involved in chemical reactions are of order 1 electron volt (eV), a fact affirmed by countless plots of electrochemical data where the abscissae are on a scale of volts relative to the potential of a reference electrode. Yet magnetic energies in laboratory fields are orders of magnitude smaller; the Zeeman splitting of the spin up ↑ and spin down ↓ states of an electron in a field of 1 tesla (T), for example, is 1.2 10^{-4} eV. Where then is the connection between electrochemistry and magnetism?

There are at least two answers. The first is that electrodeposition is a remarkably versatile (and inexpensive) method of preparing metallic films and nanostructures, including those made of ferromagnetic metals and alloys (Figure 1). A monolayer of atoms can be deposited from a bath containing a solution of metallic cations onto a centimeter-square working electrode in an electrochemical cell from a bath containing a solution of metallic cations by passing a current of 1 milliamp for about a second (Figure 2). It can be removed just as easily by reversing the polarity of the electrodes and running the current in the opposite direction. Electrodeposition of permalloy ($Fe_{19}Ni_{81}$) from a bath containing Fe^{2+} and Ni^{2+} ions is an established industrial process. The problem of obtaining smooth, uniform films is solved by a combination of clever electrode design, flow control and judicious use of the chemical additives that make electrochemistry seem as much an arcane art as an exact science. Permalloy films a few microns in thickness were for long used as cores of the thin-film electromagnets that form the write heads for high-density magnetic recording [1]. These have recently been superseded by thinner films of soft nanocrystalline Fe-Co-Ni or Fe-Co alloys which have a polarization in excess of 2 T [2], twice as large as permalloy. Weak uniaxial anisotropy needed to control the magnetization reversal process is induced by depositing the alloys in a magnetic field.

Besides alloys, it is also possible to deposit binary multilayers from a single bath by exploiting the fact that the deposition rates for different metals depend both on the concentrations of the ions in solution, and on the potential used for deposition. Copper/cobalt multilayers for spin valves, for example [3] can be plated from a bath containing a 10^{-3} molar solution of $CuSO_4$ and a 0.1 molar solution of $CoSO_4$ by toggling the cathode potential between −0.3 V (relative to the hydrogen reference electrode) where pure Cu is deposited and −1.0 V where Co with a trace of Cu is deposited. Layer thickness is controlled by varying the time for each step. Magnetic nanowires, which may be made of a single metal like nickel, or a multilayer like Co/Cu are obtained by plating into fine pores in membranes [4]. Nanocontacts (some of which exhibit huge magnetoresistance [5]) can be produced by electrochemical growth across a gap between a fine wire and a substrate, or onto a lithographically-defined metal pattern. Patterns themselves can be written by using a scanning point anode, a method known as dip-pen nanolithography.



▲ **Fig. 1:** Some magnetic nanostructures produced by electrodeposition a) metal or alloy thin film, b) multilayer, c) nanowires d) multilayer nanowires, e) dot array f) nanocontact.



▲ **Fig. 2:** A simple electrochemical cell with working electrode, reference electrode and counter electrode. The enlargements show the concentration gradient of ionic species in the electrolyte near the cathode. An applied magnetic field sets up a convective flow parallel to the electrode surface, which has the effect of narrowing the diffusion layer δ.

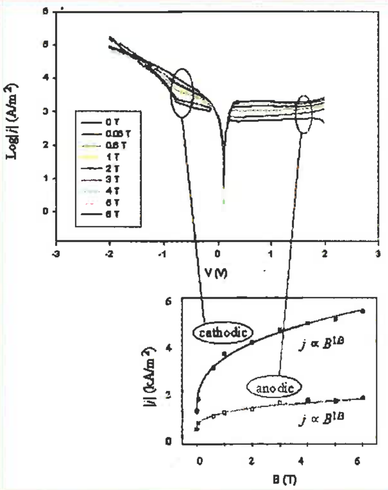
The second answer is that application of a magnetic field during electrodeposition can influence the process in unexpected ways. Consider the high-school experiment of copper plating from a $CuSO_4$ bath. According to whether its potential is less than or greater than 0.34 V relative to a standard hydrogen reference electrode, copper is either plated onto or dissolved off the copper working electrode. This information is summarized in the current-voltage characteristic of the cell, the voltamogram shown in Figure 3 [6]. Remarkably, the plating or dissolution rates can be doubled by applying a field of about 1 T,. They increase as $B^{1/3}$. In seeking an explanation of this behaviour, it is instructive to consider the magnetic forces that act on the Cu^{2+} cations in an applied field B. One is the Lorentz force $F_L = j \times B$ newtons per cubic meter (N m^{-3}) acting on the ion currents that constitute the local current density j amps per square meter (A m^{-2}). Other forces are derived from the magnetic energy

$$E = -(1/2)M \cdot B,$$

where $M = \chi_m cB/\mu_0$ is the induced magnetization of the ions with molar concentration c and molar susceptibility χ_m. Since $F = -\nabla E$, there are two force terms:

$$F = (1/2\mu_0)\,\chi_m B^2 \nabla c \;+\; (1/\mu_0)\,\chi_m cB \nabla B$$

The first of these F_c depends on the concentration gradient ∇c, the second F_B depends on the field gradient ∇B. Finally, whenever



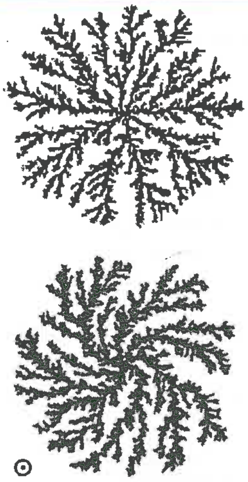
◀ **Fig. 3:** Voltamograms (polarization curve) for copper, showing the effect of applied magnetic field on the cathodic and anodic branches. The magnitude of the current density |j| is plotted on a log scale against the potential of the working electrode.

there is convective movement in the cell, there is also a damping term $F_d = \sigma v\times B\times B$ which depends on σ, the conductivity of the electrolyte, and its velocity v.

With some care, field gradients may be eliminated over the volume of an electrochemical cell, but the concentration gradients cannot be removed. Indeed they are essential to drive the diffusion of ions towards the cathode, which is the current-limiting process at most potentials used in the plating process (Figure 3). The electric field in the cell is largely screened by the supporting electrolyte, and most of the potential drop in the cell occurs at the charged double layer which is established within a few nanometers of the cathode surface, where the reduction of the metal cations occurs. A concentration gradient is established in a diffusion layer near the electrode, as indicated in Figure 2. If this layer has thickness δ, the diffusion equation $\partial c/\partial t = -D\nabla c$ gives a limiting current

$$j_l \approx nFDc_0/\delta$$

where F = 96,485 coulombs is the molar charge and c_0 is the ionic concentration in the bulk of the solution. Typically, the diffusion coefficient $D \approx 10^{-9}\,m^2s^{-1}$ for ions in solution, so the diffusion layer thickness for typical current densities in the diffusion-limited region is ≈ 100 μm. Close to the rest potential, where little current flows in the cell, the currents are limited by the kinetics of the $Cu^{2+} \leftrightarrow Cu^{+} \leftrightarrow Cu^{0}$ reduction reaction. There is no field effect here. The influence of the field appears to be restricted to the diffusion-limited regions. It is now appreciated that the $B^{1/3}$ variation arises from the Lorentz force, which creates a convective flow parallel to the surface whenever the field is not parallel to the current [8]. This in turn reduces the thickness δ of the diffusion layer, and enhances the current j, as originally proposed by Aogaki. Convincing evidence of the hydrodynamic nature of the effect is that a similar enhancement can be achieved by gentle stirring, and the field effect is progressively eliminated by increasing the viscosity of the electrolyte [6].



▶ **Fig. 4:** The effect of a magnetic field on a fractal electrodeposit grown in a flat cell.

▼ **Table 1:** Magnetic forces acting in a typical electrochemical cell [8].

Force		Expression	Typical magnitude (N m⁻³)
Lorentz force	F_L	$j\times B$	10^3
Field gradient force	F_B	$(1/\mu_0)\,\chi_{m}cB\nabla B$	10^2
Paramagnetic force	F_c	$(1/2\mu_0)\,\chi_m B^2\nabla c$	$4\ 10^4$
Damping force	F_c	$\sigma v\times B\times B$	10

[Typical values; $j = 10^3$ A m^{-2}, $B = 1$ T, $\chi_m = 10^{-8}$ m^3 mol^{-1}, $c_0 = 10^3$ mol m^{-3} (1 M), $\nabla B = 10$ T m^{-1}, $\sigma = 100$ S m^{-1}, $v = 0.1$ m s^{-1}, $\delta = 100$ μm]

A glance at Table 1 shows that the Lorentz force is *not* the largest magnetic force in the copper cell. The Cu^{2+} ions have a paramagnetic $3d^9$ configuration, and there is a force associated with the concentration gradient in the diffusion layer. The paramagnetic gradient force F_c is forty times greater in magnitude than the Lorentz force, yet it is ineffectual in influencing diffusion! The reason for this apparent paradox is that diffusion is driven by the entropic force $RT\nabla c$ which is enormously greater than F_c ($\approx 2\ 10^{10}$ N m^{-3}), and in the same direction. The Lorentz force is effective precisely because it acts in the direction *perpendicular* to the concentration gradient where it can induce convection. It should be noted that modest field gradients of order 100 T m^{-1}, like those produced by a small permanent magnet, can produce similar effects to the Lorentz force on the flow pattern in the cell. The gravitational force $\Delta\rho g$ that drives natural convection is $\approx 10^2 - 10^3$ N m^{-3}.

The field gradient and Lorentz forces can be deliberately enhanced by using electrodes with microscale or even nanoscale features. The current density is augmented around these features, and particular patterns of vortex flow are induced by a magnetic field [9]. When the electrode itself is ferromagnetic, field gradients of up to 10^5 T m^{-1} or more can be created by patterning or surface roughness. These gradients are similar to those used in high-gradient magnetic separation [10]. They will attract paramagnetic species such as Cu^{2+} or O_2, and repel diamagnetic species such as Zn^{2+} or CO_2; the altered concentrations can influence reaction rates via the thickness of the double layer. It has recently been shown that the oxygen reduction reaction $4H^+ + 4e + O_2 \rightarrow 2H_2O$ which is a limitation in solid polymer electrolyte fuel cells can be significantly increased by magnetic field gradients produced by including hard magnetic particles in the cathode catalyst layer to concentrate oxygen in the vicinity [11].

Other effects of a magnetic field have been seen on the morphology of the ramified fractal electrodeposits grown in flat electrochemical cells with a central cathode and a ring anode [12]. A magnetic field induces chirality when applied perpendicular to the cell, and axial asymmetry when applied in-plane, effects which can again be explained by the field-induced flow patterns in the cell [13]. At present it seems that all the various effects of magnetic fields in electrochemistry are somehow related to mass transport.

Magnetoelectrochemistry offers opportunities to investigate unexplained phenomena, such as the field-induced shift in rest potential associated with ferromagnetic electrodes [14], or the enhanced dissolution rate of certain crystals [15]. New magnetic nanostructures can be produced using electrochemical scanning probe methods and a new level of control may be exerted over industrial catalytic and electroplating processes by appropriately designed field patterns. Challenges include the deposition of films of hard magnetic rare-earth alloys. The odd couple has given birth to an exciting new area of magnetism, which is sure to turn up surprises, insights and new practical knowledge. Just as in other cross-disciplinary fields, there are rewards for those willing to play with a child.

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