

# Final report on the project “Frequency dependent double layer capacitances etc” (K112034)

## Introduction

Two issues were the subjects of this three-year project (extended by one year): First to perform electrochemical experiments in ionic liquids; second, to elaborate a double layer impedance theory for extremely high surface area electrodes. Both subjects were closely related to that the interfacial capacitance (“double layer capacitance”) often appears as if were frequency dependent. In some cases, it is indeed, inherently dependent. For analyses of these effects/situations, see the overview papers [1,2] written recently (in the framework of the present project).

## Ionic-liquid electrochemistry studies

### a. Motivation

Before 2015, since 2008, I have done many electrochemical measurements with single crystalline noble metal electrodes (mostly Au(111) and Au(100)) in a characteristic ionic liquid; 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIPF<sub>6</sub>). These measurements were done in the framework of cooperation with the University of Ulm, because these measurements require very clean conditions in glove boxes – such clean conditions we did not and still do not have. The typical measurements were as follows: cyclic voltammetry (CV) for general characterization of the system; electrochemical impedance spectroscopy (EIS) for the determination of the double layer capacitance; immersion measurements for the determination of the potential of zero total charge (*pztc*); finally *in-situ* STM imaging, for exploring and characterizing ordered structures. By 2015 we focused attention to the following open questions: How to interpret the impedance spectra (capacitance spectra) of the metal/ionic liquid interface? What is the connection of the capacitance spectra and the immersion transients? What other types kind of processes proceed in the interphase and what are the characteristics of their kinetics?

## **b. Measurements with HOPG**

Prior to 2015 our main statement on the frequency dependence of the double layer capacitance was that the capacitive (charging) current in ionic liquids comprises an "infinitely fast", a fast, and a slow components; the individual components needed interpretation. In other words, the double layer capacitance spectra, on the complex plane, comprise a high and a low frequency arc, whose physical meaning was unclear at that time. In 2016 we made a big step ahead by finishing a set of experiments, using HOPG (highly oriented pyrolytic graphite, a synthetic graphite) electrodes, rather than gold. This was a series of cyclic voltammetry, impedance spectroscopy and in-situ STM measurements; the individual measurements were just the same as the previous ones but the Au(100) electrodes were replaced by HOPG ones. With HOPG electrodes we found that the low frequency arc (i.e. the slow component of charging) was missing from the capacitance spectra. As it was well seen on the in-situ STM images, the HOPG surface appeared to be fairly stable under the ionic liquid. In contrast, under same conditions the Au(100) surface showed changes within the half-an-hour time frame of the STM imaging: step edges moved, monoatomic height islands and etch pits appeared even in minutes. The slow component of charging could thus be associated with the slow rearrangement of the Au surface; the fast components - on the basis of exclusion - could be associated with the double layer charging. In other words, the double layer is rearranged following a potential change slowly rather than instantaneously (with a time constant in the order of magnitude of ms). For the details, see [3].

## **c. Immersion measurements**

A basic property of the electrochemical double layer is its "neutral point", the potential of zero total charge, *pztc*. This quantity can be determined through measuring immersion current transients. That is, while keeping electrode potential continuously controlled and constant, we immerse the electrode in the electrolyte and measure the current. The integral of the current transient is zero if the potential has been held just at the *pztc*. We have performed many such immersion measurements together with our cooperating partner in Ulm since 2011. Since the measurement is difficult from technical point of view, many modifications, improvements, re-measurements were needed in the first four years. Finally, in 2015 we succeeded to perform a good series of measurements with the Au(100)/BMIPF<sub>6</sub> system; *pztc* value of this system has been determined. The key point of this measurement was to find the way how to distinguish between the initial part and the long tail of the transient; that is, how to separate the effects of the fast and slow processes. For the details, see [4].

#### **d. The closing-up stage of the ionic-liquid electrochemistry project**

By 2017, we had a fairly self-consistent picture on the behavior of the noble metal-ionic liquid interface, and decided to summarize what we had learnt in the years 2008-2016 on these systems. To a final, closing publication, we needed a couple of other measurements on different metals (on Ag(100) and Pt(100) single crystals) and in different ionic liquids. Having done these, we could finish the ionic-liquid electrochemistry project carried out together with the Ulm colleagues by writing a final publication [5]. One of its last paragraphs of its Conclusion expresses the most important scientific achievements of our cooperation, of this OTKA project (and also of my career) as well.

„ (1) The frequency dependence of the double layer capacitance implies that the double layer rearrangement processes following potential changes are not instantaneous, but are much slower than those of the “classical” aqueous double layers. As we found little if any potential dependence of the capacitive quantities, our results do not provide support for the related contemporary theories of equilibrium capacitance. “

(The other point of the conclusions is worth to be mentioned: “(2) With in situ STM we found in certain cases ordered anion and cation structures. The Au(100) surface can act as a template to form an organized overlayer.”)

Maybe this cooperative work will be resumed in the near future if a copy of my DEIS (dynamic EIS) setup can be implemented in Ulm. The reason for it is that the electrochemical measurements (CV and EIS) with ionic liquids always require very clean conditions – or fast measurements (or both), because with fast measurements the danger of surface contaminations is diminished. These days we are working on a developing a DEIS setup, which is a combination of CV with EIS; on the basis of a previous, similar device, developed for the characterization of high surface area carbon materials [6]. The new setup is now being validation with well-known aqueous electrochemical systems – with measuring diffusion-controlled currents. For the analysis of these currents, for the decoupling of the charge transfer and the diffusion a new theory has recently been developed [7,8].

#### **Frequency dependence associated with the high surface electrode area of the electrodes**

The second research topic was to contribute to the theories on porous, extremely high surface area electrodes. I did not do so. The reason for this is such a comprehensive theory on the electrochemical impedance of porous electrodes (similar to what I planned to elaborate) has

recently appeared (J. Huang, J. Zhang, Theory of Impedance Response of Porous Electrodes: Simplifications, Inhomogeneities, Non-Stationarities and Applications. *J Electrochem Soc* 163 (2016), A1983) and hence our plan has been rendered redundant. Nevertheless, I wrote a chapter exactly on the subject of frequency dependence associated with the high surface electrode area of the electrodes in an Elsevier encyclopedia [9]. This article represents my present level of understanding of this area (which was in the focus of my attention thirty years ago).

## **Miscellaneous results:**

There is a number of other of published papers in which we acknowledge the support of the OTKA. These do not belong to the core of the project; however, they are based on the methodologies related, or developed during the project. First, we have to mention a study, in which and the bipotentiostat and its the data acquisition system (originally developed for the impedance measurements by Gábor Mészáros) got an important role [10-14]. The publication of [15] deals with electrode kinetics issues; studied also by impedance spectroscopy. As such, it has common methodology roots with the project. Similarly to the measurements of István Bakos, who made a number of electrochemical characterization measurements for colleagues in our Institute [16-23].

## **Summary**

There are four recent items in my publication list (see footnotes 1,2,5, and 9) which summarize my recent or long-term activities related to electrochemical interfaces. The major part of these papers deal with frequency-dependent double layer capacitances (on various systems, ionic liquids and also in aqueous solutions) and support the conclusion as follows:

It could be demonstrated that on many and diverse, apparently ideal, ideally polarizable electrochemical interfaces that charging / discharging following potential changes are not instantaneous hence the double layer is not (solely) of electrostatic nature – as assumed in „classical” double layer theories. Such a statement urges theoreticians to taking into account the physico-chemical interactions (i.e. other than electrostatic ones) to account for the slow double layer rearrangement processes.

- 1 **T. Pajkossy** and R. Jurczakowski, Electrochemical impedance spectroscopy in interfacial studies, *Current Opinion in Electrochemistry*, **1** (2017) 53-58
- 2 **T. Pajkossy**, Slow Charging/Discharging Processes of the Electrochemical Double Layer, *Bulgarian Chem. Comm.*, **50D** (2018) 90 – 98
- 3 C. Müller, K. Németh, **S. Vesztergom**, **T. Pajkossy**, and T. Jacob, The interface between HOPG and 1butyl-3-methyl-imidazolium hexafluorophosphate, *Phys.Chem. Chem. Phys.*, **18** (2016) 916-925.
- 4 C. Müller, **S. Vesztergom**, **T. Pajkossy**, and T. Jacob, Immersion measurements of potential of zero total charge (pztc) of Au(100) in an ionic liquid, *Electrochim. Acta* **188** (2016) 512-515
- 5 **T. Pajkossy**, C.Müller, and T. Jacob, The metal–ionic liquid interface as characterized by impedance spectroscopy and in situ scanning tunneling microscopy, *Phys.Chem.Chem.Phys.*, **20** (2018) 21241-21250
- 6 **T. Pajkossy**, **G. Mészáros**, **I. Felhósi**, T. Marek, and L. Nyikos, A multisine perturbation EIS system for characterization of carbon nanotube layers, *Bulgarian Chem. Comm.*, **49C** (2017) 114 – 118
- 7 **T. Pajkossy**, Analysis of quasi-reversible cyclic voltammograms: Transformation to scanrate independent form, *Electrochem. Comm.* **90** (2018) 69
- 8 **T. Pajkossy**, **S. Vesztergom**, Analysis of voltammograms of quasi-reversible redox systems: Transformation to potential program invariant form, *Electrochim. Acta* **297** (2019) 1121
- 9 **T. Pajkossy**, Electrochemistry of Fractal Surfaces. In: Wandelt, K., (Ed.), *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*, vol. 5, pp 121–124. Elsevier (2018); valamint Elsevier’s Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*, doi: 10.1016/B978-0-12-409547-2.13306-2.

**Additional publications:**

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- 10 M. Lindner, M. Valášek, J. Homberg, K. Edelmann, L. Gerhard, W. Wulfhekel, O. Fuhr, T. Wächter, M. Zharnikov, V. Kolivoška, L. Pospíšil, **G. Mészáros**, M. Hromadová, and M. Mayor: Molecular Tripods. Importance of the Anchor Group Position (Para versus Meta) in Tetraphenylmethane Tripods: Synthesis and Self-Assembly Features , *Chem. Eur. J.* **22** (2016) 13218.
- 11 M. Lindner, M. Valášek, J. Homberg, K. Edelmann, L. Gerhard, W. Wulfhekel, O. Fuhr, T. Wächter, M. Zharnikov, V. Kolivoška, L. Pospíšil, **G. Mészáros**, M. Hromadová, and M. Mayor: Molecular Tripods. Importance of the Anchor Group Position (Para versus Meta) in Tetraphenylmethane Tripods: Synthesis and Self-Assembly Features , *Chem. Eur. J.* **22** (2016) 13218.
- 12 Š.Nováková-Lachmanová, J. J. Šebera V. Kolivoška, J. Gasiora, **G. Mészáros**, G. Dupeyre, PP.Lainé, M.Hromadová, Correlation of electrochemical properties of expanded pyridinium compounds with their single molecule conductance, *Electrochim. Acta* **264** (2018) 301
- 13 T. Sebechlebska, J. Sebera, V. Kolivoska, M. Lindner, J.Gasior, **G. Meszaros**, M. Valasek, M. Mayor, M. Hromadova, Investigation of the geometrical arrangement and single molecule charge transport in self-assembled monolayers of molecular towers based on tetraphenylmethane tripod, *Electrochim. Acta* **258** (2018) 1191
- 14 J. Sebera, V. Kolivoska, M. Valasek, J.Gasior, R. Sokolová, **G. Meszaros**, W. Hong, M. Mayor, M. Hromadova, Tuning Charge Transport Properties of Asymmetric Molecular Junctions, *J. Phys. Chem.C* **121** (2017) 12885
- 15 **É. Fekete**, B. Lengyel, T. Cserfalvi, and **T. Pajkossy**, Electrochemical dissolution of aluminium in electrocoagulation experiments, *J. Solid State Electrochem.*, **20** (2016) 3107.
- 16 Á. Vass, I. Borbáth, **I. Bakos**, Z. Pászti, G. Sáfrán, and A. Tompos, Stability issues of CO tolerant Pt-based electrocatalysts for polymer electrolyte membrane fuel cells: comparison of Pt/Ti<sub>0.8</sub>Mo<sub>0.2</sub>O<sub>2</sub>-C with PtRu/C, *Rect. Kin. Mech.Catal.* (2018)
- 17 **I. Bakos**, I Borbáth, Z.Pászti, A. Tompos, Design and investigation of molybdenum modified platinum surfaces for modeling of CO tolerant electrocatalysts, *Top. Catal.* **61** (2018) 1385
- 18 Á. Vass, I. Borbáth, **I. Bakos**, Z. Pászti, I.E. Sajó, A. Tompos, Novel Pt Electrocatalysts: Multifunctional Composite Supports for Enhanced Corrosion Resistance and Improved CO Tolerance, *Top. Catal.* **61** (2018) 1300

- 19 I Borbáth, D. Gubán, **I. Bakos**, Z Pászti, G Gajdos, I.E. Sajó, Á Vass, A. Tompos, Exclusive formation of alloy phases via anchoring technique - from bimetallic catalysts to electrocatalysis, *Catal. Today* **306** (2018) 58
- 20 D. Gubán, A. Tompos, **I Bakos**, Z.Pászti, G. Gajdos, I. Sajó, I Borbáth, CO oxidation and oxygen reduction activity of bimetallic Sn–Pt electrocatalysts on carbon: effect of the microstructure and the exclusive formation of the Pt<sub>3</sub>Sn alloy, *React. Kinet. Mech. Cat.* **121** (2017) 43
- 21 D. Gubán, A. Tompos, **I Bakos**, Á. Vass, Z. Pászti, E.Gy. Szabó, I.E. Sajó, I. Borbáth, Preparation of CO-tolerant anode electrocatalysts for polymer electrolyte membrane fuel cells, *Int J Hydrogen Energy* **42** (2017) 13741
- 22 Á. Vass, I Borbáth, Z. Pászti , **I. Bakos**, I.E. Sajó, P. Németh, A. Tompos, Effect of Mo incorporation on the electrocatalytic performance of Ti–Mo mixed oxide–carbon composite supported Pt electrocatalysts, *React. Kinet. Mech. Cat.* **121** (2017) 141