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Double layer capacitance of the platinum group metals in the double layer region

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Abstract

The interfacial impedance for the platinum-group metals, in simple binary electrolytes, in their so-called double layer region, is generally assumed to be ideally capacitive. In this communication, mainly addressing the Ir(1 0 0) / 0.1 M HCl system, we demonstrate that this is not necessarily the case when the anion of the solute is specifically adsorbed on the electrode. The frequency dependence is attributed to the relatively slow exchange of anions at the outer Helmholtz plane with the adsorbed ones (i.e. those at the inner Helmholtz plane).

Keywords: Interface; Impedance; Adsorption; Iridium; Double layer capacitance

1. Introduction

Consider a platinum-group metal electrode immersed in an aqueous electrolyte. If within the potential range bordered by the hydrogen- and oxygen evolution reactions no Faradaic reaction proceeds, the cyclic voltammogram (CV) consists of various adsorption-related peaks/humps separated by region(s) of low currents, called double layer region(s). A textbook example is the CV of polycrystalline platinum in sulphuric acid solution: the hydrogen-adsorption and oxide-formation regions are separated by an approximately 0.2 V wide flat double layer region [1]. A similar, but a somewhat better defined, widely studied system is Pt(1 1 1) in 0.1 M $HClO_4$ [2]: in this case the double layer region separates those of hydrogen and hydroxide adrption. In this communication, we demonstrate by voltammetry and impedance measurements, using as an example the Ir(1 0 0) + 0.1 M HCl system, that for the platinum group metals – for which specific adsorption is omnipresent – even in the double layer region ion adsorption may give a relevant – sometimes dominant – contribution to the double layer impedance/capacitance; in other words, the dynamic behaviour of the double layer region is mostly determined by the adsorbed ions.

2. Impedance aspects of ion adsorption

Consider the double layer capacitance, C, of a metal electrode in contact with an aqueous electrolyte. Assume that at potential E there is no Faradaic reaction proceeding at the interface, then C is calculated from the impedance spectrum, $Z(\omega)$ by $C(\omega) = 1/([Z(\omega) - Z(\omega \to \infty)]Ai\omega)$, where ω, $Z(\omega \to \infty) = R_s$, A, and i are the angular frequency, the solution resistance, the electrode area, and the imaginary unit, respectively. For an ideal case the $C(\omega)$ complex function is a frequency-independent real constant. Such a case can be experimentally realized with "inert" electrodes of the uniform surface immersed in a solution from which no specific adsorption takes place (examples: Hg in NaF solution [3] and Au(1 1 1) in $KClO_4$ solution [4]). However, there are several factors causing the $C(\omega)$ function to be non-constant; in the context of the present paper, the most important is the adsorption of solute species. The frequency

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dependence can be traced back to that of the surface excess of the adsorbate, Γ which does not immediately follow the interfacial potential change. From the mathematical point of view there exist two simple cases:

1. The solution contains a non-adsorbing electrolyte – the base electrolyte ensuring bulk conductivity – and the adsorbate is present as a minor component. The theory for this case (developed by Frumkin and Melik–Gaykazyan [5] and others [6–8]) leads to an impedance function which is the same as that of the equivalent circuit of Fig. 1a; the shape of the $C(\omega)$ function – depending on the adsorption rate, manifested in the equivalent circuit as R_{ad} and W- is an arc (Fig. 1b). This model could be used for the interpretation of the impedance spectra of various adsorption processes on Hg [9,10] and on the single crystal electrodes, like those of halide ions on Au [4,11], and of hydrogen, hydroxide and sulphate adsorption on Pt(1 1 1) [12–15].
2. One constituent of the base electrolyte – in most cases the anion of a binary electrolyte – is specifically adsorbed on the electrode in a certain potential range. The theory of this case (originally developed by Dolin and Ershler [16]) predicts a semi-circular $C(\omega)$ spectrum (like the uppermost arc in Fig. 1b), and accordingly, the diffusional element W is missing in the equivalent circuit of Fig. 1a. This is so, because the adsorbing species is a majority component of the electrolyte, its transport towards the electrode surface proceeds by migration rather than by diffusion. One can find many such impedance/capacitance spectra in the literature; most of them are taken on various – polycrystalline or single crystalline – Pt electrodes in acidic solutions [17–22]. These spectra exhibit semi-circular capacitance arcs, or one of the two limits due to the limited frequency range of the impedance measurement.

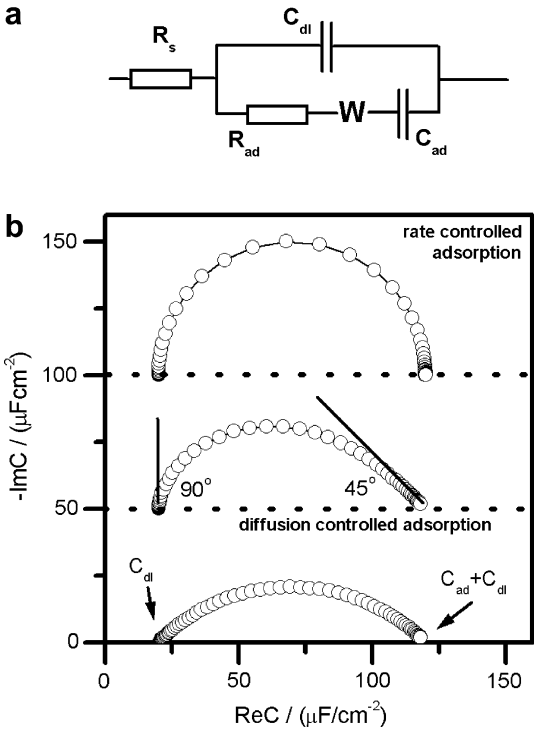

Fig. 1. (a) The equivalent circuit of the interface when there is an adsorbing component of minor concentration in a non-adsorbing base electrolyte. R_s and R_{ad} are the solution and adsorption resistances, C_{dl} and C_{ad} are the double-layer and adsorption capacitances, respectively, W is the diffusional (Warburg) impedance. (b) Capacitance spectra (with clockwise decreasing frequencies) due to adsorption at slow, medium, and fast rates. The spectra are shifted vertically for sake of clarity.

3. Experimental

The cyclic voltammograms, the CO displacement charges, and the impedance spectra presented in the forthcoming part have been measured on one and the same single crystal electrode, by employing the same experimental procedures as in our previous publications, in particular in the ones dealing with Ir single crystal electrodes [23,24].

4. Results and discussion

In Fig. 2 the results for Ir(1 0 0) in 0.1 M HCl solution are shown. In the voltammograms two adsorption regions are seen, bordering a flat double layer region between 0 V and 0.3 V. In the same graph the surface charge is also plotted, as calculated from the current during the anodic scan and using the integration constant obtained from a CO charge displacement measurement (the potential of zero total charge, $pztc = -0.13$ V vs. SCE). As this charge - potential curve reveals, the surface charge within the double layer region (denoted by C and D) is around 200 μC/cm^2, slightly increasing in the positive direction. Taking into account that one full monolayer charge on Ir(1 0 0) is 218 μC/cm^2 (calculated from basic data of Ir), we may conclude that about 90–100% of a complete ad layer is present within the double layer; most probably the adlayer is formed from chloride ions. This conclusion is supported by two findings: (i) the two adsorption regions – attributed to the replacements of H^+_{ads}/Cl^-_{ads} and $Cl^-_{ads}/\ OH^-_{ads}$ – shift in the opposite direction with Cl^- concentration (Fig. 2b); and (ii) one can get almost indistinguishable CVs in 0.1 M HCl and in 0.1 M HCl + 0.1 M $HClO_4$ solution (Fig 2b, curves c and d). Since the perchlorate anions are known to adsorb on the metal surface much weaker than the chloride, we can again conclude that all features – including those of the double layer – are due to the chloride content of the solution.

Impedance spectra measured in the double layer region and plotted as complex capacitances yield arc-like spectra (Fig. 3a); these spectra can be very well fitted[1] with the equivalent circuit of Fig. 1a. However, W appears as an empirical element of $(i\omega)^{-1/2}$ frequency dependence, rather than an element due to diffusion. In the present case, W obviously has nothing to do with diffusion, since the ions

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[1] The χ^2 values were found always smaller than 10^{-4}, and little if any systematic deviations between measured and fitted spectra were observed.