

Modulation of Double Layer Capacitance by EIS Measurements

R. Antaño-Lopez, M. Keddám and H. Takenouti

UPR 15 – CNRS, P and M Curie University,
C.P. 133, 4 Place Jussieu, 75252 Paris Cedex 05, France

Introduction

The coupling of double layer capacitance C_d and the faradaic impedance Z_F is one of the main topics that remain yet badly studied. Generally, when Z_F was derived on the basis of reaction mechanism, a constant C_d is connected in parallel. The comparison between experimental EIS data (Z_{ex}) and calculated one allowed validating the reaction mechanism [1]. However, It is often observed experimentally that C_d depends upon the *dc* potential. Recently, we devised a new experimental setup that allows measuring simultaneously the modulation of double layer capacitance at the frequency at which the electrode impedance is carried out [2]. We have demonstrated then that C_d changes indeed with a perturbing *ac* signal and that the time constants observed in Z_{ex} and C_d are essentially the same. Therefore, the measurements of C_d modulation may constitute a new alternative method to evaluate the surface relaxation processes of reaction intermediates.

To validate this hypothesis, C_d -modulation measurements at an ideally polarized interface (Hg electrode in 1M KCl) and a fast redox system where no adsorption process is believed to take place, (5 mM ferri-ferro cyanide on Pt electrode in 1M KCl) were performed.

Principles

The composite potential signals, $\Delta E_{Cd}(\Omega) + \Delta E_{EIS}(\omega)$ was applied at the electrode interface and the current response to these two signals was recorded. ω is a low frequency *ac* signal (100 to 0.01 Hz) at which Z_{ex} was measured. Ω is a high frequency *ac* signal (1 or 10 kHz) used for measuring the modulation of C_d . One may thus express this response as $\Delta C_{\Omega}(\omega)/\Delta E_{\omega}$. Details of the experimental setup and signal processing were described in the reference [2].

Results and Discussion

3.1 Ideally polarized electrode system.

Hg was filled in a U shape PTFE tube and immersed in 1M KCl. A semi-spherical Hg surface was used as the working electrode, and its surface area was 0.21 cm². By varying *dc* polarization potential, C_d at 1 kHz and its derivative $\Delta C_{\Omega}(\omega \rightarrow 0)/\Delta E_{\omega}$ were determined from admittance ($1/Z_{ex}$). It is worth recalling that C_d measurements may allow determining the zero charge potential (ZCP) if it is postulated that C_d is minimum at this potential [3].

When n-butanol was added into the solution, desorption of this compound was observed by C_d two peaks at both sides of potential away from PCZ. The modulation of C_d was measured at the cathodic desorption potential. The relaxation of C_d was observed in a low frequency range ($f < 1$ mHz). A further investigation is however necessary to attribute without ambiguity the observed relaxation phenomenon to the adsorption of n-butanol.

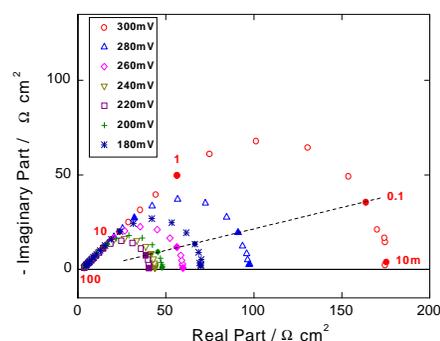


Figure 1: Pt / 5mM ferri-ferro cyanide in 1M KCl.
The rotation of disk = 600 rpm.

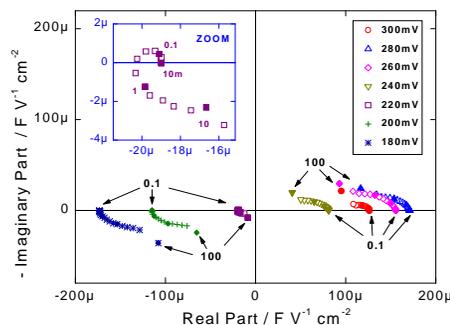


Figure 2: $\Delta C_{\Omega}(\omega)/\Delta E_{\omega}$; $\Omega=1$ kHz, $\Delta E = 10$ mV rms.

3.2 Fast oxygenation – reduction process.

The redox process of ferri-ferro cyanide is certainly one of the most frequently studied systems in electrochemistry because of its high reversibility and also its remarkable reproducibility. The charge transfer is believed to take place directly without adsorption of reaction intermediate. This is the reason why we selected this system to examine whether the modulation of C_d will occur in this system.

Figure 1 presents Nyquist plot of results obtained near the equilibrium potential (0.22 V vs. SCE), and a typical shape of a fast redox reaction where the Nernst-type diffusion impedance can be seen.

Figure 2 presents the modulation of C_d registered simultaneously to the results displayed in Figure 1. The sign of $\Delta C_{\Omega}(\omega)/\Delta E_{\omega}$ changes with the direction of current flow and the relaxation time constants are close to the diffusion process. An unexpected fact is that the equilibrium potential and ZCP (0.225V) defined as $\Delta C_{\Omega}(\omega)/\Delta E_{\omega} = 0$ are very close. A slow relaxation process, illustrated in the insert seems to correspond to the desorption of species that is not involved in the reaction examined here, and may be attributed to that of the Prussian blue as suggested by [4].

References

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