ELECTROCHEMICAL RESPONSE IN PRESENCE OF MAGNETIC FIELD. KINETIC AND DIFFUSION PROCESSES

O. Devos[a], O. Aaboubi[b], J. Amblard[b], J.P. Chopart[b] and A. Olivier[b]

[a] Laboratoire de Physique des Liquides et Electrochimie
LPLE - UPR15 – CNRS, University Pierre et Marie Curie
4, Place Jussieu, 75252 Paris cedex 05 - France
[b] Dynamique des Transferts aux Interfaces
DTI – UMR 6107 – CNRS, UFR. Sciences
BP 1039, 51687 Reims cedex 2 – France

INTRODUCTION

An homogeneous magnetic field B applied parallel to an electrode surface increases the electrolytic current by generating a controlled magnetohydrodynamic (MHD) convection at the electrode/electrolyte interface. It is well known that diffusion limiting current increases with the magnetic flux density. We propose to show the results obtained on various electrochemical systems in presence of B. The mass transport process was studied and the electrochemical kinetic as well by using stationary and transient techniques such as electrochemical impedance spectroscopy (EIS) and MHD transfer function.

RESULTS AND DISCUSSION

Reversible electrochemical system

A diffusion limited system was investigated, *ie*, oxydo-reduction of potassium ferri-ferrocyanide. According to the diffusion-convection equations at steady-state, the limiting current was proportional to $B^{1/3}$ and $C^{*4/3}$ where C* is the bulk concentration (Fig.1) (1).

Mixed electrochemical system

Figure 2 shows the impedance diagrams carried out for zinc electrodeposition from a basic media at 3/4 of the limiting current. The diagrams exhibits two capacitive loops. In the high frequency range, the semi-circle characterizes the kinetic of charge transfer whereas the capacitive loop in the low frequency range highlights the diffusion process. Both loops were influenced by B. This investigation led the diffusion mechanism to be identified. Moreover, it was shown that the electrochemical kinetic was not modified in presence of B (2).

Irreversible electrochemical system

Nickel electrodeposition from a Watt's bath is known to be not limited by the mass transport process. Nevertheless, Figure 3 shows that B influences the inductive loop in the low frequency range which characterizes the adsorption process. This investigation showed that the MHD convection increased the mass transport of protons involved as a secondary reaction in the electrochemical mechanism (3).

The lateral convection generated by B in the vicinity of the electrode surface was highlighted by SEM image of a nickel deposit in presence of an organic inhibitor (Fig.4) (4).

CONCLUSION

This work showed that the electrolytic current modifications created by B, even very confined, resulted either directly or indirectly from convection generated thereby. Magnetic field was without any effect on the charge transfer process.

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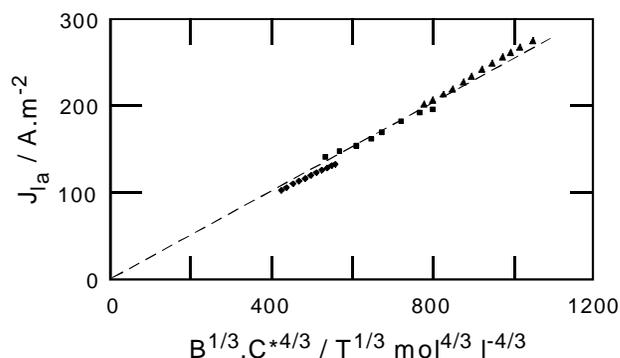
Figure 1. Anodic limiting current against $B^{1/3}.C^{*4/3}$ parameter. (♦) C*= 0.15M, (■) C*= 0.2M, (◄) C*= 0.25M.
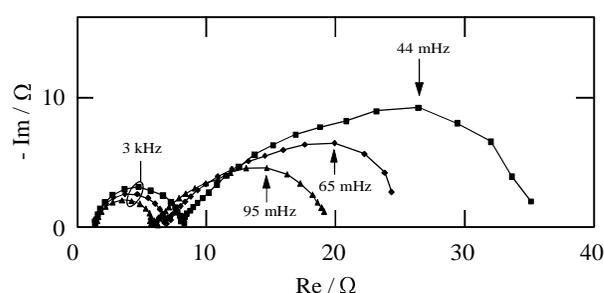
Figure 2. Electrochemical impedances in the Nyquist plane for various B. (■) B = 0.3 T, (♦) B = 0.6 T, (▲) B = 0.9 T. [Zn(II)] = 0.2 M, [KOH] = 7 M, η = - 70 mV.
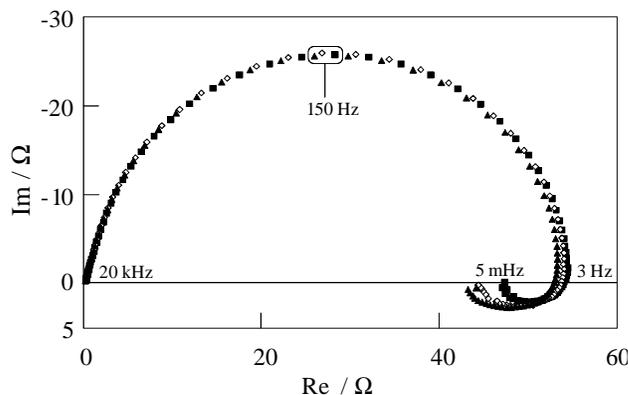

Figure 3. Electrochemical impedances in Nyquist plane for nickel electrodeposition. Watts solution, T = 30°C, E = - 0.84 V *vs* SCE. (■) B = 0, (◇) B = 0.3 T, (▲) B = 0.6 T. The electrolyte resistance has been subtracted.

Figure 4. SEM image of H_2 bubble traces on a stationary nickel deposit prepared at -1 V/SCE from a Watts bath containing 5 mM 2-butyne-1,4-diol - B = 0.6 T.