# Magnetohydrodynamic and paramagnetic phenomena in electrochemistry with diamagnetic and ferromagnetic millielectrodes

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There are three kinds of body forces operating in electrolytic solutions in the magnetic field: the magnetohydrodynamic force (MHD) F_B (=$\mathbf{i} \times \mathbf{B}$), and the two paramagnetic forces, i.e., the $F_{\nabla B}$ force (~$\mathbf{B} \cdot \nabla B$) and the $F_{\nabla C}$ force (~$|\mathbf{B}|^2 \nabla C$), where $\mathbf{i}$, $\mathbf{B}$ and C are the current density vector, the magnetic induction and the concentration of a paramagnetic species in solution, respectively.[1] These three forces manifest themselves differently, depending on the experimental conditions. Thus, diamagnetic disk millielectrodes (e.g., Au) with their plane parallel to the flux of a homogeneous magnetic field of an electromagnet yield convective current-potential response analogous to that observed with rotating electrodes; that response is generated and controlled by F_B.[2,3] The same electrodes placed in the inhomogeneous field of a strong permanent magnet yield also convective behavior that is controlled by both F_B and $F_{\nabla B}$.[1]

Now if the millielectrodes themselves are made of permanent magnets (e.g., Au-coated Nd-Fe-B disks) they yield diffusion-controlled behavior even at conditions where a gold disc electrode shows behavior dominated by density gradient driven natural convection.[4] Analysis shows that both paramagnetic body forces $F_{\nabla B}$ and $F_{\nabla C}$ are responsible for those phenomena. Further analysis, however, also shows that $F_{\nabla C}$ alone should be able to balance the gravity forces in the diffusion layer, canceling out natural convection. That was demonstrated by the reduction of nitrobenzene on a gold electrodes held in a homogeneous field with its vector perpendicular to the electrode surface (Figure 1).[5] The force able to balance
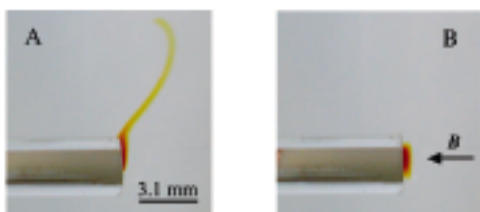
Figure 1. A gold disk electrode (1 mm diameter) in a nitrobenzene solution (0.1 M) in CH_3CN/0.5 M tetrabutylamonium perchlorate 40 s after potential steps in the diffusion-controlled range. A: $|\mathbf{B}|$=0. $|\mathbf{B}|$=3.3 T, $\theta = 0°$.

gravity was proportional to $|\mathbf{B}|^2$, and that was considered as a strong evidence for the identity of the magnetic phenomena at play.[5] Magnetic confinement of the diffusion layer by the $F_{\nabla C}$ force was utilized in the electrochemical polymerization of 3-methylthiophene, where canceling natural convection increases the current efficiency from 0.028 to 0.037 at 0.05 M of monomer concentration and from 0.051 to 0.071 at 0.1 M.[6] Even with the magnetic field parallel to the electrode surface (θ=90°) Lorenz forces causing MHD convection, in combination with $F_{\nabla C}$ forces keeping the flow pattern in

contact with the electrode, increase the current efficiency even more, to 0.048 at 0.05 M of monomer concentration and to 0.076 at 0.1 M.[6] (At higher monomer concentrations (>0.2 M), the rate of radical coupling is evidently fast enough so that, even in the absence of a magnetic field, no natural convection effects are observed and the current efficiency (0.7-0.8) is not affected by the magnetic field.)

Finally, magnetic fields shift the open circuit potential (OCP) of ferromagnetic electrodes (Fe, Co, and Ni) in corroding solutions.[7] The OCP changes observed (a) follow the series Fe>Co>Ni; (b) increase with the magnetic flux density; (c) reach a maximum with disk electrodes approximately 1 mm in diameter; and (d) depend on the orientation of the electrode. When the surface of the electrode is oriented parallel ($\theta = 90°$) or perpendicular ($\theta = 0°$) to the magnetic field, the open circuit potential moves in opposite directions (positive and negative, respectively) with the largest changes occurring when the electrode surface is parallel to the magnetic field. Nonconvective sleeve electrodes produce the same behavior. The overall experimental evidence suggests that the magnetic field changes the OCP by modifying the surface concentrations of the paramagnetic participants in the corrosion process of the ferromagnetic electrode; this in turn is accomplished by imposing a field-gradient driven mode of mass transfer upon paramagnetic species in solution (magnetophoresis). Simulations of the magnetic field around the ferromagnetic electrode at the two extreme orientations considered show that in one case ($\theta = 90°$) field gradients actually repel, while in the other case ($\theta = 0°$) they attract paramagnetic species in the vicinity of the electrode.[7]

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