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Detection of 2D phase transitions at the electrode/electrolyte interface using electrochemical impedance spectroscopy

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ABSTRACT

The capacitance of the electric double layer, C_{DL} , formed at the electrode/electrolyte interface is generally determined by electrochemical impedance spectroscopy (EIS). However, C_{DL} values obtained using EIS data often depend on the *ac* frequency of the potential perturbation used in EIS. The reasons for the observed frequency dispersions can be various, and hence extracting valuable information about the status of the electrified interface is not possible with the required certainty. In this work, using well-understood electrochemical systems, namely Pt(111) electrodes in contact with a series of acidic sulfate ions containing electrolytes, we provide strong evidence that 2D phase transitions in the adsorbate layers and, in general, structural effects at the electrode/electrolyte interface are in many cases responsible for the frequency dispersion of the double layer capacitance. These empirical findings open new opportunities for the detection and evaluation of 2D phase transition processes and other structural effects using EIS, even in presence of simultaneously occurring electrochemical processes. However, further theoretical elaboration of this effect is necessary.

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1. Introduction

Research techniques which use alternating current (*ac*) probing signals are among the most informative non-destructive methods in physical chemistry and electrochemistry. Electrochemical impedance spectroscopy (EIS) is often used as an indispensable tool for in-depth characterisation of the electrode/electrolyte interface [1–5]. EIS allows for the elucidation of physical models of electrochemical systems and for obtaining detailed information about processes taking place simultaneously at electrified interfaces.

Conventional EIS is based on the determination and analysis of two parameters at different *ac* probing frequencies: (i) the absolute value of the impedance, $|Z|$, which is the ratio between the amplitudes of the probing *ac* signal (e.g. electrode potential) and the response (e.g. *ac* current), and (ii) the phase (time) shift, δ , between the former and the latter. Due to specific properties of electrochemical systems, both $|Z|$ and δ depend on the frequency, ω , of the *ac* signal. The ultimate goal of EIS investigations is to solve the inverse problem [6]: it is necessary to find a suitable *physical* model of the system and to estimate its parameters using the impedance data as a function of the frequency, $|Z|(\omega)$ and $\delta(\omega)$.

According to the classical approach developed by Dolin and Ershler in 1940 [7] and by Randles in 1947 [8], a general EIS model of the electrochemical interface consists of at least three major parts (Fig. 1). The first part is related to the impedance of the electrolyte Z_{el} , which can often be approximated by a resistance if the electrolytes are liquids: $Z_{el} = R_s$. The second part is related to the impedance due to electrochemical processes involving the interfacial charge transfer (Faradaic processes) with the associated impedance Z_F . It should be noted that particular equations describing Z_F depend on many factors, such as the mechanism of the electrochemical reactions, their kinetics or mass transport modes [9]. Finally, the third part of the model is the impedance of the interface itself, Z_i . The response of the latter is normally of capacitive nature. The Dolin–Ershler–Randles approach is to express the model using a formula for the total impedance, Z_{tot} : $Z_{tot} = Z_{el} + (Z_i^{-1} + Z_F^{-1})^{-1}$, which corresponds to a general equivalent circuit as shown in Fig. 1. The parallel combination of Z_F and Z_i reflects the underlying hypothesis that the current due to electrochemical processes can be roughly considered as a “leakage” of the interfacial “capacitor”.

Whilst theories describing Z_F for various reactions and mechanisms are relatively well developed [3,10,11], the interpretation of the interfacial impedance (Z_i) is unfortunately not straightforward. The main constraint is that the *ac* perturbation probing the electrode/electrolyte interface reveals that a seemingly capacitive behaviour of the so-called interfacial electric double layer often does not obey the rules of an ideal capacitance and it turns out that the measured capacitance of the double layer depends on the applied *ac* frequency. This empirical fact can be formally described using a so-called constant phase element

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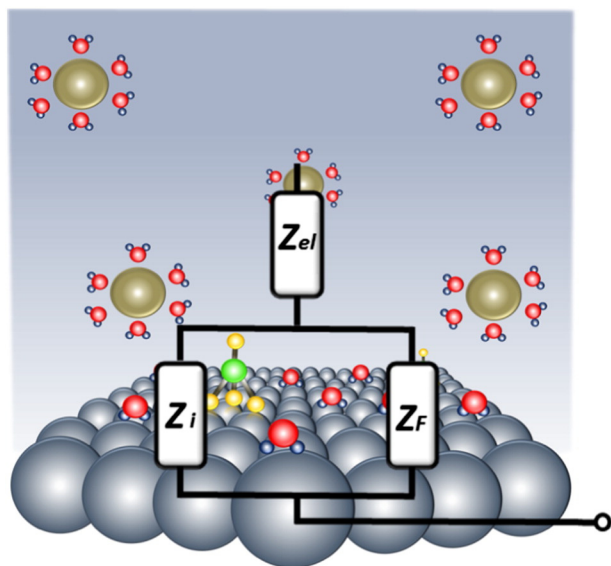


Fig. 1. A generalised physical model (equivalent electric circuit, EEC) describing the electrode/electrolyte interface according to the Dolin–Ershler–Randles approximation. The impedance spectra of electrochemical interfaces contain the response of the ionically conducting electrolyte, Z_{el} , the response of the interface itself, Z_i , and the contributions originating from electrochemical (Faradaic) reactions, Z_F .

(CPE) with a specific formula given as $Z_i = C_{DL}^{-1}(j\omega)^{-\varphi}$, where C_{DL} is the parameter, which is proportional to the double layer capacitance, and $\varphi \leq 1$ is the CPE-exponent, which is directly related to the above-mentioned “frequency dispersion”. When $\varphi = 1$, the CPE behaviour corresponds to that of an ideal capacitor. Remarkably, responses of numerous systems of different natures can be *formally* represented by a simple exponential formula as presented above [12]. Nevertheless, the above-discussed CPE phenomenon complicates the analysis of EIS data and significantly decreases the informative power of the method itself.

In different periods of the development of EIS, numerous hypotheses and theories were proposed to explain the CPE behaviour of the double layer [9,12–19]. The essential idea of those hypotheses is that the observed non-ideal behaviour is exclusively due to a “chaotic performance” of the double layer caused by one of the following reasons: (i) a low concentration of working electrolyte or the presence of contamination [9,19], (ii) roughness of electrodes [9,14,15,17], (iii) disturbing electrochemical (Faradaic) reactions or non-uniform (or fractal) properties of the electrodes themselves [9,15,17,18], and (iv) other specific phenomena and effects which can be classified as measurement “artefacts”. Unfortunately, numerous experimental facts suggest that none of these theories can explain the whole variety of experimental observations on this subject. Moreover, some of them even contradict those concepts. Likely, there could be more than one reason for the frequency dispersion in each particular case.

Concerning the response of electrified interfaces between solid electrodes and liquid electrolytes, recent experiments with well-defined single crystal metal electrodes provide evidence that in many cases the CPE-behaviour of the electrochemical interface is not a consequence of its “chaotic performance”. On the contrary, it is likely a consequence of structural effects at the boundary between electrodes and electrolytes. Pajkossy [13], Kolb and Pajkossy [20] and Motheo et al. [21] suggested that 2D and 3D structuring effects in the electric double layer caused by adsorbates hinder its ability to respond ideally to the *ac*-probing.

In this manuscript, we extend our previous work on the elucidation of the nature of the *ac*-response of the electrochemical interface [22–24] using one of the most well understood model systems in electrochemical science, namely the interface between Pt(111) electrodes and

aqueous sulfuric acid solutions. Specifically, we further test the hypothesis of Pajkossy, Kolb and Motheo et al. by changing important parameters in this system such as the electrolyte concentration, the nature of the electrolyte components and the presence of disturbing Faradaic reactions. Our findings provide probably the best evidence confirming the above-mentioned hypothesis that structural effects at the electrode/electrolyte interface govern the CPE-behaviour during *ac*-probing. These findings open up new opportunities for the detection of 2D phase transitions and other structuring effects using impedance spectroscopy.

2. Experimental

Two Pt(111) crystals (MaTeck, Germany, 5 mm diameter, oriented better than 0.1° , roughness 30 nm) were used to ensure high reproducibility of data. The electrochemical cell for preparation and characterisation of single crystal electrodes was described in detail elsewhere [25]. Pt(111) electrodes were selected instead of Au(111) as the former exhibits much lower surface mobility of Pt atoms at room temperature, simplifying data interpretation. The following chemicals were used to prepare working electrolytes: H_2SO_4 (Merck, Suprapur) and K_2SO_4 (Aldrich, 99.99% trace metal basis).

The EIS measurement scheme was the same as in Ref. [24], Frequencies between 30 kHz and 1 Hz with 5 mV amplitude of the probing signals were used. Issues related to modelling and fitting of large experimental EIS datasets are reported in detail elsewhere [26]. The quality of the measured impedance spectra was evaluated using the “linear” [27] and “logarithmic” [28] Kramers–Kronig check procedures. The output of the fitting procedure was controlled by the root-mean-square deviations and estimated individual parameter errors using home-made “EIS Data Analysis 1.0” software to ensure the validity of the model and correctness of the fitting, as described in detail elsewhere [29,30].

A mercury–mercury sulfate reference electrode (MMS) was kept in a separate compartment and separated from the working electrolyte with an ionically conducting ceramic insert. A polycrystalline Pt wire was used as counter electrode. All potentials are referred to the RHE scale. A VSP-300 potentiostat (Bio-Logic, France) was used to control the electrochemical measurements. Measurements involving rotating disc electrodes (RDE) were performed using a Pine RDE 710 instrument (USA).

3. Results and discussion

3.1. Cyclic voltammetry and impedance analysis

Fig. 2 shows a cyclic voltammogram typical for Pt(111) single crystal electrodes in contact with 0.05 M H_2SO_4 electrolyte. The voltammogram reveals several processes involving the interfacial charge transfer at different electrode potentials. Broad peaks between 0.05 V and ~ 0.35 V disclose surface limited adsorption and desorption of hydrogen. The potential region between ~ 0.35 V and ~ 0.55 V is attributed to adsorption/desorption of (bi)sulfate anions with a pair of sharp peaks due to order/disorder phase transitions in the (bi)sulfate adsorbate layer to form predominantly a $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ superstructure with co-adsorbed H_2O molecules at the surface with an anion coverage of 0.2 monolayer (ML), as indicated in Fig. 2. It should be noted that the above-mentioned superstructure co-exists with a denser adsorbate structure, namely a (3×1) superstructure with a corresponding (bi)sulfate adsorbate coverage of $1/3$ ML [31]. A pair of relatively small peaks in the potential region between approximately 0.7 V and 0.9 V is associated with an order/disorder phase transition, as revealed by electrochemical scanning tunnelling microscopy [31].

In order to explore the potential regions where the order/disorder and disorder/order phase transitions take place, impedance spectra have been recorded between 0.37 V and 0.92 V. In this potential region, the physical model of the interface (expressed in terms of EEC) is

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