

TEC-TRANSFER FUNCTION ANALYSIS OF NICKEL ELECTROCRYSTALLIZATION

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Temperature is well known as a parameter capable of exerting dramatic effects on processes taking place at the electrode/electrolyte interface. Drastic alterations of Faradaic currents can thus be produced as temperature is varied, whatever the kind of cell used, isothermal or not. For the particular case of mass-transport-controlled systems, huge increases of limiting currents have been reported [1].

Hence the thermo-electrochemical transfer function (TECTF) has been experimentally studied and compared to the theoretical model [2, 3], although its use has been so far mainly restricted to fast systems under mass-transport control.

It was deemed necessary to broaden the field of TECTF applications by studying a system known to be irreversible, namely nickel electrocrystallization from a Watts solution. A temperature modulation of the potentiostatically-controlled electrode allows the frequency analysis of the current response to be conducted. The potentiostatic TECTF $(\partial I/\partial T)_E$ that had already proved fruitful for mass-transport analysis reveals as well to be highly outstanding for the analysis of adsorption phenomena [4].

RESULTS

EIS impedance

A Nyquist plot of EIS results leads to a good overlap, frequency for frequency, between the case of the isothermal cell and that of the non-isothermal cell (Fig.1). Although a slight frequency variation may be observed, the polarisation resistance (the low frequency real point) is strictly the same for both cases. We show below that such a slight variation, hardly quantifiable from the mere EIS data, becomes more obvious with the TECTF analysis.

TEC-Transfer function

The comparison (Fig.2) between the Nyquist plots of calculated and experimentally measured $(\partial I/\partial T)_E$ leads to one single loop (for a given potential) exhibiting the same amplitude. Such a loop results from the adsorption state of the working electrode.

The analysis of the TECTF transfer function in the case of Ni electrocrystallization from a Watts solution allows the adsorption step to be isolated and quantified with a far better accuracy than using conventional EIS methods. Nevertheless, the electrochemical parameters deduced are quite close to those previously determined in the case of an isothermal cell [5].

REFERENCES

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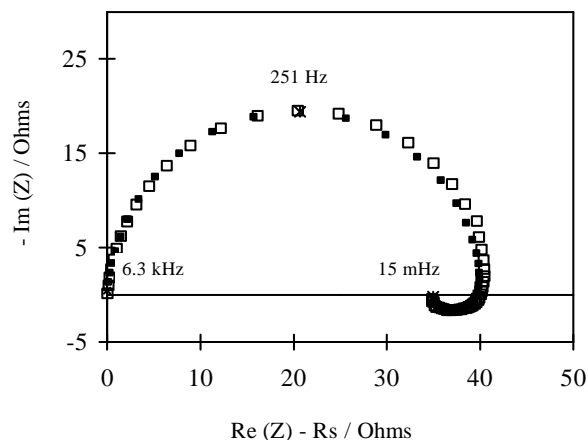


Fig.1 - Comparison between EIS loops obtained either with an isothermal cell (■) maintained at $T_b = 307$ K, or with a non-isothermal cell (□) for the same electrode temperature $T_e = T_b + \Delta T = 307$ K. $E_p = -0.85$ V/SCE.

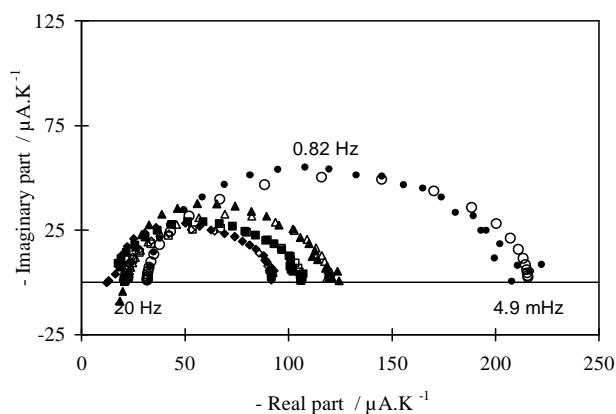


Fig.2 - Confrontation between TECTF data calculated (open symbols) and TECTF experimental data (dark symbols) obtained at $T_b = 299$ K & $\Delta T = 2.5$ K, for various values of the cathodic potential:
(◆) - 0.9 V/SCE; (■) - 0.93 V/SCE;
(▲) - 0.95 V/SCE; (●) - 1.2 V/SCE.