MAGNETIC FIELD INFLUENCE ON ELECTROCHEMICAL PROCESSES

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1. Introduction

Electrochemical reactions play an important role in various types of industrial processes including electrolysis (conversion of substances), metal processing and finishing, batteries and fuel cells, and waste water treatment. From an industrial viewpoint, primary considerations are obviously of economic nature. The product yield in space and time and the specific energy consumption are of utmost importance for the return of investments. Magnetic fields might be a tool to increase the space time yield as well as to decrease the energy consumption of specific electrochemical processes. The effect of magnetic fields on electrochemical reactions were so far mainly attributed to an enhanced mass transfer due to electromagnetically induced convection [1]. A possible effect of the magnetic field on reaction kinetics has been argued by several researchers, too. Recently, the latter point of view started to gain acceptance due to a number of newly published results, but remains still controversial. In the present paper, the convective effect of the Lorentz force is the sole object of consideration.

2. Increase of space time yield

The space time yield \( \rho_p \) [kg m\(^{-3}\) s\(^{-1}\)] of product \( P \) in the absence of competing reactions may be defined as

\[
\rho_p = a_e j \frac{M_p}{\nu_e F}.
\] (1)

Here, \( a_e \) denotes the electrode area per volume, \( j \) the current density, \( M_p \) the molar mass of the product, \( \nu_e \) the number of electrons involved in one reaction and \( F \) the Faraday constant, respectively. The variables of equ. (1) accessible to the chemical engineer are \( a_e \) and \( j \). Both should be maximised in order to increase \( \rho_p \).

Electrochemical reactions belong to heterogeneous chemical processes. Therefore various transport phenomena have to be taken into account. If the mass transport to or from the electrodes determines the reaction rate, the maximum current density is as well limited by mass transfer. Typical industrial processes under mass transfer control are for instance copper refining and many electroorganic synthesis, like the Monsanto process.

The maximum current density attainable under mass transport control is the limiting current density \( j_l \). It may be related to the diffusion coefficient \( D \) of the reacting specie, its concentration \( c \) in the bulk of the cell and the thickness of the Nernst diffusion layer \( \delta_N \) around the electrode by [2]

\[
j_l = \nu_e F D \frac{c}{\delta_N}.
\] (2)

The thickness of the diffusion layer again is determined by the flow conditions near the electrode. This is where Magnetohydrodynamics (MHD) comes into play.
The Lorentz force

\[ \mathbf{F} = \mathbf{j} \times \mathbf{B} \]  

(3)

is the vector product of a current density \( \mathbf{j} \) and a magnetic field \( \mathbf{B} \). This Lorentz force represents a body force inside the electrolyte able to influence its flow. Since the current density is an inherent feature of electrochemical processes, only a suitable magnetic field has to be added to generate a Lorentz force. In economic terms, no running costs are added to the process, provided the magnetic field originates from permanent magnets.

Fig. 1 shows the anodic limiting current density in a small cell with vertical electrodes for the classical \( \text{K}_4[\text{Fe(CN)}_6]/\text{K}_3[\text{Fe(CN)}_6] \)-redox system under different conditions in terms of the magnetic field influence. A permanent magnet has been placed behind the anode of the cell in such a way, that the main field component was parallel to the electrode surface. By changing the orientation of the permanent magnet Lorentz forces either in upward or downward direction could be imposed on the electrolyte. At the anode \([\text{Fe(CN)}_6]^{4-}\) is oxidised to \([\text{Fe(CN)}_6]^{3-}\), which has a smaller density than the former complex. Therefore in the unforced case, a natural convection develops, which is directed upwards at the anode and downwards at the cathode. If a steady state is reached, a limiting current given by this natural convection is established. The limiting current increases with the concentration as it would be expected from eqn. (2), although this simplified relation hides the nonlinearities caused by the flow in

\[ \delta \varepsilon \].

In Fig. 2 four shadowgraphs of the electrolytic solution in the cell are given. The arrows denote the direction of the Lorentz forces near the electrode. Both images in the upper part of Fig. 2 show configurations, where only the anode is equipped with a permanent magnet. It is
clearly to be seen that the Lorentz force despite their concentration in a small volume along the anode determines the flow in the whole cell completely. If one applies additional magnets behind the cathode, depending on the orientation of the force fields a twin vortex structure may be generated, or the single large vortex typical for the one side forcing might be intensified. Dictated by the cell geometry, in all configurations edge vortices are present. If the Lorentz force $F_L$ has the same direction as the buoyancy force $F_B$, the limiting current density in Fig. 1 is increased by a factor of almost two over the whole range of concentrations. In the contrary, the configuration where the Lorentz force counteracts buoyancy shows only a slight increase and sometimes even a decrease of the limiting current density. Reduced convection alone could hardly explain this since, as can be deduced from the upper left subfigure of Fig. 2 and has been measured by Particle Image Velocimetry, the velocity magnitudes are similar in both cases. A possible explanation might be the formation of dead zones, when both forces are antiparallel. As mentioned afore, the anodic product is lighter than the bulk solution, therefore it will tend to accumulate in the upper left edge vortex thus preventing the covered electrode area from taking part in the reaction. Therefore the measured absolute current and the mean current density calculated with the geometric electrode area would be decreased.

3. Decrease of the specific energy consumption

Many industrial electrochemical processes such as chloralkali or water electrolysis take place under activation control, i.e. the rate determining step is not connected to mass transport in the electrolyte but to the processes of adsorption/desorption, surface diffusion and electron transfer. The cell voltage $U_C$ which has to be applied at the electrodes in order to maintain an electrochemical reaction can be divided into several components

$$U_C = U_0 + \eta_a + \eta_c + I \Sigma R.$$ (4)

Here $U_0$ denotes the purely thermodynamicaly determined reversible cell voltage, $\eta_a$ is the anodic and $\eta_c$ the cathodic overvoltage, respectively. $I \Sigma R$ describes the voltage drop due to the several resistances in the cell (electrolyte resistance, membrane resistance). Whereas neither the reversible cell voltage nor the overvoltages could be influenced by fluid dynamic means, the resistance of the electrolyte might be accessible in the case of processes developing gaseous products. The gas holdup in the cell increases the averaged electrolyte resistance and can lead to other unfavorable side effects like foaming and membrane degradation [3].

As has been shown in [4] the fluid velocity near the electrodes has a strong influence on the electrode area covered with gas bubbles which is, therefore, blocked for the current. Depending on the fluid velocity almost all bubbles can be removed from the electrode, reducing the Ohmic resistance accordingly.

As has been already demonstrated, the magnetic fields of suitable placed permanent magnets are capable of producing a Lorentz force density accelerating the electrolyte near the electrode. Fig. 3 shows Laser Doppler Anemometry measurements near the gill of a model louver. In this case louver and counter electrode have been immersed in a
larger vessel containing a 0.2 molar NaOH. The reaction has therefore been a water electrolysis. Only one gill of the anode was equipped with permanent magnets, the velocity measurements took place in the plane in front of this gill. \( y \) denotes the wall distance and \( u \) the mean velocity. In the case without Lorentz force a wall jet can be seen that is driven by the rising oxygen bubbles evolving at the anode. The velocity is positive in the \( y \) range covered in the diagram. In the direct vicinity of the anode, velocity measurements have been prevented by the high void fraction, which caused an intensive light scattering. If the Lorentz force points upwards, the mean velocity gradient becomes steeper near the electrode. For \( y \geq 1.5 \text{mm} \) a back flow occurs. In the case that Lorentz force and buoyancy are opposed, the velocity farther away from the wall increases compared to the unforced case. At first sight, this seems paradoxical. A possible explanation could be the redistribution of oxygen bubbles due to the downward force: the bubbles migrate from the region near the electrode into the outer fluid and accelerate it due to buoyancy.

So far complementary measurements of the cell voltage are still to be performed. Therefore the presumed effect on the energy consumption has not been verified, but could be concluded from the pertinent literature.

4. Conclusions

Magnetic fields in conjunction with present electric fields may be used to influence significantly the momentum transfer in electrochemical cells and reactors. The effects shown here demonstrate the large influence of magnetic fields of moderate strength and extension on mass transfer and flow conditions in the cells.
References


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