Investigation of the electrochemical stability of conducting polymer films and thin metal layers in modified electrodes - electrocatalytic activity and degradation

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1. Abstract

Electrochemical technology touches almost every aspect of everyone's life. In fact, much of modern technology depends on the capabilities that electrochemical processes have made possible. Electrochemical devices are used in numerous applications ranging from cordless power tools, mobile phones and laptop computers to hybrid electric vehicles, railroad signaling systems and aerospace applications, from lambda sensors to carbon monoxide detectors. In recent years there has been great progress in research on electronic and electrochemical devices based on organic materials. The operation of these devices is based on electrochemical processes, therefore, it is beyond doubt that a better understanding of these processes is a prerequisite for the development of novel, improved electrochemical reactors (e.g. batteries or fuel cells), electrochemical sensors and other applications. On the other hand, the monitoring of the degradation of the different components is of great importance for the efficient use of these devices. It is well known that (electrochemical) corrosion or degradation processes cause immense damage every year in many industry sectors and to our economic infrastructure. Since corrosion is driven by electrochemical processes, the study and the better understanding of electrode processes are also needed to develop new corrosion protection methods. The results of the present research project (e.g. the development of a new measuring system and novel measuring techniques) may lead to the development of novel and improved electrochemical devices.

It is confidently hoped that the results concerning the degradation of conducting polymer films and thin metal layers as well as the new information gained about electrochemical processes and complex electrochemical reaction mechanisms of theoretical and practical importance make possible a better understanding of the degradation processes in modified electrodes and electrode materials.

2. Introduction

In recent years there has been great progress in the development, production and use research on electronic and electrochemical devices based on organic materials (e.g. ion-selective electrodes, sensors, microelectrode arrays, actuators, fuel cells, laminate-type organic constructs such as chip on board structures, composite films, solar cells, etc.). In such devices polymers are often deposited on polycrystalline thin metal layers, however, microelectronic devices which utilize polymers coated with patterned thin metal films have also been developed. Many of the above mentioned devices work in an electrochemical environment and can be considered to be “modified electrodes” (“chemically modified electrodes”, “surface modified electrodes”, “polymer modified electrodes”, etc.). According to the literature the distinguishing feature of a modified electrode is that a generally quite thin film (from monomolecular to a few micrometers thick multilayer) of a selected chemical is bonded to or coated on the electrode surface to endow the electrode with the chemical, electrochemical, optical, electrical, transport, and other desirable properties of the film in a rational, chemically designed manner, but more complex structures also exist, they may contain more than one modifying substance, or more than one layer. It is beyond question that the monitoring of the degradation of the different (functional) layers is of great importance for the efficient use of these devices.

In accordance with the above considerations, the main objectives of the current project were:

- Development of new electrochemical techniques for the monitoring of the degradation of conducting polymer films and thin metal layers in modified electrodes.
- A better understanding of the degradation processes in modified electrodes and electrode materials.
- Design and development of a new, complex electrochemical measuring system.
- Gaining new information on electrochemical processes of theoretical and/or practical importance.
- A better understanding of complex electrochemical reaction mechanisms.
- Improvement of the performance of the “bending beam” technique.

3. Summary of the results

3.1. *Objective 1. Development of new electrochemical techniques for the monitoring of the degradation of conducting polymer films and thin metal layers in modified electrodes.*

Results that became available by the application of dual potentiodynamic control to the two working electrodes of a rotating ring-disk electrode (RRDE) have been reviewed and discussed [1,2,3]. It is a widespread opinion that the electrochemical behavior of gold in aqueous media has been thoroughly studied, and the interfacial tension changes ($\Delta\gamma$) of gold in sulfuric acid solutions can be explained by monolayer oxide formation/removal and adsorption phenomena. However, there are some peculiarities to consider. For instance, a sudden change in the slope of the $\Delta\gamma$ vs. electrode potential curve recorded during the negative-going scan of the cyclic voltammogram can be observed in the oxide reduction region of gold. The method of dual dynamic voltammetry, i.e. applying dynamic potential programs to the generator and the collector electrodes of a generator-collector system simultaneously, is a promising new method for studying the mechanisms of electrochemical processes [4]. By applying this method to a gold/gold rotating ring-disk electrode (RRDE) it could be shown [5,6,7] that the sharp change in the slope of the interfacial tension vs. potential curve recorded in the oxide reduction region of gold in sulfuric acid solutions is accompanied by the formation of soluble, electrochemically reducible gold species which can be detected at the ring electrode [8,9].

Electrochemical and mechanical properties of thin polymer films deposited on gold or platinum have been investigated in aqueous solutions by combining electrochemical methods (CV, EIS, EQCM) with SEM, X-ray crystallography and the bending beam method [10]. At sufficiently positive electrode potentials, degradation of the polymer takes place on both metals. In some cases structural changes of the polymer layer (the change in the film stress) caused by overoxidation could be detected by using the electrochemical bending beam method. To highlight these features, PEDOT (poly(3,4-ethylenedioxythiophene)) and PPD (poly(o-phenylenediamine)) films have been selected as illustrative examples. The morphological changes of the films during degradation were analysed by scanning electron microscopy (SEM). Changes of the effective mass of the Au|PEDOT film were studied by EQCM. Impedance spectra recorded before and after overoxidation were analyzed. The results support the mechanistic picture, according to which the originally compact and strongly adherent polymer films undergo structural changes during oxidation. As it can be seen from the SEM images of Au|PEDOT the overoxidation process results in the formation of cracks in the polymer layer and leads to partial delamination of the polymer film from the underlying metal. X-ray diffraction results showed that besides degradation, the crystallinity of the PEDOT film was also gradually improved with increasing number of overoxidation cycles. These changes may result in the generation of sites with novel catalytic and binding properties that may be advantageous for specific applications.

Many electrochemical systems are intrinsically nonstationary and are affected by time-dependent phenomena. The requirement of stationarity in the classical version of impedance spectroscopy appears to be in conflict with the essential properties of the object, therefore a post-experimental mathematical/analytical procedure is necessary for the reconstruction of the "true" impedance values. We could show [11,12,13] that the 4-dimensional analysis method, originally proposed by Stoynov, can not only be used for the correction of existing (experimentally measured) impedance data, but it also opens up the possibility of the estimation of impedance spectra outside the time interval of the measurements. As an illustrative example the method has been applied for the determination of the charge transfer resistance (R_{ct}) of poly(3,4-ethylenedioxytiophene) (PEDOT) modified electrode as a function of time, including the R_{ct} value corresponding to the time instant just after overoxidation of the polymer film. After the overoxidation the charge transfer resistance decreased continuously with experiment time to a value somewhat higher than the R_{ct} of the pristine electrode. The results imply that a "healing process" may occur at the film/substrate interface. A better understanding of this effect may have an impact on practical applications. The scheme of the mathematical procedure is shown in Fig. 3.1.1.

As illustrative examples, the method has been applied for the determination of the charge transfer resistance of a polymer modified electrode corresponding to the time instant just after overoxidation of poly(3,4-ethylenedioxytiophene) (PEDOT) films deposited on gold and glassy carbon substrates [14,15].

By comparing the properties of the GC|PEDOT|0.1 M H_2SO_4 and the Au|PEDOT|0.1 M H_2SO_4 electrodes a possible mechanistic explanation for the observed behavior has been proposed [15]. This is based on the assumption that in the case of the GC|PEDOT|0.1 M H_2SO_4 electrode two processes may occur simultaneously during the impedance measurements: (a) reduction of the oxidized surface of the GC substrate, including the reduction of the oxygen-containing surface functionalities and (b) readsorption of the polymer chains (polymer chain ends) on the surface.

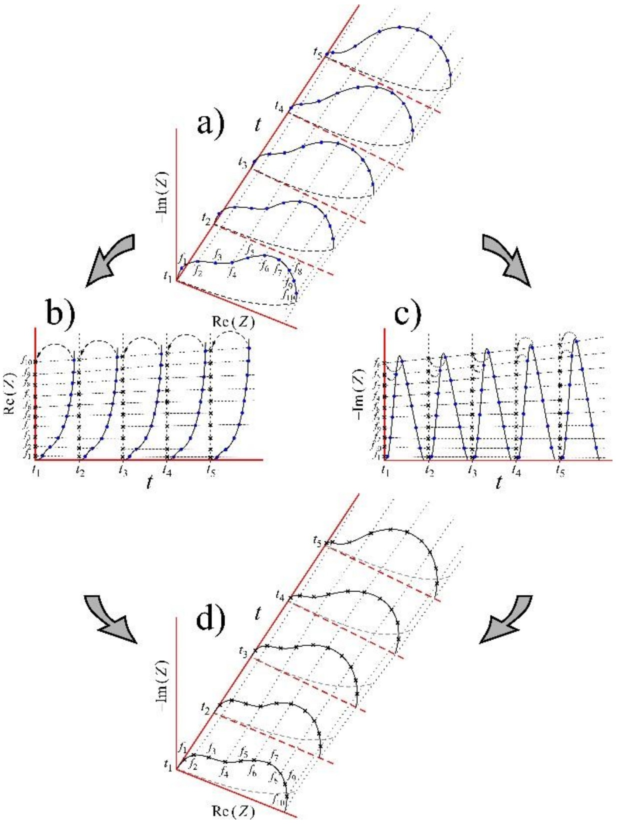

Figure 3.1.1. Scheme of the mathematical procedure. a) 3-D representation of the impedance and time evolution in Re(*Z*), –Im(*Z*) and *t* coordinates. Re(Z): real part of the complex impedance, Im(Z): imaginary part of the complex impedance, *t*: time,. •: measured data points (impedances) corresponding to the frequencies f_i, t_i: starting time of the i-th frequency scan. b) Iso-frequency dependencies and calculation of the instantaneous (corrected) Re(*Z*) values (×) by interpolation of the measured Re(*Z*) data. b) Iso-frequency dependencies and calculation of the instantaneous (corrected) –Im(*Z*) values by interpolation of the measured Im(*Z*) data. d) 3-D representation of the “reconstructed” instantaneous impedances related to the beginning of each frequency scan. ×: corrected data points (impedances) corresponding to the frequencies f_i

3.2. *Objective 2. A better understanding of the degradation processes in modified electrodes and electrode materials.*

Bending beam probes have been prepared by vacuum evaporation and by using electrodeposition. Au|PEDOT and Pt|PEDOT modified electrodes have been prepared by electrochemical methods in collaboration with the Department of Electrochemistry of Saint Petersburg State University. Au|PEDOP films have been prepared in collaboration with the

Department of Organic Chemistry of Eötvös Loránd University. The electrodes have been tested by electrochemical methods, by scanning electron microscopy (SEM) and by X-ray crystallography (in cooperation with the Institute of Physics, Eötvös Loránd University). Modified electrodes on RRDE tips have been prepared by electrochemical deposition, and tested by dual cyclic voltammetry. Electrochemical characteristics (voltammetric curves, impedance spectra) of Au|PEDOT layers in contact with electrolyte solution of different composition and pH has been investigated systematically.

The electrochemical mechanical and degradation properties of Au layers have been investigated by the electrochemical bending beam method and dual dynamic voltammetry. By applying the dual dynamic voltammetric method to an Au/Au rotating ring-disk electrode (RRDE) it could be shown that the sharp change in the slope of the interfacial stress vs. potential curve recorded in the oxide reduction region of gold in sulphuric acid solutions is accompanied by the formation of soluble, electrochemically reducible gold species (i.e. the degradation of the gold layer) which can be detected at the ring electrode [5,6,7,8,9]. By using scanning electron microscopy (SEM) method, an attempt was made to interpret the electrochemical mechanical properties of Au layers observed by the electrochemical bending beam method and dual dynamic voltammetry.

Conducting polymer layers (PEDOT, PEDOP, PoPD) have been deposited electrochemically on different substrates including glassy carbon. The properties of the modified electrodes and the degradation of the films have been investigated by electrochemical methods (voltammetry, impedance spectroscopy, electrochemical bending beam method), by scanning electron microscopy (SEM) and by X-ray crystallography [16].

Results of recent studies on the electrochemical stability and degradation properties of poly(3,4-ethylenedioxythiophene) films are summarized, with particular emphasis on the structural changes induced by overoxidation and electrochemical degradation. The most important electrodeposition methods for the preparation of PEDOT films in surfactant free aqueous media have also been summarized, and several experimental techniques suitable for monitoring the degradation process have been discussed. Morphological changes in PEDOT films during overoxidation have been analyzed. Overoxidation mechanisms proposed in the literature have been surveyed [17,18].

Electrochemical, mechanical and morphological properties of thin poly(3,4-ethylenedioxy-thiophene) (PEDOT) films deposited on gold were investigated in aqueous sulfuric acid and sodium sulphate solutions. At sufficiently positive electrode potentials overoxidation of the polymer took place and resulted in morphological changes and structure evolution. These effects were monitored by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and X-ray diffraction [19,20]. Significant changes in the film stress caused by overoxidation were detected by using the electrochemical bending beam method. Results of the EIS measurements proved that the charge transfer process at the metal/film interface is more hindered in case of the degraded film. According to SEM images the overoxidation/degradation of PEDOT films can result in random-like but quite well-ordered arrays of islands and trench-like structures. The diffraction peaks of PEDOT (see Fig. 3.2.1.) became sharper and more intensive during the subsequent oxidation cycles indicating an increase in the degree of crystallinity of the polymer.

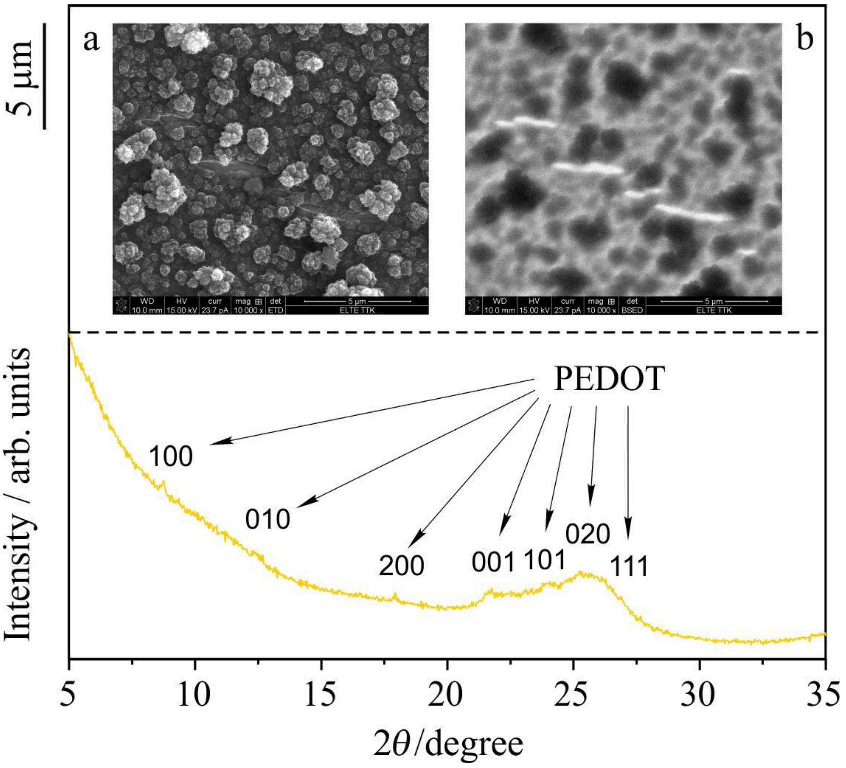

Figure 3.2.1. Structure of the oxidized PEDOT film after “mild” overoxidation: X-ray diffractogram. Inserts: (a) SEM image using secondary electrons. (b) The corresponding backscattered SEM image taken from the same area. The length of the vertical black bar left to the images corresponds to 5 μm.

Composite Au/PEDOT-MnO_2 and glassy carbon/PEDOT-MnO_2 electrodes have been prepared by electrochemical methods. The electrodes have been tested by cyclic voltammetry and impedance spectroscopy. The degradation process of the composite films have been followed by cyclic voltammetry, impedance spectroscopy and dual cyclic voltammetry []. Au and glassy carbon/ PEDOT, PEDOP / MoO_2, Fe_2O_3, Pd, Pt composites have been prepared and characterized by voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy (SEM). The degradation properties and electrocatalytic activity of polymer films and composite electrodes have been investigated by impedance spectroscopy, voltammetry, dual dynamic voltammetry, and the electrochemical bending beam method [21].

3.3. *Objective 3. Design and development of a new, complex electrochemical measuring system.*

A Zahner IM6 electrochemical workstation together with two XPOT external potentiostats has been purchased and installed. All necessary software has been installed. The new electrochemical measuring system has been extensively tested. Electrodes and insulator tubes for thin layer measurements has been purchased from the University of Warsaw. A new design of testing tubes for permittivity measurements of thin layers has been developed.

With the help of the new system independent and dynamic potential programs could be applied simultaneously to the RRDE disk and the ring. In some tests cyclic voltammograms were recorded simultaneously at the two electrodes. The symmetrical triangular waveforms driving the potentials of the two electrodes were identical, however, with a “phase shift” (the vertex potentials and the potential sweep rates for the two signals were the same, Fig. 3.3.1). By applying this “phase-shifted double cyclic voltammetry” method we were able to show that the reduction of the surface oxide layer of the polycrystalline gold disk immersed into sulfuric acid solutions is ac-companied by the formation of electroreducible side product(s), which can be detected on the ring. In fact, this was a rather unexpected result, since it is a common opinion that the electrochemical behavior of gold in aqueous media has been thoroughly studied, and the electrochemistry of gold is frequently viewed in very simple terms as involving only double-layer charging/discharging and monolayer oxide formation/removal phenomena.

The dual voltammetric technique can also be used to study electrode processes in different ways. For instance, if the “disk electrode” is polarized at a sufficiently low and the “ring electrode” at a sufficiently high scan rate, a 3D map can be constructed using the measured potential and current data, which may reveal the electro-active intermediates or products that are formed in the electrode process(es) taking place on the disk. Another possibility is the continuous measurement of the impedance of the collector electrode during the application of a potential program to the generator electrode.

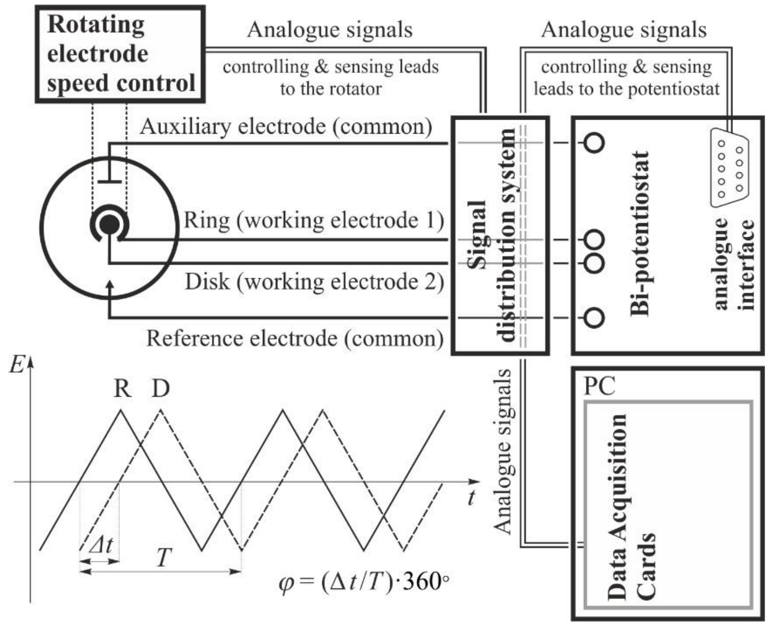

Figure 3.3.1. Scheme of the measuring system.

The combination of dual voltammetry, impedance spectroscopy and the bending beam technique offers substantial advantages for the monitoring and understanding of electrode processes. The advantages are not only more efficient detection of intermediates and increased selectivity, but also the possibility of observation of species which cannot be detected with conventional techniques [1,9].

The problems with electrical cross-talk, i.e. an interference between the current/voltage characteristics of the two working electrodes in four-electrode (generator/collector) systems have been investigated in the special case of the rotating ring–disk electrode (RRDE) [22,23]. Cross-talk arises in electrochemical cells of finite resistance due to the superposition of the electrical fields of the working electrodes, and often causes serious difficulties in the interpretation of measurement results. We presented an algorithm for modelling the rotating ring–disk electrode (RRDE) immersed into a finite resistance solution of a redox couple. We could show that based on the analysis of the Kirchhoff (Laplace) matrix of the simulation mesh, the effect of electrical cross-talk may be accounted for in such experiments. The intensity of cross-talk is found to be heavily influenced by the selection of the reference point for potential measurements; in practice this is the position of the reference electrode or the tip of the Luggin probe. The devised model is validated by means of a simple and demonstrative experiments [23].

Products of titanium dissolution in the active state are investigated in fluoride containing 1 M H_2SO_4 solutions [24]. The novel method of dual dynamic voltammetry, applied to Ti disk/Pt ring rotating ring–disk electrodes, is utilized for the simultaneous detection of different dissolution products. Potential regions where certain products (primarily, Ti(III) and H_2) are formed are identified by a 3D electrochemical map constructed based on the ring–disk electrode measurements. Besides dissolution in the form of Ti(III) species and hydrogen evolution, the formation and prompt oxidation of Ti(II) can also be presumed under the applied conditions.

3.4. *Objective 4. Gaining new information on electrochemical processes of theoretical and/or practical importance.*

The reduction of perchlorate ions on ruthenium and rhodium films has been investigated by the electrochemical bending beam method, voltammetry and impedance spectroscopy.

The effect of oxonium&hydroxide ion diffusion on the hydrogen evolution reaction in unbuffered aqueous electrolyte solutions of mildly acidic pH values has been investigated. It has been demonstrated that the cathodic polarization curves measured on a Ni rotating disk electrode in these solutions can be modeled by assuming two irreversible reactions, the reduction of H+ and that of water molecules, both following Erdey-Gruz–Volmer–Butler kinetics. Interestingly, both digital simulation and the analytical model hint that hydroxide ions, when present in the solution layers bounding the electrode surface have an infinitely large diffusion coefficient. This feature can be explained by assuming what we call a “directed Grotthuss mechanism” of transport.

Palladium and platinum are good catalysts. One of the main research interest is the partial substitution of the metal amount of such catalyst using polymer-metal composites. PEDOT is one of the common used polymers in industries, due to its optical transparency in its conducting state, high stability, moderate band gap and low redox potential. Therefore we investigated PEDOT/palladium and PEDOT/platinum composites and their special electrocatalytic properties. PEDOT/palladium and PEDOT/platinum composites and their special electrocatalytic properties has been investigated in both in argon and air saturated 0.1 M sulphuric acid solutions [25]. Several PEDOT/palladium composite samples were prepared by the immersion of PEDOT films into 0.005 M $PdCl_2$ - 0.1 M H_2SO_4 solution, using different preparation methods with varied film reduction and immersion parameters. The obtained composite systems were studied by cyclic voltammetry and electrochemical impedance spectroscopy. The morphology and the palladium content of the composites were studied by scanning electron microscopy. The cyclic voltammograms of the PEDOT/palladium composite samples showed little difference in the potential range of E = (-0.25 – +0.6) V vs. SSCE, compared to those of PEDOT films. On the other hand, significant hydrogen reduction peaks could be observed at more negative potentials in case of the composite samples. The impedance spectra of the composite samples showed no significant potential dependence, besides, the small frequency double layer capacity values were similar in case of the composites of the same surface area and film thickness. One of the composite samples showed a distinct Warburg section at medium frequencies what may be related to the structure caused by the electroless composite preparation method. Scanning electron microscopy measurements showed that the palladium crystals formed spikes, aggregates and snowflakes on top of the PEDOT film, depending on the preparation method used. The distribution of palladium was considerably inhomogeneous, while the average palladium content of the samples did not differ to a large extent. A PEDOT/platinum composite on a platinum rotating disk electrode was also prepared and studied. The cyclic voltammograms of the PEDOT/platinum composite sample showed significant rotation rate dependence in air saturated solution, contrary to PEDOT. Furthermore, the Levich equation was fulfilled in case of the composite sample, suggesting the presence of a sluggish, diffusion-controlled reaction in air saturated solution. The impedance spectra of the composite sample confirmed the rotation rate dependence. A detailed analysis of the results is in progress, and the results will be published in scientific journals.

In the implant dentistry the biocompatible titanium screws are integrated in the gingivitis or jawbone then the crown is attached atop the implants. Different constituents in the saliva, e.g. the fluorid additive of the toothpastes, mouthwashes (in as typical concentration ranges as of 200-20,000 ppm) may deteriorate the surface layer of implants and tooth enamel. The titanium ion release from the implant to the saliva might cause unfavorable metallosis cases. The aim of the work reported in [26] was to study the effect of fluoride ion addition on the corrosion process of titanium dental implants in physiological Ringer solutions. The chemical composition of the Ti implant was determined using SEM/EDS, prompt gamma activation (PGAA), and neutron activation (NAA) analyses, respectively. The investigations were carried out in physiological Ringer solution in the 0-500 ppm F^- concentration range at 37 °C. The solution pH-s were adjusted with addition of lactic acid to pH 3, and lactic acid and $NaHCO_3$ to pH 6. The kinetic evaluation of the impedance diagrams recorded on the open circuit potentials have revealed the significant weakening of the protectiveness of the passive layer formed on titanium in the fluoride-containing Ringer solutions. The effect of fluoride ion is greater at pH 3 and 37 °C than at pH 6 or ambient temperature. The shift of the open circuit potentials to more negative values due to the F^- addition at pH 3 is more significant to such extent that might cause the breakdown of the passive layer and lead to fast passive state dissolution rate of titanium. Products of titanium dissolution in the active state were investigated in fluoride containing 1 M H_2SO_4 solutions [24,26].

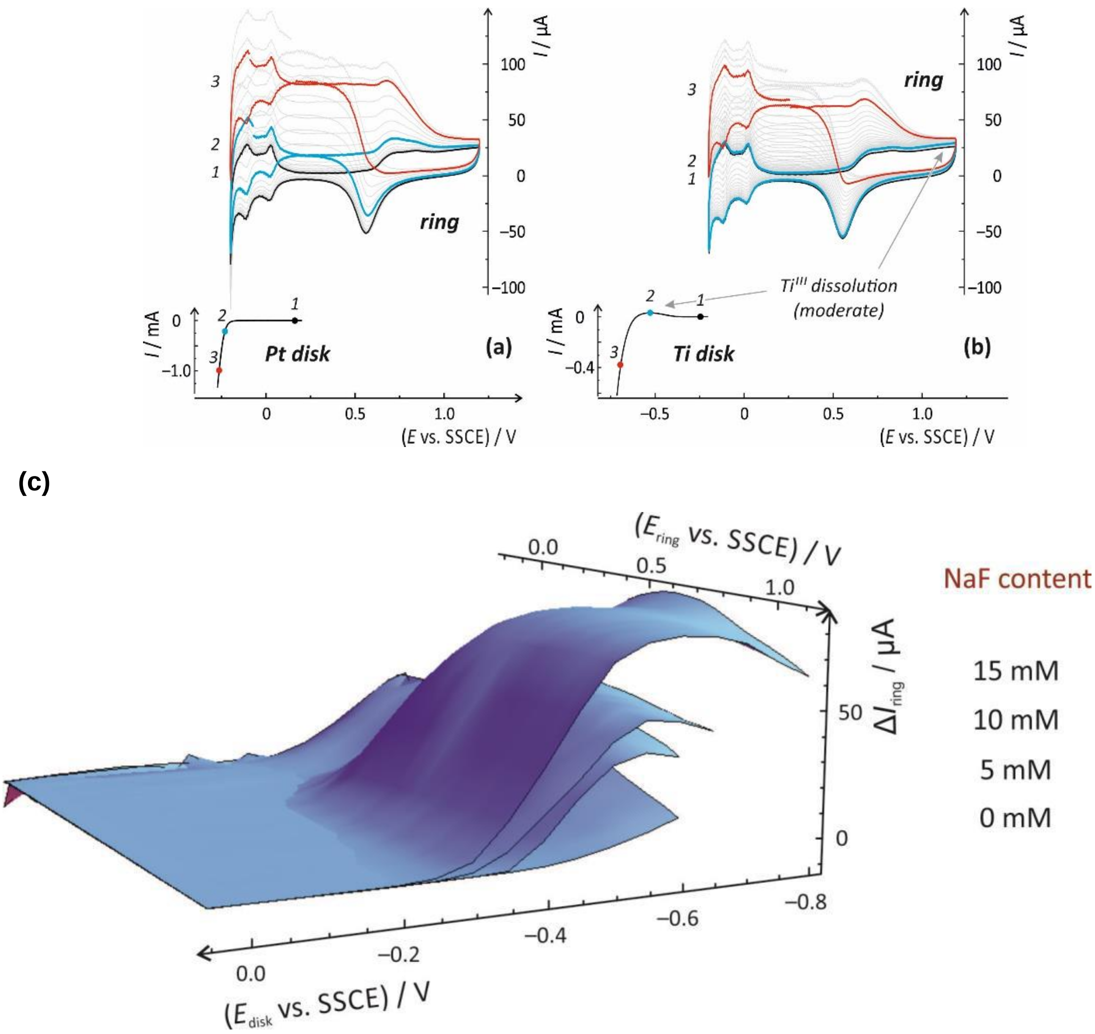

Figure 3.4.1. (a) Hydrogen evolution resulting by a slow, negative-going scan on the platinum disk and oxidation of the produced hydrogen on the platinum ring of a Pt/Pt RRDE in 1 M H_2SO_4. (b) Slow, negative-going scan on the titanium disk and oxidation of the formed products and intermediates on the platinum ring of a Ti/Pt RRDE in 1 M H_2SO_4. In both cases the disk electrode was polarized towards negative potentials at 0.25 mV/s sweep rate while on the ring cyclic voltammograms were recorded between –200 mV and 1200 mV vs. SSCE at 100 mV/s scan rate. (c) Illustration of the effect of varying the fluoride ion concentration on the detectable ring current changes during fast ring scanning measurements. Measurements were taken in 1 M H_2SO_4 solutions containing NaF at different concentrations as indicated. A reference disk potential of 0 V vs. SSCE was used for creating the presented surfaces.

The novel method of dual dynamic voltammetry, applied to Ti disk/Pt ring rotating ring–disk electrodes, was utilized for the simultaneous detection of different dissolution products. Potential regions where certain products (primarily, Ti(III) and H_2) are formed were identified by a 3D electrochemical map constructed based on the ring–disk electrode measurements (see Fig. 3.4.1). Besides dissolution in the form of Ti(III) species and hydrogen evolution, the formation and prompt oxidation of Ti(II) can also be presumed under the applied conditions.

Some elements of the theoretical background of the thermodynamics of interfaces have been discussed [27,28]. We provided a brief overview of the mathematical background to the thermodynamic theory of surfaces interfaces and of some of the mathematical concepts and techniques relevant to the study of thermodynamics, including the theory of homogeneous functions and partly homogeneous functions, Euler's theorem, and Legendre transformation. Some general aspects of the thermodynamics of systems with surfaces and interfaces were discussed, and a concise treatment of interfaces within the framework of classical thermodynamics was given. A reasonably simple thermodynamic treatment of interfaces, together with a brief description of the models widely used in the literature, was presented, and the characteristics of the Gibbs „dividing plane" model and the Guggenheim „interphase" model was outlined. In an another paper [29] the basic thermodynamic functions of an ideal monatomic gas (fundamental relations and thermodynamic potential functions) have been selected as illustrative examples.

3.5. *Objective 5. A better understanding of complex electrochemical reaction mechanisms.*

The electrochemical reduction of ClO_4^- ions at different electrodes has been discussed in [30]. Based on thermodynamics alone, perchlorate is expected to be a powerful oxidizer. Perchloric acid, for example, should be able to oxidize water to oxygen in aqueous solutions. In contrary to this, perchlorate ions are usually considered as stable anions in electrochemistry; therefore perchloric acid and its salts are often used as supporting electrolytes in different experiments (e.g., investigation of dissolution, deposition, or corrosion of metals and semiconductors), and many observations revealed that perchlorate salts show considerable stability in electrochemical environment. This behavior can be explained by the concept of "kinetic stability," that is, the stability of perchlorate in aqueous solutions is governed by kinetics and not a result of thermodynamics. Nevertheless, evidence for the occurrence of the reduction process has been reported e.g. for Rh, Pt, WC, Al, Ti, Ir, Ru, Re, Tc, and Sn electrodes. Besides the significance of perchlorate reduction for the fundamental electrochemistry nowadays a very practical reason, the so-called perchlorate contamination challenge, came into foreground orienting the attention toward the reductive elimination of perchlorate ions. Perchlorates are used as oxidizer component and primary ingredient in solid propellants for rockets, missiles, and fireworks. Therefore dissolved ammonium, potassium, magnesium, or sodium salts are present as contaminant in groundwater and surface waters originating from improper disposal of the solid propellants and from the wastewaters of the manufacturing plants. Perchlorate salts are also used in optoelectronics,20 electronic tubes, car air bags, and leather tanning. According to the above, the problem of perchlorate reduction constitutes an intersection of several branches of science, such as electrochemistry (anodic dissolution of metals, discharge of oxonium ions), (electro)catalysis, corrosion science passivity of metals, coupling of cathodic and anodic processes), civil, environmental and medical sciences, etc.

The reduction of perchlorate ions on ruthenium and rhodium films has been investigated by the electrochemical bending beam method, voltammetry and impedance spectroscopy [31].

The effect of H^+ and OH^- diffusion on the hydrogen evolution reaction has been studied in unbuffered aqueous electrolyte solutions of mildly acidic pH values [32]. It has been demonstrated that the cathodic polarization curves measured on a Ni rotating disk electrode in these solutions can be modelled by assuming two irreversible reactions, the reduction of H^+ and that of water molecules, both following Erdey-Grúz–Volmer–Butler kinetics. The reduction of H^+ yields a transport-limited and thus, rotation rate-dependent current at not very negative potentials. At more cathodic potentials the polarization curves are dominated by the reduction of water and no mass transfer limitation seems to apply for this reaction. Although at the first look the two processes may seem to proceed independently, by the means of finite-element digital simulations we could show that a strong coupling (due to the recombination of H^+ and OH^- to water molecules) exists between them. We also developed an analytical model that can well describe polarization curves at various values of pH and rotation rates. The key indication of both models is that hydroxide ions can have an infinite diffusion rate in the proximity of the electrode surface, a feature that can be explained by assuming a directed Grotthuss-like shuttling mechanism of transport.

Products of titanium dissolution in the active state are investigated in fluoride containing 1 M sulfuric acid solutions [24,26]. Dual dynamic voltammetry, applied to Ti disk/Pt ring rotating ring–disk electrodes, has been utilized for the simultaneous detection of different dissolution products. Potential regions where certain products (primarily, Ti(III) and H2) are formed have been identified by a 3D electrochemical map constructed based on the ring–disk electrode measurements. Under the conditions applied, besides dissolution in the form of Ti(III) species and hydrogen evolution, the formation and prompt oxidation of Ti(II) can also be presumed [24].

Electrochemical behavior of poly-(3,4-ethylenedioxythiophene) composites with manganese dioxide (PEDOT/MnO_2) has been investigated by cyclic voltammetry and electrochemical quartz crystal microbalance at various component ratios and in different electrolyte solutions [33]. The electrochemical formation of PEDOT film on the electrode surface and PEDOT/MnO_2 composite film during the electrochemical deposition of manganese dioxide into the polymer matrix was gravimetrically monitored. The mass of manganese dioxide deposited into PEDOT at different time of electrodeposition and apparent molar mass values of species involved into mass transfer during redox cycling of PEDOT/MnO_2 composites were evaluated. Rectangular shape of cyclic voltammograms of PEDOT/MnO_2 composites with different loadings of manganese dioxide was observed, which is characteristic of the pseudocapacitive behavior of the composite material. Specific capacity values obtained from cyclic voltammograms were about 169 F g^{-1}. The specific capacity, related to the contribution of manganese dioxide component, was about 240 F g^{-1}. It was found that during the redox cycling of PEDOT/MnO_2 composite films with various MnO2 content, the oppositely directed fluxes of counterions (anions and cations) occur, resulting in a change of the slope of linear parts of the $\Delta f - E$ plots with changing the mass fraction of MnO_2 in the composite film.

Time dependence of the electrochemical impedance of overoxidized Au|poly(3,4-ethylenedioxytiophene) (PEDOT)|0.1 mol·dm-3 sulfuric acid (aq.) and glassy carbon|poly(3,4-ethylenedioxytiophene) (PEDOT)|0.1 mol·dm-3 sulfuric acid (aq.) electrodes has been investigated [14,15]. To follow the changes occurring at the film/substrate interface after the overoxidation procedure, successive impedance measurements were carried out. Although the system is intrinsically nonstationary, the charge transfer resistance (R_{ct}) corresponding to different time instants could be determined by using the so-called 4-dimensional analysis method. The same post-experimental mathematical/analytical procedure could be used also for the estimation of the charge transfer resistance corresponding to the time instant just after overoxidation of the PEDOT film. The increase of the charge transfer resistance of the overoxidized system with respect to that of the pristine electrode suggests that during overoxidation the electrochemical activity of the film decreases and the charge transfer process at the metal/film interface becomes more hindered. After the overoxidation procedure, when the electrode potential was held in the “stability region” (at E = 0.4 V vs. SSCE in the present case) the R_{ct} decreased continuously with experiment time to a value somewhat higher than that of the pristine electrode. Fig. 3.5.1. shows the schematic representation of the suggested process in connection with the Au|PEDOT system. In the beginning, i.e. in the pristine films, the sulfur atoms of the PEDOT chains are connected to the gold surface. As already mentioned in the introduction, during overoxidation at sufficiently positive potentials a significant fraction of the polymer chains become detached from the substrate surface (i.e. "desorption", "deactivation" or "delamination" occurs). In parallel with this process the oxidation of the electrode leads to the formation of a gold oxide layer.

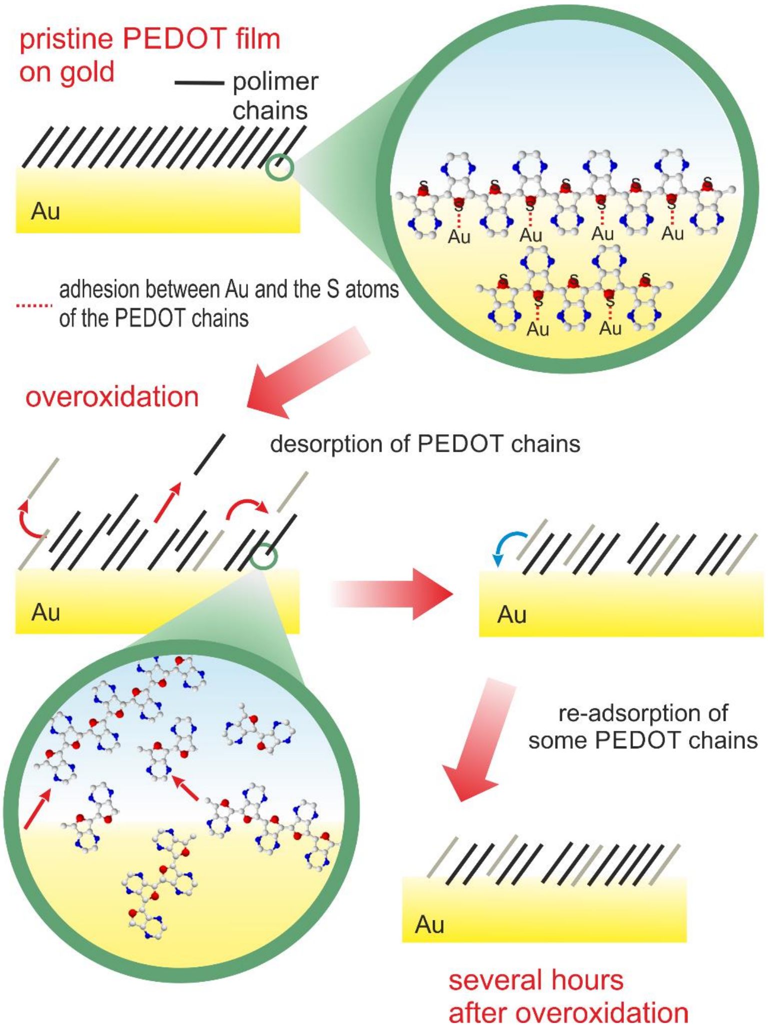

Figure 3.5.1. The suggested mechanism of the desorption and re-adsorption polymer chains during the overoxidation process and after overoxidation (when the potential is held in the "stability region").

This atomic oxide layer can block the active surface temporarily and ad interim hinders the adhesion interactions with the polymer chains. This effect may be operative in the present case too. On the other hand, after the overoxidation treatment, at a less positive potentials the readsorption of the polymer chains (polymer chain ends) becomes possible. This means that during overoxidation the "effective" coverage of the substrate by the polymer decreases, and at less positive potentials the coverage may start to increase again. The direction of the change in R_{ct} is in agreement with this hypothesis.

Poly(3,4-ethylenedioxypyrrole) films on gold substrate were prepared by electropolymerization of ethylenedioxypyrrole monomer (EDOP) under potentiodynamic conditions in aqueous sodium sulfate solutions [34]. The aim of this work was to characterize the gold | poly(3,4-ethylenedioxypyrrole) electrodes in aqueous sulfuric acid solutions and to compare the results with those of other studies that investigated similar systems. However, the experimental results obtained for the PEDOP modified electrodes significantly deviated from the expectations based on studies with similar systems. According to the results, two distinct types of polymer films were formed depending on the storage history of the monomer solutions. By using "fresh" monomer solutions polymer films with nearly ideal capacitive behavior were obtained and almost rectangular-shaped cyclic voltammograms could be observed in a rather broad potential range. Impedance spectra revealed that the charge transfer resistance between the substrate and the film was low. According to the SEM images the polymer layer on the gold substrate was relatively smooth with some small and short cracks. In contrast, working with "old" monomer solution that was not properly stored, the shapes of the cyclic voltammograms recorded at the Au | PEDOP | 0.1 M sulfuric acid (aq.) electrode exhibited two peaks, a reduction peak at about -0.2 V vs. SSCE and an oxidation peak close to 0.2 V vs. SSCE, and the charge transfer resistances were considerably higher than those estimated for the electrode prepared using "fresh" monomer solutions. SEM images showed that the surface of the polymer film was extremely rough, with several wrinkles, creases and large cracks. This behavior was quite unexpected, because the two types of samples were prepared in the same way and only the storage histories of the two commercial monomer solutions were different. It is known that despite some differences in interpretation of literature results on the electropolymerization of monomers and oligomers, there seems to be a general consensus that long conjugated oligomers are poorly (if at all) electropolymerizable because of the increased stabilization of their extended cation radicals, which prevents further coupling toward the formation of polymers. Nevertheless, it is accepted in the literature that "extending oligothiophene length beyond certain limit apparently brings them to an "island of reactivity" toward electropolymerization". On the other hand, the conjugation length of the polymer chains, which is a primary indicator of conductivity, may also be influenced by oligomerization. It is known that rather short conjugation lengths are usually sufficient for reasonable conductivity. Intuitively, conjugation should be important in two respects. First, carrier generation upon oxidation or reduction should be facilitated with high conjugation lengths since the resulting radical cation or anion will be more highly delocalized. Second, higher conjugation lengths ought to facilitate intermolecular charge transport by providing more frequent π-π overlap between adjacent backbones.

Nevertheless, it is clear from our results, that the conjugation length is longer in the case of the PEDOP film prepared from “fresh” monomer solution.

3.6. *Objective 6. Improvement of the performance of the “bending beam” technique.*

There are a variety of materials that can be used to prepare opto-electrochemical cells. The most common ones include glass (Pyrex and quartz), Teflon, and Kel-F. A practical consideration in selecting these materials is that the materials should be easily processable, inert to the electrochemical reactions, and cost-effective. For most electrochemical reactions, a Pyrex glass cell is used because it is easy to make and glass is generally a very low cost material. When the reaction involves media that are corrosive to glass (e.g., high pH, hydrofluoride, etc.), Teflon, Kel-F or other plastic materials should be used instead. However, in the presence of some organic solvents, the plastic materials might decompose leading to contamination and hence interference in sensitive measurements. In order to carry out more accurate measurements the electrochemical bending beam system in our laboratory has been modified and improved: new (Pyrex glass) containers and accessories for opto-electrochemical cells have been designed and constructed. A special optical window arrangement was developed, which can be used for many purposes, including measurements using a multibeam optical sensing technique (see Fig. 3.6.1).

Thin gold, platinum, rhodium, chromium and titanium metal layers on bending beam probes were prepared by vacuum evaporation (in cooperation with the Technical University Budapest, Dr. F. Ujhelyi). Ruthenium layers were prepared by electrodeposition. The experimental methods for the determination of stress changes at electrified solid-liquid interfaces have been surveyed in [35]. Results of bending beam experiments have been summarized in [36].

Fig. 3.6.1. Photo of a new opto-electrochemical cell

Some critical remarks have been made [37] concerning the use of the bending beam method in electrochemical systems. Possible sources of systematic errors in optical methods used for the experimental determination of stress evolution of silicon and germanium as lithium-ion battery electrode materials have been discussed.

Several methods developed for the experimental determination of (interfacial or film) stress changes in electrochemical systems containing solid-liquid interfaces have been reviewed, as well as the kind and quality of information that can be obtained using these methods are discussed ("bending beam" method and related techniques, piezoelectric method, extensometer method, and the method based on the measurement of contact angle [35,36].

4. Overall conclusions, publication statistics

Many electronic and electrochemical devices based on organic materials (e.g. ion-selective electrodes, sensors, microelectrode arrays, actuators, fuel cells, laminate-type organic constructs such as chip on board structures, composite films, solar cells, etc.) work in an electrochemical environment and can be considered to be "modified electrodes". The operation of these devices is based on electrochemical processes, therefore, it is beyond doubt that a better understanding of these processes is a prerequisite for the development of novel, improved electrochemical reactors (e.g. batteries or fuel cells), electrochemical sensors and other applications. On the other hand, the monitoring of the degradation of the different components is of great importance for the efficient use of these devices. It is well known that (electrochemical) corrosion or degradation processes cause immense damage every year in many industry sectors and to our economic infrastructure. However, experimental studies concerning the electrochemical and mechanical stability of modified electrodes are scarce and often are no more than broad outlines of little practical use. We hope that the results of the present research project (e.g. the development of a new measuring system and novel measuring techniques, the findings concerning the degradation of conducting polymer films and thin metal layers as well as the new information gained about electrochemical processes and complex electrochemical reaction mechanisms of theoretical and practical importance, etc.) make possible a better understanding of the degradation processes in modified electrodes and electrode materials, may help to fill in the gap in this area of knowledge, and may lead to the development of novel and improved electrochemical devices.

The results of the project have been published in peer-reviewed international scientific journals (so far, 21 papers), and in 6 book chapters (see the attached list of publications: Q1:7 (D1:4), Q2:2, Q3:6, Q4:1, 5 papers in new scientific journals (journal ranking information is not yet available)). In addition, the results of the project have been presented at more than a dozen international scientific conferences.

With regard to the dissemination of information, it is remarkable to mention that 2 BSc and 3 MSc theses have been completed within this project, and 3 research papers (including 1 award-winning essay) have been presented at the National Scientific Students' Associations Conference ("OTDK") [21,25,38,39,40,41,42,43].

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