

THESES OF THE DOCTORAL DISSERTATION

INVESTIGATION OF ADSORPTION, UNDERPOTENTIAL  
DEPOSITION AND FILM FORMATION PROCESSES WITH THE  
ELECTROCHEMICAL QUARTZ CRYSTAL NANOBALANCE  
TECHNIQUE

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## § 1. INTRODUCTION

Investigation of adsorption, underpotential deposition (UPD) and film formation phenomena are in the foreground of electrochemical research. The common with the research of these topics is in the *in situ* characterization of boundaries between electrodes and liquid electrolytes, and that of the resulting films. The deep understanding of the happenings at the interface is critical to control a number of processes, especially those in which the surface status and kinetic parameters can change at different stages or with time. On the other hand the formed layer can be of special use and applications, therefore they thorough knowledge is of particular importance.

In this work we demonstrate the applicability of the electrochemical quartz crystal nanobalance (EQCN) technique to explore some of these processes. They include the study of the influence of  $\text{Na}^+$  and  $\text{Cs}^+$  ions on platinum electrodes in acid media and adsorption and film formation properties of indole and 4-aminoindole at different electrodes. Furthermore we show a salient example of hyphenating EQCN with other technique: the results of simultaneous acquisition of electrochemical impedance spectroscopy (EIS) and gravimetric data in cyclic electrode potential scans to characterize nonstationary electrode processes. Non-stationarity in this context means that the system does not show the same properties in the forward and backward potential scans and also in cycle-to-cycle sequences.

The reason for developing hyphenated electrochemical techniques for solving research problems, like those mentioned above, is the following. Application of voltammetric techniques often requires multiple cycling of the electrode potential to distinguish different constituents contributing to the direct current, like the double-layer charging, electron transfer processes, diffusion, or specific adsorption. However, multiple cycling is not always acceptable for nonstationary systems and particularly for surfaces the properties of which irreversibly change from cycle to cycle. Therefore, other *in situ* techniques need to be concurrently applied to complement voltammetric techniques for an extended characterization of these systems in a single potential scan. The choice of the techniques in this case is not trivial as multiparameter measurements can be unacceptably long, and the response analysis could become ambiguous. The optimal combination would obviously require acquisition of a maximum amount of independent and self-consistent data from a minimal number of measurements.

In one part of the work, we demonstrate that simultaneous acquisition and analysis of impedance and gravimetric data in one cyclic potential scan is advantageous for a detailed electrochemical characterization of nonstationary electrode | electrolyte interfaces. Scanning the potential is necessary to compare the surface status and continuously monitor changes at different stages of the electrode process. On the other hand, by combining potentiodynamic EIS (PDEIS) and EQCN, it is possible to elucidate self-consistent physical models of the interface at various electrode potentials providing deeper physical insight into the system under investigation. The two model systems for the demonstration of the method were the electrochemical UPD of atomic layers of *i*) Ag on Au and *ii*) Cu on Pt. In these systems, the deposition of monolayer amounts of Ag and Cu occurs at potentials more positive than those for the bulk phase deposition. Both processes, however, are difficult to investigate using conventional voltammetric techniques due to their high nonstationarity. An additional reason to select these model systems was that there were no EIS studies which characterize them.

Platinum is one of the most thoroughly studied and used electrode materials. It demon-

strates exceptionally good catalytic activity toward numerous technologically important reactions. Adsorption energies for reaction intermediates at Pt surfaces are very close to the optima for oxygen reduction, hydrogen evolution, and hydrogen oxidation, making Pt highly active toward these catalytic processes vital for future energy production. From this point of view, understanding of adsorption phenomena at the Pt | electrolyte interface is of increasing importance. Attention has been paid to the adsorption of anions, and much less knowledge is accumulated on the influence of different cations. In this work we present and interpret the significant deviation from the usual behaviour of platinum that was observed in the presence of Cs<sup>+</sup> ions. First of all we give insight into the deviations from the normal behaviour of Pt in the hydrogen adsorption / desorption region observed by using merely the EQCN technique. Furthermore we compare the influence of two cations, Na<sup>+</sup> and Cs<sup>+</sup>, on the adsorption of \*H, \*OH, and \*O at polycrystalline Pt in acidic sulfuric media. To this end we use EIS, cyclic voltammetry, and EQCN.

The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry. This intense interest is due to wide range of promising applications of these compounds in the fields of energy storage, electrocatalysis, organic electrochemistry, bio-electrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection etc. After the discovery of conducting polymers the researchers tried to polymerize every kind of simple organic molecules. Some of them, like aromatic amines and heterocyclic compounds became very popular within this field. Electropolymerization of indole and its derivatives has also been studied, and a wide range of applications for these polymers from corrosion protection via Li-ion batteries to ion sensors and electrochromic devices has been suggested. However, there are still controversial issues in the literature concerning the structure and the behaviour of the formed polymers. Our attention turned to indole and 4-aminoindole for several reasons. First, the electrochemical behaviour of 4-aminoindole has not been studied yet, albeit due to its structure, the free site in the para position to the amino group, the formation of a polyaniline-like polymer might also be expected. Second, it was hoped that by using EQCN technique, the application of which has been neglected in these studies, several controversies that can be found in the electrochemical literature of the indole compounds including their adsorption and electropolymerization could be resolved. In this work we report the results obtained and their possible explanation concerning the adsorption and electrooxidation of indole and 4-aminoindole as well as the characterization of the resulting surface films in different aqueous acid solutions by EQCN technique. Attention is paid to the crucial role of the oxygen in these processes.

## § 2. RESULTS AND CONCLUSIONS

### 2.1 Results connected to the development of EIS-EQCN technique

1. We showed that the simultaneous acquisition and analysis of impedance and gravimetric data by EIS-EQCN in one cyclic potential scan can be advantageous for a detailed electrochemical characterization of nonstationary electrode | electrolyte interfaces. Both data sets complement each other in elucidating different aspects of the interfacial dynamics.
2. We characterized two surface-limited UPD processes by EIS-EQCN: *i*) Ag UPD on Au

and *ii*) Cu UPD on Pt. The EIS and gravimetric data appeared to be consistent with each other and with the data previously published in the literature. EIS physical models of the electrochemical interface during Ag and Cu UPD processes were elucidated in terms of equivalent circuits based on EQCN and EIS data recorded simultaneously. Ag UPD on Au could be described with a model containing two reversible adsorption processes (where one has diffusion limitations) which occur simultaneously, while Cu UPD on Pt could be modelled with a circuit describing a slow irreversible UPD.

3. Ag UPD on Au in  $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$  is a complex process which is accompanied by changes of the electrode surface and perchlorate anion coadsorption. EIS-EQCN provided an opportunity to simultaneously monitor adsorption of anions and cations by the variation of the frequency curve with electrode potential and the respective adsorption capacitance curves which are available from the impedance analysis. The latter shows that the anion coadsorption dynamics changes at different Ag UPD stages. Initial Ag deposition induces coadsorption of one  $\text{ClO}_4^-$  anion per about six Ag adatoms, while the later stages change this ratio to 1/4 at 0.2 V (vs. mercury-mercury-sulfate in cc.  $\text{K}_2\text{SO}_4$ ). Further perchlorate adsorption likely meets steric complications at the final stages of the Ag UPD.
4. New kinetic information on "intrinsically" nonstationary Ag UPD was obtained from EIS-EQCN through the evaluation of the apparent rate coefficients  $k_a f_a(\theta)$ . The  $k_a f_a(\theta)$  values range from  $0.015 \text{ cm s}^{-1}$  to  $0.045 \text{ cm s}^{-1}$  which is between the standard rate constants  $k_0$  of Ag bulk deposition on Ag for different Ag surfaces reported previously. The  $k_a f_a$  values demonstrate a complex dependence on the electrode potential due to the occupancy related factor  $f_a$  and appeared to be different in the anodic and cathodic scans as a result of surface alloying.
5. Surface alloying between Ag and Au additionally contributes to the resonance resistance variation  $\Delta R(E)$ . The latter increases constantly in the presence of Ag adatoms in both cathodic and anodic scans.
6. Analysis of the EIS-EQCN data shows that in contrast to Ag UPD a specific adsorption of  $\text{ClO}_4^-$  does not contribute significantly to Cu UPD on Pt in  $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ . Instead, the double layer capacitance dependencies demonstrate that a competitive OH adsorption influences the UPD process to a large extent, especially at the early stages of Cu deposition. Another difference between two UPD systems is that the Cu adsorption and desorption do not modify the Pt surface:  $\Delta R(E)$  remains almost constant in the cyclic potential scan.

## 2.2 Results connected to the investigation of cationic adsorption

1. Alone the results of the electrochemical quartz crystal nanobalance experiments furnish evidences that a competitive adsorption of  $\text{Cs}^+$  ions and  $\text{H}^+$  ions exists in the hydrogen UPD region. The unusual EQCN frequency change in the double layer region can be explained by the desorption of  $\text{Cs}^+$  ions, and the simultaneous adsorption of bisulfate and/or sulfate ions as well as water molecules. The cation adsorption on platinum electrode depends on the adsorption ability of the ions, which is the highest in the case of  $\text{Cs}^+$ , and it is the very reason why this effect cannot be detected in the presence of other alkali metal ions.

2. The influence of two cations,  $\text{Na}^+$  and  $\text{Cs}^+$ , on the adsorption of  $^*\text{H}$ ,  $^*\text{OH}$ , and  $^*\text{O}$  at polycrystalline Pt in acidic sulfuric media has been further investigated. Noncovalent interactions at the interface caused by alkali cations change drastically the interface status, which should be taken into account while model electrocatalytic experiments are performed.
3. Using impedance analysis it was possible to separate at least two adsorption processes: (bi)sulfate and hydrogen adsorption. Nanogravimetry additionally resolves the contribution from  $\text{Cs}^+$ . Specific adsorption of  $\text{Cs}^+$  at Pt surface significantly affects hydrogen adsorption, while it has almost no effect on the dynamics of sulfate ion adsorption. Specifically adsorbed alkali cations, however, are desorbed by the onset of  $^*\text{OH}(^*\text{O})$  adsorption. Nevertheless, they likely remain in close proximity to the surface, probably in the second  $\text{H}_2\text{O}$  layer, and largely contribute to the formation of the  $^*\text{OH}$  and  $^*\text{O}$  adsorbed species from the surface water. This can be important for the catalytic processes that involve these species as the reaction intermediates.
4. Additional information is provided by the potential dependence of the exponent of the constant phase element, which describes the response of the double electric layer. 2D phase transitions in the adsorbate layer decrease the exponent values, significantly confirming the general observations reported earlier in the literature.

### 2.3 Results connected to the investigation of adsorption and film formation abilities of indole and 4-aminoindole

1. The results of electrochemical quartz crystal nanobalance experiments reveal several interesting features on the adsorption and electropolymerization of indole and 4-aminoindole in acid media. These compounds undergo a strong oxidative adsorption at platinum electrode, which does not occur at gold. The presence of the amino-group on the molecule even strengthens this effect. The adsorption is due to the hydroxide-oxide layer on the Pt surface, because it reacts with the monomers. When the oxygen had been carefully removed and the experiment was started with reduced Pt the adsorption phenomenon could not be observed.
2. The adsorbed layer does not inhibit the electropolymerization at higher positive potentials, which has been reported for amino-substituted indoles.
3. The presence of molecular oxygen in the system leads to the overoxidation of the deposited polymer therefore, even the traces of oxygen should be removed in order to have good quality polymer. This effect might be responsible for the contradictory findings that have been reported so far for polyindoles and indole derivatives. Despite the effect of the substrates on the adsorption behaviour, the electropolymerization process occurs unhindered and in a similar manner at both Pt and Au electrodes.
4. The relatively small difference in structure has a huge effect on the nanogravimetric response of the deposited materials. While in the case of indole the charge compensating processes during the redox transformations are the ingress or egress of anions, in the case of 4-aminoindole most probably a partial deprotonation of the film compensates the excess charges. These are readily detectable with the EQCN, and reveal already during the polymerizations: the shape of frequency change vs. time function serves as evidence for these statements.

## § 3. PUBLICATIONS

### Research Articles

The Dissertation is based on the following articles:

1. B. B. Berkes, G. Inzelt, Electrochemical nanogravimetric studies on the electropolymerization of indole and on polyindole, *Electrochimica Acta* – submitted
2. B. B. Berkes, G. Inzelt, E. Vass, Electrochemical nanogravimetric study of the adsorption of 4-aminoindole and the surface layer formed by electrooxidation in aqueous acid media, *Electrochimica Acta* **96** (2013) 51-60.
3. B. B. Berkes, G. Inzelt, W. Schuhmann, A. S. Bondarenko, Influence of Cs<sup>+</sup> and Na<sup>+</sup> on Specific Adsorption of \*OH, \*O, and \*H at Platinum in Acidic Sulfuric Media, *Journal of Physical Chemistry C* **116** (2012) 10995-11003.
4. M. H. Huang, J. B. Henry, B. B. Berkes, A. Maljusch, W. Schuhmann, A. S. Bondarenko, Towards a detailed in situ characterization of non-stationary electrocatalytic systems, *Analyst* **137** (2012) 631-640.
5. B. B. Berkes, A. Maljusch, A. S. Bondarenko, W. Schuhmann, Simultaneous acquisition of impedance and gravimetric data in a cyclic potential scan for the characterization of non-stationary electrode/electrolyte interfaces, *Journal of Physical Chemistry C* **115** (2011) 9122-9130.
6. B. B. Berkes, A. Székely, G. Inzelt, Effect of Cs<sup>+</sup> ions on the electrochemical nanogravimetric response of platinum electrode in acid media, *Electrochemistry Communications* **12** (2010) 1095-1098.

Other scientific papers:

7. B. B. Berkes, G. Inzelt, Generation and electrochemical nanogravimetric response of the third anodic hydrogen peak on a platinum electrode in sulfuric acid media, *Journal of Solid State Electrochemistry* – submitted
8. B. B. Berkes, Á. Nemes, C. E. Moore, F. Szabó, G. Inzelt, Electrochemical nanogravimetric study of the electropolymerization of 6-aminoindole and the redox transformations of the polymer formed in aqueous media, *Journal of Solid State Electrochemistry* – submitted
9. B. B. Berkes, The 2012 Joseph W. Richards summer research fellowship - Summary report Catalytic activity for ORR of a platinum-free electrocatalyst in phosphoric acid, *The Electrochemical Society Interface* **21** (2012) 93-94.
10. B. B. Berkes, J. B. Henry, M. H. Huang, A. S. Bondarenko, Electrochemical Characterisation of Copper Thin-Film Formation on Polycrystalline Platinum, *ChemPhysChem* **13** (2012) 3210-3217.
11. Á. Kriston, B. B. Berkes, P. Simon, G. Inzelt, K. Dobos, Á. Nemes, Unusual surface mass changes in the course of the oxygen reduction reaction on platinum and their

explanation by using a kinetic model, *Journal of Solid State Electrochemistry* **16** (2012) 1723-1732.

12. G. Inzelt, B. B. Berkes, Á. Kriston, Electrochemical nanogravimetric studies of adsorption, deposition and dissolution processes occurring at platinum electrodes in acid media, *Pure and Applied Chemistry* **83** (2011) 269-279.
13. G. Inzelt, B. B. Berkes, Á. Kriston, A. Székely, Electrochemical nanogravimetric studies of platinum in acid media, *Journal of Solid State Electrochemistry* **15** (2011) 901-915.
14. G. Inzelt, B. B. Berkes, Á. Kriston, Temperature dependence of two types of dissolution of platinum in acid media. An electrochemical nanogravimetric study, *Electrochimica Acta* **55** (2010) 4742-4749.
15. G. Inzelt, B. B. Berkes, Á. Kriston, Two Types Dissolution of Platinum in Acid Media. An Electrochemical Nanogravimetric Study, *ECS Transactions* **25** (2010) 137-156.

### Book Chapter

- B1. M. Huang, J. B. Henry, B. B. Berkes, A. Maljusch, W. Schuhmann, A. S. Bondarenko, Simultaneous acquisition of impedance and gravimetric data for the characterization of the electrode | electrolyte interfaces, in: *Lecture Notes on Impedance Spectroscopy. Measurement, Modeling and Applications*, volume 3, (Ed.) O. Kanoun, CRC Press - Taylor and Francis Group, London, 2012, pp. 35-41.

### Presentations, Conference Participations

- E1. G. Inzelt, B. B. Berkes, Nanogravimetric Study on the Adsorption and Electropolymerization of Indole and Indole Derivatives and on the Redox Behavior of Polyindoles, *63rd ISE Meeting*, Prague, Czech Republic, August 19-24, 2012
- E2. B. B. Berkes, G. Inzelt, Study of Formation and Redox Behaviour of Polyindoles by Electrochemical Quartz Crystal Microbalance, *International Workshop on the Electrochemistry of Electroactive Materials WEEM – 2012*, Hódmezővásárhely, Hungary, June 3-8, 2012
- E3. B. B. Berkes, G. Inzelt, Adsorption and electropolymerization of indole and indole derivatives, *Third Regional Symposium on Electrochemistry*, Bucharest, Romania, May 13-17, 2012
- E4. B. B. Berkes, G. Inzelt, Nanogravimetric Studies of Formation and Redox Behaviour of Polyindole and Its Derivatives, *International Workshop: Polymers at Electrodes A Quarter of a Century later*, Bad Schandau, Germany, November 6-9, 2011
- E5. B. B. Berkes, A. Maljusch, A. S. Bondarenko, W. Schuhmann, Simultaneous acquisition of impedance and gravimetric data in a cyclic potential scan. Characterization of UPD of Ag on Au and Cu on Pt, *EIRELEC 2011*, Adare, Ireland, May 16-18, 2011
- E6. B. B. Berkes, Á. Kriston, P. Simon, G. Inzelt, Investigation of oxygen reduction reaction on Pt by using electrochemical quartz crystal nanobalance and numerical simulation, *Second Regional Symposium on Electrochemistry*, Belgrade, Serbia, June 6-10, 2010

- E7. G. Inzelt, B. B. Berkes, Á. Kriston, Electrochemical nanogravimetric studies of platinum in acid and neutral media, *Second Regional Symposium on Electrochemistry*, Belgrade, Serbia, June 6-10, 2010
- E8. B. B. Berkes, G. Inzelt, Á. Kriston, Electrochemical nanogravimetric studies of platinum in acid media, *61th ISE Meeting*, Nice, France, September 26-October 1, 2010
- E9. G. Inzelt, B. B. Berkes, Á. Kriston, Two types of platinum dissolution in acid media, *216th ECS Meeting*, Vienna, Austria, October 4-9, 2009

## Posters

- P1. B. B. Berkes, A. Maljusch, A. S. Bondarenko, W. Schuhmann, Simultaneous acquisition of impedance and gravimetric data in a cyclic potential scan for the characterization of non-stationary electrode|electrolyte interfaces, *62th ISE Meeting*, Niigata, Japan, September 11-16, 2011, s13-P-015
- P2. Á. Kriston, T. Szabó, Á. Nemes, S. Vesztergom, B. B. Berkes, T. Horváth, N. Molnár, K. Dobos, The application of multi-level simulation during the development of a hydrogen fuel cell vehicle, *61th ISE Meeting*, Nice, France, September 26-October 1, 2010, s15-P-030
- P3. Á. Kriston, B. B. Berkes, P. Simon, G. Inzelt, Investigation of oxygen reduction reaction on Pt by using electrochemical quartz crystal nanobalance and numerical simulation, *61th ISE Meeting*, Nice, France, September 26-October 1, 2010, s15-P-005

## Informative

- I1. B. B. Berkes, Tüzelőanyag-cellák (Hungarian), *Természet Világa*, **143** (2012) 63-65.
- I2. Á. Kriston, T. Szabó, B. B. Berkes, Á. Nemes, *Környezetvédelem*, Városi közlekedés hidrogénalapon, (Hungarian), **17** (2010) 16-17.