MODIFIED ELECTRODES

Ph.D. thesises

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I. Introduction

It is well known that the same electrochemical process can proceed with orders of magnitude difference in rate on different electrode surfaces. The electrode is not just part of the charge transfer process, but it does have catalytic effect, as well. Accordingly, one of the main scopes of electrochemical research is the development of new electrodes. The modification of electrode surfaces influences significantly the properties, which is determined primarily by the modifier. The original electrode is just an electron source or sink. At the beginning the research focused on the preparation of new modified electrodes, and later their possible applications were concerned. The intensive work resulted in using modified electrodes in many fields of science and even in daily life. An application area is the chemical and biochemical sensors. Furthermore better catalytic effect and selectivity could be achieved with modified electrodes in organic synthesis. Metals can be protected against corrosion by modifying the surface.

The processes of the surface modification can be classified in two groups by the interaction between the surface and the modifier, physisorption and chemisorption. There are various methods for modification, and the choice depends on the surface and the modifier, too. Physical adsorption is suitable for binding bigger molecules, e.g., polymers to the electrode surface. Smaller molecules can be linked to the active sites of the surface by their functional groups. Other compounds can be bound to the modified electrodes thus increasing the number of possible modification processes.

Modified electrodes are used in the electrochemical group of the Department of Physical Chemistry at University of Szeged. The fields of investigation involve conductive polymers, corrosion, enzyme electrodes, fullerene electrodes, self-assembling monolayers. I have investigated the latter three types of modified electrodes.

II. Aims and scopes

Our first aim was to develop an enzyme electrode in which the enzyme was trapped into a Nafion film physisorbed onto an electrode surface. We meant to investigate the influence of the composition of the film forming solution, e.g., Nafion and water content on the enzyme activity. We intended to study the binding of the enzyme and the possibility of repetitive application of our enzyme electrodes.

We wanted to study physisorbed surface layers that were electroactive themselves and the electrochemical transformation of them could mean the formation of some electrocatalytic surfaces. From this aspect we proposed to investigate C_{60} fullerene layers in solutions of decreased water content to form C_{60} films in various oxidation states. Our further goal was the synthesis of new derivatives of C_{60} in solid phase and the investigation of their possible catalytic effects.

Our third aim was to form chemisorbed self-assembling layers, to which electroactive compounds can be bound and probably longer conductive chains can be built, as well. These molecular “wires” might be suitable for linking various compounds, e.g., enzymes to surfaces also providing the electric contact. We wanted to study the chemisorption of different aminothiol compounds on gold surfaces (their surface amounts, and their structures). We intended to link benzoquinone to these modifiers by the reaction of amine group and benzoquinone. For this purpose we wanted to test which aminothiol could be the best for binding quinone firmly, what could be the correlation between the reactivity and the structure, and what could be the effect of the modifier on the electrochemistry of quinone. For the formation of molecular “wires” we meant to study the extension of the chains with various diamine compounds to get as long chains as possible.

III. Experimental

The electrochemical methods used (amperometry, voltammetry, coulombmetry) were complemented with other measurements if they were possible. The response of the enzyme electrode was followed by potentiometric method measuring the hydrogen peroxide formed in the reaction of the enzyme. The behavior of fullerene films was studied by cyclic voltammetry. The structural rearrangement was verified by infrared spectroscopy (IR), as well. The semiconductive properties of fullerene were investigated by photoelectrochemical studies. The electrochemical investigations of self-assembled layers were carried out by cyclic voltammetry, too. The adsorption of aminothiol sublayers was also studied by quartz crystal microbalance (QCM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The protonation of aminothiol layers was studied with impedance spectroscopy. The layer extensions with quinone and diamine compounds were followed by infrared spectroscopy.

IV. Thesises

1. Formation and investigation of enzyme electrodes

We succeeded in working out a simple method to prepare a glucose sensor based on glucose oxidase enzyme. The enzyme was dissolved in a buffer solution (type I) and then mixed with acetone (type II) and Nafion solution. This mixture was cast onto a glassy carbon electrode, and dried. The enzyme electrode prepared was suitable for determining glucose by measuring the oxidation current of hydrogen peroxide formed in the enzyme reaction. Adding of glucose resulted in a rapid current response, which was proportional to the glucose concentration. We carried out experiments to optimize the activity and the stability of the enzyme electrode. We found that the composition of the layer forming solution influenced the detected current, i.e., the activity of the enzyme. We investigated the effect of the enzyme concentration, the effect of Nafion and water content. Our results showed that the increased enzyme concentration enhanced the current response, the sensitivity. Changing the Nafion content in the layer forming solution, we observed, that the current increased up to 0.9 % Nafion, but it decreased at larger amounts. The large Nafion content might worsen the transports in the films, while the low Nafion content could not give films suitably entrapped enzymes. The decrease of water content, adding acetone to the layer forming solutions, increased the enzyme activity, and the amount of entrapped enzymes increased an order of magnitude. The enzyme electrodes were suitable for repetitive using, although the current became gradually noisier due to the damaging effect of hydrogen peroxide accumulated in the surface layer.

2. Investigation of electrodes covered by fullerene films

2.1. We established that the three-electron reduction of fullerene films in aqueous solutions containing K^+ could be separated into three consecutive one-electron reductions by decreasing the water content with the addition of dimethylformamide. We found that depending on the water content, the reduction changed from a reversible one-electron reaction to an irreversible three-electron reaction. Besides the water content, the concentration of the electrolyte and the pH of the solution influenced the processes, as well. We assumed a competition for the reduced C_{60} between alkali metal ion and Brønsted acids present in the solution. This competition resulted in the formation of various amounts of alkali fullerides and hydrogenated fullerenes. We observed that the hydrogenation of C_{60} retarded the film reduction. At optimal conditions (amount of dimethylformamide, $[K^+]$, oxygen-free solution) reversible reduction-oxidation of fullerene films could be carried out. We suggested that movement of alkali metal ions in to and out of the film, together with the release of entrapped dichloromethane used to make the films caused a significant structural rearrangement of the fullerene layers. We assumed that the structure of the film became more open after one reduction-oxidation cycle (pretreatment), and it resulted in considerable difference in the behavior. For instance, such pretreated films showed more than an order of magnitude larger quantum efficiency in the photoelectrochemical oxidation of ascorbic acid.

2.2. We also observed that after pretreatment, hydrogenation of the bulk of the film was possible causing the formation of various H_xC_{60} $(1 \leq x \leq 3)$ compounds. The extent of hydrogenation depended on the potential range, and on the acid content of the solution used. The formation of hydrogenated fullerenes was an irreversible process, its oxidation occurred at very large potentials, giving the possibility of electrochemical studies in a quite large range. The oxidation did not form the neutral C_{60} back, we over-oxidised the films. We found that the H_xC_{60} film was an n-type semiconductor (its flatband potential was 0.3 V more negative than the intrinsic semiconductor C_{60}), and its quantum efficiency was even larger than that of pretreated C_{60} film.

2.3. The electrochemical transformation of fullerene films in various solutions gave rise the possibility of studying the electrocatalytic effect of fullerene derivatives in various oxidation state. We found that they could act as catalysts in certain electrochemical processes. For instance, HC_{60} was active in oxygen reduction, and its activity was more pronounced after pretreatment of the films. This was attributed to the structural rearrangement. The films became more porous, more penetrable for oxygen. Solid C_{60}^{2-}, formed at larger water content, was shown to have catalytic effect on the reduction of formaldehyde. We assumed that the reaction produced methanol. We also found that the pretreatment of the films could produce some side products that could catalyze the oxidation of dimethylamine and sulfite ion. That was probably due to some unknown fullerene derivatives formed during the pretreatment, and we assumed at least three of such products.

3. Formation and investigation of self-assembled layers

Various aminothiols were attached to gold surfaces by chemisorption. We determined the adsorbed amounts by the reductive desorption of the modifiers. We measured that aromatic aminothiols adsorbed with a little larger surface concentration than aliphatic ones, but none of them could reach the possible saturation amount. Although the surface coverages were similar, we observed different behavior due to the change of compactness of the layers. We investigated the electrochemical reaction of cytochrom c on such modified electrodes. It was found that the electrochemical response was not stable on aminoalkanethiol modified surfaces, and it was much better on aromatic aminothiol covered ones. The change was interpreted by the protonation of primary amines at neutral pH, while the aromatic amines carried partial negative charge at the same conditions.

3.2. We investigated the possibility of the reaction between each modifier (so-called sublayer) and quinone. The aminothiols studied could be classified in two groups: the first one where the aminothiols bound quinone with covalent bonding, the second one where the modifiers interacted with quinone mainly noncovalently. The aminoalkanethiols and 4-aminothiophenol were in the first group. On these modifiers we found three types of quinone, besides di- and monoaminosubstituted quinone, we assumed and verified the presence of nonsubstituted quinone. We suggested that the nonsubstituted quinone on these modifiers could bind to monoaminosubstituted ones. Other aromatic aminothiols could be put in the second group. These compounds bound quinone rather by noncovalent interaction than through their amino groups.

3.3. We established that the attached quinone (either covalently or noncovalently) could be reacted with diamine compounds. The terminal amine group could be reacted with quinone again, and thus molecular chains, "molecular wires" could be built with several quinone units at increasing distance from the surface. It seemed that the conductivity of these chains was good enough that the quinone units in different distance showed similar oxidation – reduction rates. We observed that the effect of the sublayer on the behavior of the chains decreased with increasing length, i.e., the influence of the spacers became determining. We observed that the oxidation-reduction potentials of quinone units systematically changed in the consecutive reactions of quinone and amine. That phenomenon was suggested to be the consequence of the positive charge of protonated terminal amine groups. The redox potential of quinone units could be tuned by changing the binder aminothiols and the spacer diamines, as well. Comparing the reactivity of various diamines we observed no significant difference among diaminoalkanes with different chain length (n=2-10). We assumed similar reactivities due to the flexibility of those spacers. However, the extension of the layers with diaminocyclohexane and benzidine was much less effective. In those cases the spacers had more rigid structure and that could mean steric hindrance causing lower reactivity toward quinone.

V. List of publications

Papers:

1. Á. Szűcs, V. Budavári, J. B.Nagy, M. Novák: Electrochemical behavior of C_{60} films in dimethylformamide + water mixtures. *J. Electroanal. Chem.*, 528, 153 (2002); IF: 2,027 (2002)

2. V. Budavári, Á. Szűcs, Cs. Somlai, M. Novák: Noncovalently bonded quinone on self-assembled molecular layers. *Electrochim. Acta*, 47, 4351 (2002); IF: 2,078 (2002)

3. Á. Szűcs, V. Budavári, O. Berkesi, M. Novák: Electrochemical hydrogenation of C_{60} fullerene films. *J. Electroanal. Chem.*, 548, 131 (2003); IF: 2,027 (2002)

4. Viktória Budavári, Árpád Szűcs, Albert Oszkó and Mihály Novák: Formation and electrochemical behavior of self-assembled multilayers involving quinone. *Electrochim. Acta*, 48, 3499 (2003); IF: 2,078 (2002)

Lectures, posters:

1. V. Budavári: Electrochemical investigation of Nafion-embedded glucose oxidase enzyme. (Nafionba ágyazott glükóz-

oxidáz enzim elektrokémiai vizsgálata.) XX. Kémiai Előadói Napok, Szeged, 1997, Abstract 101. (lecture)

2. M. Novák, V. Budavári: Nafion-based glucose oxidase sensor with organic solvent. 48th Meeting, International Society of Electrochemistry, Paris, France, 1997, Abstract No. 815 (lectrure)
3. V. Budavári, M. Novák: Some properties of polyamino-quinone self-assembled films on gold. 50th Meeting, International Society of Electrochemistry, Pavia, Italy, 1999, Abstract No. 716 (lecture)
4. V. Budavári, M. Novák: Electrochemical behavior of poly amino quinone layers. (Poliaminokinon rétegek elektrokémiai tulajdonságai.) XXII. Kémiai Előadói Napok, Szeged, 1999, Abstract 60. (lecture)
5. V. Budavári: Charge transfer characteristics of poly amino quinone layers. (Poliaminokinon rétegek töltésátviteli sajátságai.) MTA, Elektrokémiai Munkabizottság ülése, Szeged, 1999 (lecture)
6. Á. Szűcs, V. Budavári, J. B.Nagy, M. Novák: Electrocatalytic reactions on the intermediates of the reduction of fullerene films. 53rd ISE Meeting, Düsseldorf, Germany, 2002, Book of Abstract 23 (poster)

7. M. Novák, V. Budavári, Á. Szűcs: Structural effect on the electrochemical properties of self-assembled multilayers. 54th ISE Meeting, Sao Pedro, Brasil, 2003, Book of Abstract 15 (poster)

8. M. Novák, V. Budavári, Á. Szűcs: Electrochemical hydrogenation of C_{60} fullerene films. 54th ISE Meeting, Sao Pedro, Brasil, 2003, Book of Abstract 15 (poster)