

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

Claus Müller, Soma Veszteg^{1,2}, Tamás Pajkossy^{1,3}, Timo Jacob¹

Institute of Electrochemistry, University of Ulm, 89069 Ulm, Germany

Helmholtz-Institute-Ulm (HIU), Helmholtzstrasse, 89069 Ulm, Germany

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 (BMIPF₆). 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.

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 (BMIPF₆) is targeted in the present study. The other constituent is a well-defined crystal face of gold: Au(100). The Au(100) | BMIPF₆ 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.

¹ ISE member

² Permanent address: Eötvös Loránd University, Pázmány Péter sétány 1/A, Budapest, Hungary, H-1117

³ Corresponding author. Permanent address: Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2, Budapest, Hungary, H-1117; e-mail: pajkossy.tamas@ttk.mta.hu

2. Determination of the *pzt*c

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 [10-12].

The second concept: the potential of zero total charge, *pzt*c, 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 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 *pzt*c, $q(E=pztc)=0$. 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 *pzt*c was first employed for real measurements by Jakuszewski and coworkers [17,18]; for the scarce attempts to determine the *pzt*c this way in aqueous electrolytes see Refs. [19,20]; in our previous double layer studies with ionic liquids *pzt*c 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 *pzt*c 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.

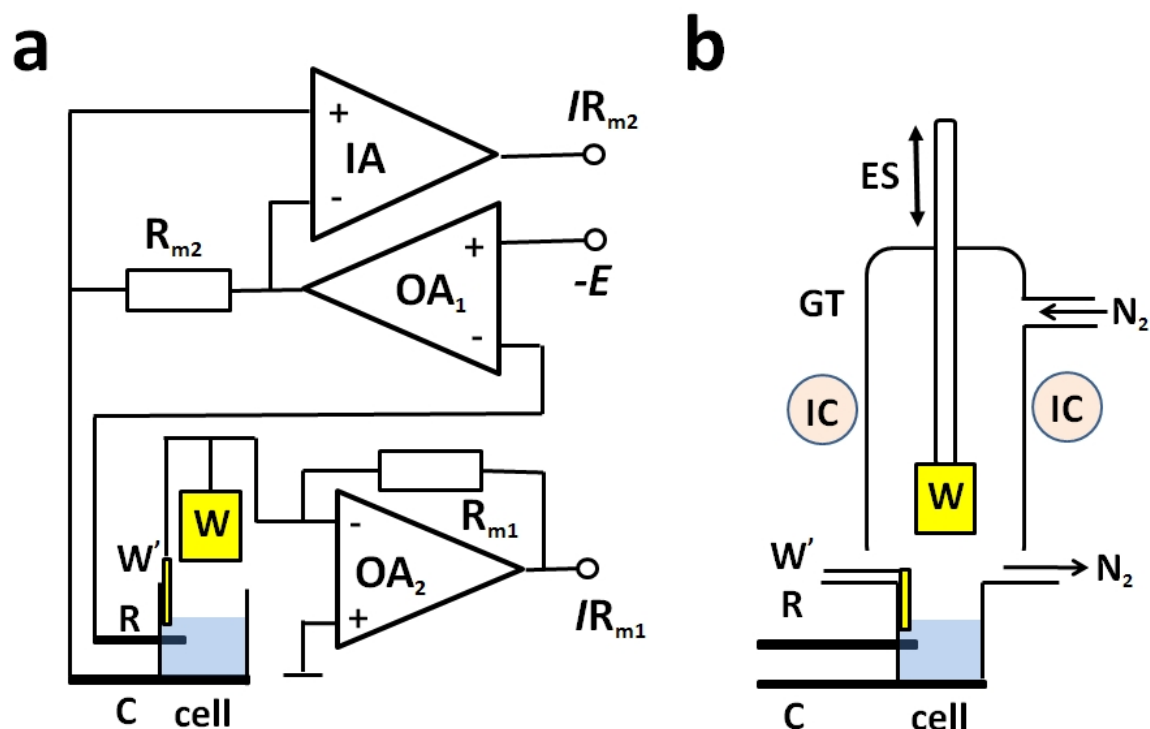


Fig. 1.

(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.

3. Experimental

The BMIPF₆ 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™ 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 (50Hz) 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 50mV/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 [20] the integrated current vs. time curves do not converge to a final value within 3 minutes. That is, some residual current in the range of nA still flows, even at those potentials at which the electrode is generally regarded to be ideally polarizable. As a consequence, the apparent charge, the integrated current, depends on the duration of the experiment. This problem – just as in our previous work [7] – can be circumvented by taking and comparing the calculated charge at one and the same, arbitrarily chosen time, 180 s.

The initial part of the transients deserve attention: whereas the $q(E)$ curves are monotonous at sufficiently positive and negative potentials, there exists a certain potential range around +0.2 V, where the transient comprises of two clearly distinguishable parts. Here the charge transient starts negative and changes to positive; that is, an initial negative current spike is followed by a positive tail of the transient, as shown in Fig. 3.

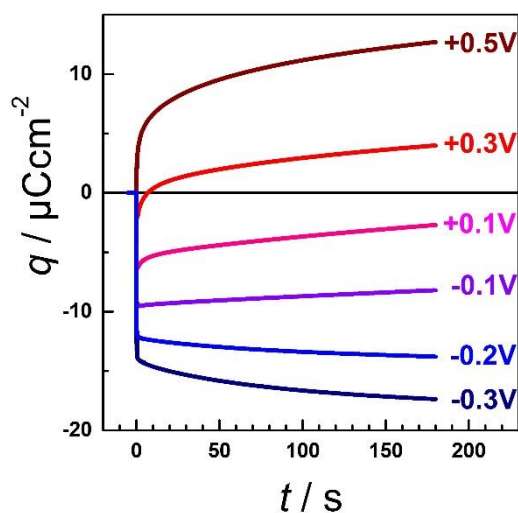


Fig. 2. Integrated immersion current transients at various potentials.

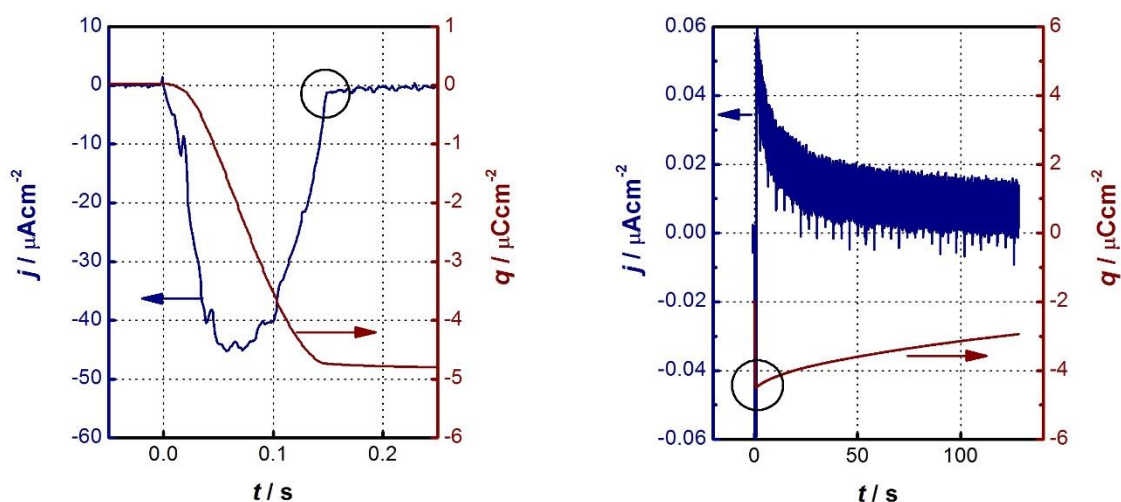


Fig. 3. Short and long time parts (a and b, respectively) of the current and charge transients (left and right axes, respectively) at +0.1V. Circles emphasize the breaks.

The initial cathodic current transient finishes after 0.15 s (Fig. 3a), right when the meniscus formation is complete. Afterwards, at 0.1V, the current is positive, and of very low value.

The two sections of the transients are discernible in a fairly broad potential range; there is a sharp break on the $j(t)$ and $q(t)$ curves, as marked by circles in Figs. 3a and b.

The charge associated with the initial ($t_1=0.2$ s) and the long-term ($t_1=180$ s) parts are plotted in Fig. 5. (Here t_1 stands for the time at which the charging transient's value has been read.)

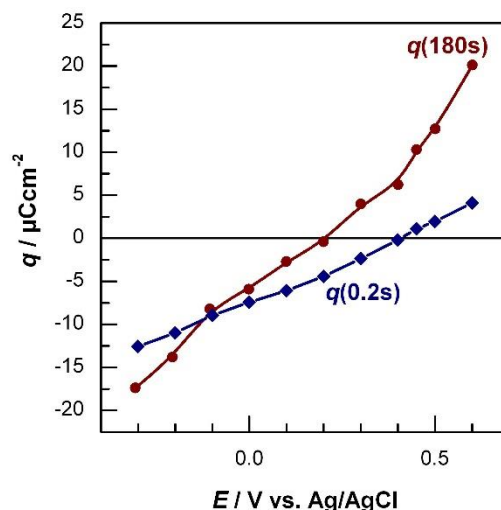


Fig. 4. The charge of the first peak (ending at $t_1=0.2$ s) and of that after 3 minutes as a function of potential

4. Discussion

The novelty of the present measurements is a result of the fast immersion; these measurements reveal that the current – and also the charging transient – comprise two parts. The slowly decaying long-term part of the transient, being in the order of magnitude of 1–10 nA/cm², often escapes one's attention. This low current might be due to two reasons: the first is some contaminations of the IL (*e.g.* water, oxygen, or manufacturing residues of the IL) the second is slow surface rearrangement processes on Au(100). Note that during *in-situ* STM measurements we have often found etch pits and slowly forming surface layers [25] — both processes may be associated with additional charge on the metal.

Were the long-time part due to Faradaic reactions, based on exclusion we might conclude that the short-time part is associated with double layer charging. Consequently, for determining the *pztc*, only those charging transients can be employed, for which the initial and subsequent parts (with the above distinction: charging and Faradaic currents, respectively) can be clearly distinguished – just as on the curves in Figs. 3a and 3b. – and the latter ignored⁴. Thus, the *pztc* is to be identified as the zero-crossing of the $q^M(t_1=0.2$ s) curve at +0.4V.

Because of dimensional reasons the slope of the $q(E, t_1=0.2$ s) curve in Fig. 4 is a capacitance. Although the measurement yields an integral value (*i.e.* q , rather than some derivative of it) the slope is a differential capacitance. The actual value is $C(t_1=0.2\text{s})=17$ μF/cm². As a crude test we can compare this estimate with capacitances at $\omega=1/t_1$ determined from *ac* impedance spectra. In Fig. 3 of Ref. [7] it can be seen that depending on the potential $C(\omega=5/\text{s})$ is between 8 μF/cm² and 30 μF/cm² — this is good order-of-magnitude correspondence with the 17 μF/cm² calculated from the $q(t=0.2$ s) data.

Provided that the initial transient is due to double layer charging, and the long-time part is due to slow surface reactions (either of Faradaic or of adsorption nature), the interpretation of our previous impedance measurement results on the Au(100)/BMIPF₆ system and on

⁴ This was not the case in our previous immersion measurements on the Au(100)/BMIPF₆ system [7] and with Au(111)/BMIPF₆ [4] – at which the immersion could be accomplished much slower than at the present experiments.

similar Au/IL systems [6,7,21] is straightforward. For those systems, the equivalent circuit of the interface was found to consist of three capacitive branches. Two of them – responsible for the high frequency part of the impedance spectra, and showing little potential and temperature dependences – hence reflect double layer charging properties. Accordingly, the third branch, which affects the low frequency part of the impedance/capacitance spectra only, expresses slow Faradaic⁵ or adsorption processes. Hence, our views in Refs. [7] and [21] on connecting *pztc* with the C_2 elements of those equivalent circuits need revision.

5. Summary and conclusions

In order to determine the *pztc* of the title system, we measured charging current transients upon immersing the electrode in the IL, using Au(100)/BMIPF₆ as model system. We found that two sections of the transient could be distinguished; the short-time and long-time parts are attributed to double layer charging and unspecified Faradaic and/or adsorption processes, respectively. Hence, from the point of view of the electrode charge the long-term part can be ignored; the *pztc* should be calculated from the short-time charging only. Based on this procedure for the given system of Au(100)/BMIPF₆ we obtained the *pztc* to be at 0.4 V vs. Ag/AgCl.

Acknowledgments

This cooperation was made possible by the exchange project of the Deutscher Akademischer Austauschdienst and the Hungarian Fellowship Board, No. 39706. The support of Hungarian funding agency OTKA (under contract No. 112034) is highly appreciated. Special thanks are due to Dr. J. Szalma for assembling the elevator unit. Further, support by the Deutsche Forschungsgemeinschaft (DFG) through grant KO 576/28-1 is gratefully acknowledged.

⁵ Although this branch was regarded to be capacitive and in the equivalent circuit appeared as a serial R-CPE-C element combination, we never but in few cases could determine C with acceptable accuracy. In other words, that branch could have expressed a Faradaic process as well as an adsorption process.

References

- 1 M. Freemantle, *Introduction to Ionic Liquids*, RSC Publishing, Cambridge, UK, 2009.
- 2 B. Kirchner (Ed.), *Ionic Liquids*, Topics Curr. Chem., vol. 290, Springer, Heidelberg, Germany, 2010.
- 3 A. Kokorin (Ed.), *Ionic Liquids: Applications and Perspectives*, InTech, Rijeka, Croatia, 2011.
- 4 P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany, 2003.
- 5 J. S. Wilkes, M. J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, *J. Chem. Soc. Chem. Comm.* 13 (1992) 965.
- 6 T. Pajkossy, D.M. Kolb, The interfacial capacitance of Au(100) in an ionic liquid, 1-butyl-3-methyl-imidazolium hexafluorophosphate, *Electrochem. Comm.*, 13 (2011) 284.
- 7 M. Gnahn, C. Müller, R. Répánszki, T. Pajkossy, and D.M. Kolb, The interface between Au(100) and 1-butyl-3-methyl-imidazolium-hexafluorophosphate, *Phys. Chem. Chem. Phys.*, 13 (2011) 11627.
- 8 A. Frumkin, A. Gorodetskaja, Kapillarelektische Erscheinungen an Amalgamen, I. Thalliumamalgame, *Z. Phys. Chem.*, 136 (1928) 451-472
- 9 A.N. Frumkin, O.A. Petrii, B.B. Damaskin, in J.O'M. Bockris, B.E. Conway, and E. Yeager (Eds), *Comprehensive Treatise of Electrochemistry*, Plenum Press New York, 1980, pp. 221-285
- 10 A.N. Frumkin, *Zero Charge Potentials*, Nauka, Moscow, 1979
- 11 O.A. Petrii, Zero Charge Potentials of Platinum Metals and Electron Work Functions (Review), *Russ. J. Electrochem.*, 49 (2013) 401.i
- 12 D.C. Grahame, The electrical double layer and the theory of electrocapillarity, *Chem. Rev.*, 41 (1947) 441.
- 13 G. Gouy, Sur la constitution de la charge électrique à la surface d'un electrolyte, *J. Phys. Radium*, 9 (1910) 457.
- 14 G. Gouy, Sur la constitution de la charge électrique à la surface d'un electrolyte, *Compt. Rend.* 149 (1910) 654.
- 15 D.L. Chapman, A Contribution to the Theory of Electrocapillarity, *Phil.Mag.* 25 (1913) 475.
- 16 A. Frumkin, Adsorptionserscheinungen und elektrochemische Kinetik, *Z. Elektrochem.*, 59 (1955) 807-822
- 17 B. Jakuszewski, Z. Kozłowski, Pomiar potencjału ładunku zerowego metoda zanurzeniowa, *Rocz. Chem.* 36 (1962) 1873-1877
- 18 B. Jakuszewski, Z. Kozłowski, S. Partyka, M. Przasnyski, S. Romanowski, Direct pulse method for measuring null charge points, *Soviet Electrochemistry*, 7 (1971) 772 (translation of *Elektrokhimiya* 7 (1971) 804).
- 19 V. Jendrašić, Immersion-electrode method for determination of the point of zero charge of solid metals, *J. Electroanal. Chem. Interfac. Electrochem.*, 22 (1969) 157.
- 20 U.W. Hamm, D. Kramer, R.S. Zhai, D.M. Kolb, The pzc of Au(111) and Pt(111) in a perchloric acid solution: an ex situ approach to the immersion technique, *J. Electroanal. Chem.*, 414 (1996) 85.
- 21 M. Gnahn, T. Pajkossy, D.M. Kolb, The interface between Au(111) and an ionic liquid, *Electrochim. Acta*, 55 (2010) 6212.
- 22 J. Clavilier, R. Albalat, R. Gómez, J.M. Orts, J.M. Feliu, Displacement of adsorbed iodine on platinum single-crystal electrodes by irreversible adsorption of CO at controlled potential, *J. Electroanal. Chem.* 360 (1993) 325.
- 23 M.J. Weaver, Potentials of Zero Charge for Platinum(111)-Aqueous Interfaces: A Combined Assessment from In-Situ and Ultrahigh-Vacuum Measurements, *Langmuir*, 14 (1998) 3932.
- 24 A. Cuesta, Measurement of the surface charge density of CO-saturated Pt(111) electrodes as a function of potential: the potential of zero charge of Pt(111), *Surf. Sci.*, 572 (2004) 11.
- 25 C. Müller, K. Németh, S. Vesztegom, T. Pajkossy, and T. Jacob, The interface between HOPG and 1-butyl-3-methyl-imidazolium hexafluorophosphate, *Phys.Chem. Chem. Phys.*, (2016) doi: 10.1039/c5cp05406k