ELECTROCHEMISTRY AND BIOELECTROCHEMICAL APPLICATION OF SOLID STATE FULLERENES

Ph.D. theses

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IV. INTRODUCTION

The new allotrope versions of carbon, the fullerenes were discovered in 1985. From the beginning electrochemistry has contributed to get known their properties, because it turned out that fullerenes are soluble in some solvents, and can be reversibly reduced. The range of electrochemical investigations has broadened when it was discovered that solid fullerenes, cast on conductive substrates are electrochemically active. During their reduction, cations are incorporated from the solution, while the conductivity of films changes similarly to the doping of semiconductors.

Earlier electrochemical experiments were done in non-aqueous solutions and in inert atmosphere, because some intermediate species, formed during the reduction reacted rapidly on exposure to water and oxygen. Later it was found that fullerene films could be reduced in aqueous solutions, as well. Water as a solvent offers many advantages for the electrochemical studies. Neither the neutral nor the reduced forms of fullerenes are soluble in water. This means that fullerene films can stay on the substrates in any oxidation form. The required potential range, where water is stable, can be adjusted by simply changing the pH of the solution, or by choosing an appropriate electrode. Many metal salts are soluble in water, i.e., we can provide various counter ions (dopants) to the reduced films. Thus, fullerene films of new properties can be formed, extending the family of carbon-based electrodes (graphite, glassy carbon) with new members. Fullerene electrodes mean a bridge between the conventional electrodes and surface modified electrodes. They can also have electrocatalytic effect in some processes.

In my Ph.D. work I studied the electrochemical properties of fullerene films in aqueous media and their possible application areas.

II. AIMS AND SCOPES

The primary aim of our research was the study of fullerene films in aqueous solutions. Beside the most common C_{60}, we wanted to extend our studies to other fullerenes, as well.

At the very beginning we wanted to prepare homogeneous and compact C_{70} films on electrode surfaces, applying the same solution casting method that was used for C_{60}. We wanted to examine the morphology, the porosity and the electrochemical activity of C_{60} and C_{70} films as the function of the preparation method. We wished to explore whether these behaviour can be influenced with the type of the electrode, with the _re-treatment of the electrode, with the solvent used for casting, or with the post modification of the cast films. We looked for a method that could give estimation for the free surface ratio, as well.

Another aim was to clarify the reduction mechanism of C_{60} in solutions containing alkali or alkali earth metal ions, to find out what happens in the potential region before the bulk reduction.

We also wanted to see, how a transition metal ion could be inserted into fullerene films. Manganese has a variety of possible oxidation states, and several forms have catalytic properties in chemical reactions. So, we were interested in the insertion of manganese ions into C_{60} films, and to investigate their properties and their possible electrocatalytic features.

We wanted to study the electrocatalytic behaviour of the fullerene electrodes with a biological active protein, cytochrome c, as well. We would have liked to find out the right conditions of preparing the electrodes to get reversible cytochrome c reaction on them.

III. EXPERIMENTAL

Cyclic voltammetry was most often used with gold and glassy carbon electrodes. In some experiment rotating disc glassy carbon was applied. Cronocoulometry was used to determine the open surface area of the fullerene-modified electrodes. Homogeneity and compactness of the fullerene films was studied by high-resolution microscopy and atomic force microscopy. The semiconducting behaviour of fullerene films was characterised by photoelectrochemical measurements. The results obtained by photoelectrochemistry were compared with the spectra in solid state and solution state, measured by absorption spectroscopy.

IV. THESES

1. Properties of fullerene films

1.1. Preparation and characterisation of the films

A solution casting technique of making C_{70} films on gold and glassy carbon electrodes was developed. Films could be reproducibly prepared and they were uniform enough for electrochemical studies. We established that the solvent and the solution volume used for the film casting, as well as the quality of the surface influenced the structure of the films. The best solvent for the film preparation was dichloromethane. Atomic force microscopy revealed that no crystals were formed on the substrates even in the micrometer scale the films were rather even. However, electrochemical measurements confirmed that fullerene films were penetrable for small molecules like water or oxygen. The open surface area in the film was estimated by two different methods. The porosity was determined by the quantity of the fullerene cast on the surface, and by the quality of the electrode. Thinner layers and C_{60} films cast on glassy carbon were opener, their porosity were larger.

1.2. Photoelctrochemical behaviour of fullerene films

Neutral C_{70} films were shown to be intrinsic semiconductors; they behaved as insulators in dark. However, photooxidation and photoredution could be measured upon illuminating them by light. The photoelectrochemical behaviour of C_{70} was slightly different from that of C_{60}. Although the bandgaps were similar, the flatband potential of C_{70} films was 250 mV more positive than that of C_{60}. The quantum efficiency spectra of both fullerenes resembled very much to the absorption spectra measured in solution or in solid state, indicating that the determining process was the light absorption of the films.

2. Electrochemical properties of fullerene films

2.1. Partial reduction

The porosity of fullerene films could be controlled by a special treatment. When such films were examined on a rotating disc electrode, clear evidences could be collected for a partial reduction before the bulk reduction of the films. Partial reduction meant, that only a few molecular layers were reduced at the electrode|fullerene and the fullerene|solution interfaces, but that was enough to develop the cation exchanging properties of films.

2.2. Reduction of C_{70} films

C_{70} films could be reduced in solutions containing alkali metal ions. The shape of the voltammograms and the reduction peak potentials varied very much with the quality and quantity of the cations on the solution side. On gold electrodes the reduction was detectable in the presence of Na^+ and K^+ ions, and on glassy carbon surfaces we could detect with Li^+, as well. The reduction was irreversible and pH independent (in the range of 3–14). Formation of conductive M_3C_{70} salt was suggested in three consecutive one-electron steps. The stability of the reduced fullerene films varied in a very wide range, some reduced films could be used as electrodes in certain reactions. The conductive behaviour of C_{70} films was also supported by photoelectochemical measurements.

2.3. Manganese doped fullerene films

A transition metal, manganese ion was incorporated into fullerene films using mixed solutions of cations. One of the cations had to have smaller hydration free energy (e.g., Na^+ or K^+) than that of the manganese ion. Manganese and the alkali metal ions were inserted together into the reduced films. The ratio of the built-in cations was controlled by the solution composition. An ion-exchange mechanism was suggested for the interpretation of that phenomenon.

3. Bioelectrochemical application of the fullerene films

Studying the electrochemical behaviour of cytochrome c on different fullerene films, it was established, that the partially reduced C_{60} films had good properties as reaction environment for the protein molecule. The neutral, the totally reduced, or the reduced and then re-oxidised films were bad for cytochrome c. It was supposed that the partially reduced films resembling to a biological membrane and also having a molecular sieve character offered the suitable conditions for the reaction.

V. LIST OF PUBLICATION

Papers:

1. **M. Csiszár**, Á. Szûcs, M Tölgyesi, J. B.Nagy, M. Novák: Electrochemistry of C_{70} fullerene films in aqueous solutions; *J. Electroanal. Chem.*, 441, 287 (1998)
   IF: 1.760; Cit.: 9
2. Á. Szûcs, M. Tölgyesi, **M. Csiszár**, J. B.Nagy, M. Novák: Electrochemistry on partially reduced fullerene films; *Electrochemica Acta*, 44, 613 (1998)
   IF: 1.591; Cit.: 6
3. Á. Szûcs, M. Tölgyesi, **M. Csiszár**, J. B.Nagy, M. Novák: Manganese-doped fullerene film electrodes; *J. Electroanal. Chem.*, 442, 59 (1998)
   IF: 1.760; Cit.: 11
4. **M. Csiszár**, Á. Szûcs, M. Tölgyesi, Á. Mechler, J. B.Nagy, M. Novák: Electrochemical reactions of cytochrome c on electrodes modified by fullerene films; *J. Electroanal. Chem.*, 497, 69 (2000)
   IF: 1.960; Cit.: 4
5. Á. Szûcs, M. Tölgyesi, E. Szûcs, **M. Csiszár**, A. Loix, L. Lamberts, J. B.Nagy, M. Novák: Electrochemistry of C_{60} films in aqueous solutions in „Fullerenes Volume 5: Recent Advances in the Chemistry and Physisc of Fullerenes and Related Materials", K. M. Kadish and R. S. Ruoff, Editors, p. 68-78, (1997)

6. Á. Szûcs, **M. Csiszár**, M. Tölgyesi, J. B.Nagy, M. Novák: Electrochemistry of C_{70} fullerene films in „Fullerenes Volume 5: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials”, K. M. Kadish and R. S. Ruoff, Editors, p.10-19, (1997)

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Lectures, posters:

1. Á. Szûcs, M. Tölgyesi, E. Szûcs, **M. Csiszár**, A. Loix, L. Lamberts, J. B.Nagy, M. Novák: Electrochemistry of C_{60} films in aqueous solutions; 48th Meeting, International Society of Electrochemistry, Paris, France, 1997, Abstract No. 1367
2. Á. Szûcs, **M. Csiszár**, M. Tölgyesi, J. B.Nagy, M. Novák: Electrochemistry of C_{70} fullerene films; 48th Meeting, International Society of Electrochemistry Paris, France, 1997, Abstract No. 1366
3. **Marika Csiszár**: Electrochemical and photoelectrochemical behaviour of C_{70} fullerene films (C_{70} fullerénfilmek elektrokémiai és fotoelektrokémiai viselkedése); XX. Kémiai Elõadói Napok, Szeged, 1997
4. **Marika Csiszár**: Fullerene-modified electrodes for the electrochemistry of cytochrome c (Fullerén-módosított felületek viselkedése a citokróm c elektrokémiai reakciójában); XXII. Kémiai Elõadói Napok, Szeged, 1999

5. **Marika Csiszár**: Electrochemical and photoelectrochemical behaviour of C_{70} fullerene films (C_{70} fullerénfilmek elektrokémiai és fotoelektrokémiai viselkedése); MTA, Elektrokémiai Munkabizottság ülése, Szeged, 1999

6. **M. Csiszár**, Á. Szûcs, M Tölgyesi, J. B.Nagy, M. Novák: Enhanced stability of the electrochemical behavior of cytochrome c on electrodes modified by partially reduced fullerene films; Poster presentation, 50^{th} Meeting, International Society of Electrochemistry, Pavia, Italy, 1999, Abstract No. 734