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Mini review

Magnetic fields in electrochemistry: The Lorentz force. A mini-review

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ABSTRACT

Some recent work on the flow induced by uniform or non-uniform magnetic fields acting on currents in an electrochemical cell is reviewed. The effects include modifying the structure and texture of electrodeposits including their chirality, controlling hydrogen bubble release, inducing microfluidic flow and influencing nucleation. Much of this depends on micro-magnetohydrodynamic flow, on a scale of microns.

Contents

1. Introduction

Although the influence of an applied magnetic field on the operation of an electrochemical cell has been studied for over 40 years [1,2], magnetoelectrochemistry remains relatively unfamiliar territory to all but a few specialized research groups. The topic is inherently interdisciplinary, melding concepts from electrochemistry, hydrodynamics and magnetism with results that are sometimes surprising. Their elucidation can lead to unexpected insights into fundamental electrochemical processes, as well as new practical applications. It is useful to distinguish the effects of a uniform magnetic field from those of a magnetic field gradient, and to consider the forces of magnetic origin in relation to others acting in the cell [3]. In this short review we focus on the electromagnetic forces acting on electric currents. The magnetophoretic forces acting on paramagnetic ions are the topic of a companion review [4]. Both types of force are usually present, because any redox process where a single electron is transferred necessarily involves paramagnetic species, but one or the other is often dominant.

2. Uniform magnetic fields

2.1. Cathodic processes

The usual way for magnetic fields to create convection in an electrochemical cell is by the magnetohydrodynamic (MHD) effect (Fig. 1). The magnetic field $\boldsymbol{B}$ acting in the cell is the externally imposed field, essentially unaltered by the flow of electrolyte or current. The interaction of the field with the local current density $\boldsymbol{j}$ induces a flow that tends to

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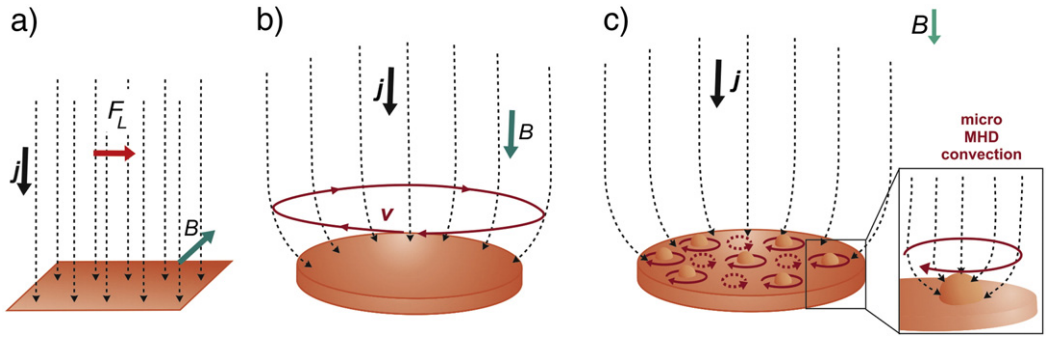

Fig. 1. Hydrodynamic flow at an electrode in a uniform magnetic field. a) Field applied parallel to the electrode surface. The primary MHD flow is parallel to the surface. b, c) Field applied perpendicular to the electrode surface. In b) the primary MHD flow is a vortex around the rim but in c) secondary micro-MHD vortices arise around protuberances on the surface.

reduce the diffusion layer thickness and enhance mass transport. The limiting current in the diffusion-controlled regime increases due to the localized magnetic stirring of the electrolyte. This convective force density has the same origin as the driving force in an electric motor. It is known as the Lorentz Force and is given by the following equation:

$$\boldsymbol{F}_L = \boldsymbol{j} \times \boldsymbol{B}. \quad (1)$$

The force is zero when $\boldsymbol{B}$ and $\boldsymbol{j}$ are parallel, and it is the largest when they are orthogonal. During electrodeposition, the Lorentz force may be comparable in magnitude to the buoyancy force driving convection, due to density variations of order 10% in the electrolyte near the cathode. A typical value of $\boldsymbol{F}_L$ for $\boldsymbol{B} = 1$ T and $\boldsymbol{j} = 1$ mA mm^{-2} is 1000 N m^{-3}. The flow pattern can therefore be modified by applying a magnetic field, or by realigning the field to alter the relative orientation of the Lorentz force and gravity [5,6]. A consequence of $\boldsymbol{F}_L$ is an increase in the electrodeposition rate, varying as $\boldsymbol{B}^{1/3}$ [7].

The benefits of large-scale convection can be more effectively achieved by mechanical agitation, but the relation between Lorentz force and local current density means that it is possible to induce flow patterns magnetically on a scale that would be otherwise unattainable. The effects may be sharply localized in spots of high current density, where a micro-MHD effect is created (Fig. 1c). Another advantage is that electrolyte flow can be driven in microfluidic channels, where transverse redox currents are flowing [8,9].

Since $\boldsymbol{j}$ is inevitably non-uniform at the edge of an electrode, there is normally an MHD flow around the rim when $\boldsymbol{B}$ is perpendicular to the electrode surface (Fig. 1b). Furthermore, uneven growth at the cathode during electrodeposition produces a locally nonuniform current distribution, giving rise to secondary micro-MHD vortices around growing asperities that protrude into the diffusion layer, as illustrated in Fig. 1c [10,11]. Mogi et al. have recently demonstrated that magnetically-prepared Ag or Cu electrodes exhibit a high sensitivity towards certain enantiomeric amino acids, offering a novel route for the synthesis of biomolecules with a high enantioselectivity [11,12]. The effect may be explained by chirality imprinted on the electrode surface, where screw dislocations grow in a sense imposed by the direction of the magnetic field [11]. Furthermore, it is suggested by Aogaki et al. that the no-slip boundary condition at the electrode surface is relaxed during electrodeposition by the formation of ionic vacancies, which facilitate the establishment of these microvortices [13]. The vacancies are thought to coagulate into nanobubbles of radius r which are stabilized by a layer of charged anions on their inner surface. The Coulomb repulsion reduces the effective surface tension γ and therefore cuts down the Laplace pressure $2\gamma/r$, which would otherwise lead to the rapid dissolution of the nanobubble. The enatiomeric sensitivity increases with decreasing electrode diameter, due to the supporting effect of the primary MHD flow, Fig. 1b. A rotating cell can also impose electrode chirality [12].

Hydrogen bubble formation and release during the electrolysis of water are strongly influenced by magnetically-induced flow [14]. Gas bubbles occlude the electrode surface, deforming the local current density. At electrodes where the average current distribution is uniform, it is found that the bubbles released are smaller when a magnetic field is present [15–17]. This is beneficial during electrodeposition, as the films produced lack the typical defects caused by hydrogen evolution [18]. Even when the field is normal to the cathode and MHD is negligible, there are still micro-MHD flows arising from the deformation of the current distribution by the spherical bubbles, which induce hydrodynamic drag forces that sweep the bubbles away from the electrode surface, thereby impeding their growth.

With a microelectrode comparable in diameter to the bubbles (<1 mm), the bubble release is often periodic and the system behaves as a gas oscillator [19], depending on the relative orientation of $\boldsymbol{F}_L$ and buoyancy (Fig. 2) [20]. In that case it is possible to see the opposite effect — hydrogen bubbles grow bigger in a vertical field applied normal to the microelectrode surface [21]. Motion tracking images using PVC particles reveal that the flow created when the current distribution is deformed around the growing bubble tends to pin it to the microelectrode. Electrochemical noise analysis provides a frequency spectrum [22], and it suggests that bubbles grow by coalescence with much smaller ones [20,21,23], something that can be observed directly, together with microbubble growth and release, using high-speed photography [21,24]. Magnetic field does modify the bubbling regime, but surface tension appears to be the critical factor.

The efficiency of water electrolysis to produce hydrogen can also be improved magnetically via MHD [25]. Micro-MHD is also responsible for the improvement of hard nickel electrodeposits containing alumina nanoparticles when they are pulse-plated in a magnetic field. The alumina content of the hard coating is increased, and its hardness is improved, partly due to the effective removal of hydrogen bubbles during plating [26].

Besides enhancing the deposition rate via the MHD effect, there are many studies which show the influence of magnetic fields on the morphology, texture, roughness and dendritic character of electrodeposits [27]. The results depend on the orientation of the field relative to the cathode surface. Aogaki and Morimoto suggest that fields applied parallel to the electrode tend to suppress three-dimensional nucleation and dendritic growth, but they promote faster, two-dimensional growth and smoother deposits due to the micro-MHD effect [10]. A perpendicular field usually produces rougher deposits. The field often induces preferred crystallographic texturing in metallic electrodeposits [28], and the effects are enhanced in continuous films as the deposit grows thicker [29]. The texturing is usually accompanied by changes in grain shape, typically from rounded to needle-like in a perpendicular field [18,30]. An example is provided by the deposition of Co, where there is a clear tendency of the film to grow along the 110 *hcp* direction when the magnetic field is parallel to the electrode surface [18]. In this configuration, the surface roughness of electrodeposited films may be enhanced [18] or reduced [29]. but the film thickness is almost always enhanced as a result of improved ion transport [15,29,31]. When