



# Immersion measurements of potential of zero total charge (*pztc*) of Au (100) in an ionic liquid



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## ABSTRACT

In order to determine the potential of zero total charge (*pztc*) we measured charging current transients upon immersing Au(100) into an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF<sub>6</sub>). In the current–time transients two sections could be identified, one attributed to double-layer charging, the other to spurious Faradaic or adsorption processes. The *pztc*, as determined from the short-time section, was found to be 0.4 V vs. Ag/AgCl.

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## 1. Introduction

The potential of zero charge, *pzc*, is one of the basic properties of the electrochemical double layer: it is the potential at which the charge density of the metal is zero. Mathematically, it represents an integration limit when the surface charge of the metal in a metal | electrolyte solution interface at electrode potential  $E$ ,  $q^M(E)$ , is calculated from the double layer capacitance. Hence its value is essential whenever the double layer structure is attempted to be characterized by calculating surface excesses, or simply to determine the sign of the electrode's charge at a given potential.

The system studied here comprises an ionic liquid (IL) in contact with a single-crystal Au(100) electrode. ILs are defined as salts which are molten at ambient temperatures [1–4]. For electrochemists, the air- and water-stable ILs, mostly the imidazolium-based ones [5] appear to be rather interesting, mostly because of their broad electrochemical stability window and unique properties. This is why 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIPF<sub>6</sub>) is targeted in the present study. The other constituent is a well-defined crystal face of gold: Au(100). The Au(100)|BMIPF<sub>6</sub> electrode was found to be a good model system for the characterization of metal|ionic liquid double layers; hence we

have previously reported the various dependencies of the interfacial impedance [6,7] along with one sort of *pzc* measurements via immersion [7]. The subject of the present report is the repeating of the latter experiments with much better time resolution and accuracy along with the interpretation of the charging curves.

## 2. Determination of the *pztc*

Potentials of zero charge are almost century old concepts introduced by Frumkin and Gorodetskaya [8]; for well-established monographs written by Frumkin and coworkers see refs. [9,10]; a recent review of *pzc* of Pt-group metals is ref. [11]. Here, for the sake of brevity, we refrain from defining *pzc* in terms of thermodynamics, as it is done therein. Instead, we give operational definitions for the two classes of the *pzc*. The first case: the potential of zero free charge, *pzfc*, which we will see is not in the scope of the present paper. In certain special cases, this quantity can be determined as a minimum location on the  $C(E)$  curves of e.g. Hg in dilute NaF solutions [12]; the  $C(E)$  curve is interpreted by the Gouy–Chapman theory [13–15].

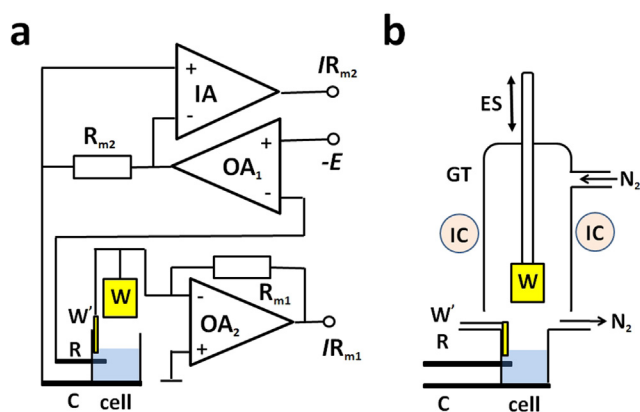
The second concept: the potential of zero total charge, *pztc*, is related to the electronic charge of the metal when the double layer is formed or eliminated. It can be defined through a measurement procedure as follows: Consider a metal and an electrolyte initially separated from each other, while a certain voltage is maintained between them. Technically this can be done, as illustrated in Fig. 1a, using a usual electrochemical cell with reference (R) and counter (C) electrodes, and a working electrode W initially out of the electrolyte. The potentiostat is switched on and keeps a potential

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**Fig. 1.** (a) Electrical scheme of the *pztc* measurement. The potentiostat is represented by its two main operational amplifiers:  $OA_1$  provides potential control and  $OA_2$  is a current-to-voltage converter. An alternative current-to-voltage conversion is performed by the  $R_{m2}$  resistor and the  $IA$  instrumentation amplifier in the counter electrode's circuit.  $C$ ,  $R$  and  $W$  stand for the counter, reference and working electrodes, respectively.  $W'$  is a very small auxiliary working electrode. (b) The immersion experiment apparatus. The counter electrode  $C$ , a gold foil, constitutes the cell bottom; the  $R$  quasi-reference electrode is a AgCl-coated Ag wire,  $W'$  is a thin gold wire. The Au(100) single crystal,  $W$ , is attached to an elevator shaft ( $ES$ ), thereby it can be lifted up and down within a glass tube,  $GT$ . Annealing of the Au(100) single crystal can be performed by using the  $IC$  induction coil under  $N_2$  atmosphere.

difference  $E$  between  $R$  and  $W$ . We stress that the potentiostat keeps  $E$  even if the electrode is out of the electrolyte (note the very small “auxiliary” working electrode  $W'$  connected parallel to  $W$  as shown in Fig. 1a). When  $W$  is immersed in the electrolyte, the double layer is formed, and its charge is supplied by the potentiostat in the form of a current transient,  $I(t)$ . Provided that no Faradaic reaction proceeds on  $W$ , the overall electronic charge on the metal ( $q^M = q$ ) is the integral of  $I(t)$ . Thus, one has to measure  $q$  at various potentials; at the *pztc*,  $q(E = pztc) = 0$ . Such a measurement is simple in principle, however difficult in practice, because the metal surface must be completely clean and oxide-free, and Faradaic reactions must be absent. Based on the idea of Frumkin [16], this operational definition of the *pztc* was first employed for real measurements by Jakuszewski and coworkers [17,18]; for the scarce attempts to determine the *pztc* this way in aqueous electrolytes see Refs. [19,20]; in our previous double layer studies with ionic liquids *pztc* measurements were also carried out [7,21].

Two comments are due here: (i) Apart from two exceptions (see below) all current–potential–time measurement methods in electrochemistry provide information on charge changes of the electrodes rather than on the charge itself. The two exceptions are: (a) when the double layer is created (like in the course of the above immersion measurement) and (b) when the double layer is completely eliminated. The CO charge displacement method [22] – often used to determine the *pztc* of Pt-group single crystalline electrodes – is an approximant of this second case: because of the incomplete elimination of the double layer certain corrections [23,24] must, however, be applied. (ii) It is difficult to rule out the occurrence of Faradaic reactions. The present manuscript shows a way to distinguish between charging and Faradaic currents.

### 3. Experimental

The BMIPF<sub>6</sub> ionic liquid was the same, cleaned and handled in the same way, as used in our previous studies [6,7]; the cylindrical Au(100) crystal of 4 mm diameter was purchased from MaTeck GmbH, Jülich, Germany. The experiments were carried out in a dedicated setup sketched in Fig. 1b whose main elements are the

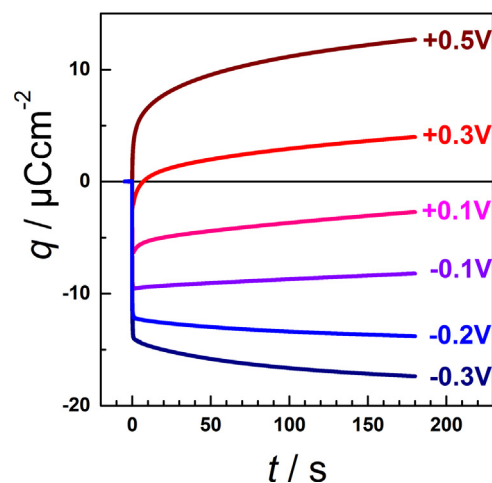
Kel-F<sup>TM</sup> cell of about 0.5 mL volume and a home-made computer-controlled moving tool (“elevator”), allowing the electrode to be immersed in the IL in a fast, controlled way to form a hanging meniscus. The electronic instruments, analog-digital-converters (ADCs) comprised a number of home-made elements. To measure current with sufficient accuracy both at the start and at the end of the quickly decaying current transients, we applied two parallel current meters, as illustrated in Fig. 1a. The short-time part of the transient has been measured as a voltage across a 10 kOhm or a 100 kOhm resistor in the counter electrode's circuit, whereas the long-time part has been recorded from the 10 Hz-filtered output of the current-to-voltage converter with  $10^7$  V/A amplification. The ADCs' data have been averaged in 20 ms intervals in order to reduce the noise of line (50 Hz) origin.

Using the setup of Fig. 1b,  $W$  could be lifted up to the position of the induction coil,  $IC$ , powered by a Himmelwerk 2000 RF power supply. Here annealing of the gold electrode was accomplished under nitrogen stream typically for 1 minute at 850 °C (as checked by an Impac ISR-12-Lo pyrometer) followed by cooling for 2 minutes. Afterwards  $W$  was lowered to just above the electrolyte; the potentiostat and the current recording was switched on, and the elevator was moved slowly downwards (by about 0.1 mm/s) until the electrode touched the electrolyte. Upon detection of this event (in the form of a sudden jump in the current signal), the elevator lifted up the electrode by 1 mm thereby forming a hanging meniscus. The current was recorded for further 5 minutes after the electrode came to rest. As a finishing step of the experiment, the cleanliness of the system was checked by taking a CV of 50 mV/s in the potential range of – 400 mV to +600 mV, yielding CVs similar to those shown in Fig. 1 of Ref. [6]. This sequence was performed as a function of potential.

The electrode immersion process was followed by a high-magnification video camera. By a frame-by-frame analysis of the recorded footage we could confirm that the formation of the hanging meniscus ends within 3–4 frames, *i.e.* after about 0.15 s, being the time resolution of the measurement. This is about one order of magnitude faster than in our previous experiments [7,21] when the metal/electrolyte contact was accomplished by simply filling up the cell. By inspecting the video frames, we found no sign of electrolyte creeping onto the cylindrical wall of the gold electrode.

### 4. Results

The integrated current transients are shown in Fig. 2. Unlike for the case of measurements in aqueous solutions [21] the integrated



**Fig. 2.** Integrated immersion current transients at various potentials.

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