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Solvent-free electrodeposition of polypyrrole as a base for the preparation of carbonised platinum microelectrodes

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Abstract

The combination of electropolymerisation of suitable monomers and pyrolysis for the local modification of the surface of Pt microelectrodes with pyrolytic carbon films is presented. For use in biological systems, carbon-based electrodes have several advantages over their inert metal counterparts. However, carbon electrodes with dimensions in the sub-μm range lack the required mechanical stability for practical applications. Platinum is employed as a robust support for carbon films to yield carbonised Pt electrodes.

Pyrrole, aniline and a polyacrylic resin were investigated for their suitability for forming uniform and stable pyrolytic carbon films on Pt support. Polypyrrole deposited from solvent-free pyrrole (pyrrole concentration higher than 14 M) was found to be most suitable for the formation of stable and crack-free carbon films on Pt electrodes. The carbonised Pt electrodes obtained were characterised electrochemically.

Keywords: Pt electrodes; Pyrolytic carbon films; Crack-free

1. Introduction

Electrodes fabricated from a large variety of different carbon materials have received considerable attention for use in electroanaytical studies [1,2] because they exhibit a good availability in a variety of inexpensive forms, a wide useful potential window due to the slow kinetics of carbon oxidation, a rich surface chemistry which can be modulated by a variety of modification reactions, a high analytical activity which can be tailored to enhance electron transfer kinetics and a decreased tendency for surface passivation or fouling in biological media. Hence, carbon-based electrodes are particularly suited for use in biological media. Several investigations involving the use of carbon-fibre electrodes whose diameters are between 5 and 15 μm, for the electrochemical investigation of processes occurring in biological systems, have been reported [3–7]. However, for a localised resolution of the processes occurring at/or within biological membranes, miniaturised electrodes with sub-μm diameter are required. For a localised and sequential probing of different spots within a single cell or on its membrane only electrodes with diameters in the sub-μm region can yield the required resolution. Carbon fibres are commercially available with minimum diameters of about 5 μm, which severely hampers further miniaturisation of carbon electrodes. Though cylindrically etched carbon fibre electrodes with radii in the threshold of 0.5–2 μm have been reported [8] and successfully applied for the detection of neurotransmitter exocytosis form single cells [9], in general, carbon electrodes with diameters less than 5 μm are too fragile and lack the mechanical stability required for practical purposes. This has largely precluded the application of carbon-based electrodes at the sub-μm level. Thus, there is need for the development of carbon electrodes small enough for sequential investigation of different spots

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within a single cell or on its membrane, yet robust enough to be of practical use.

On the other hand, the feasibility of preparing quartz-insulated Pt electrodes with radii far below 1 μm has been demonstrated [10] and emerged to a standard technique for the preparation of SECM tips. Taking this into account, we anticipated to use sub-μm Pt disk electrodes as a robust support for carbon without affecting its desirable properties.

Carbon films have been formed on suitable substrates by applying a number of methods [11], such as vacuum evaporation [12–14], laser photo-activation of sites on graphite or carbon substrates [15], screen printing [16–18] and pyrolysis of low molecular weight hydrocarbons on quartz or glass ceramic [19–24]. The localised modification of Pt surface with carbon material, especially at the sub-μm level can only be realised through the localised deposition of a polymer that can subsequently be transformed into pyrolytic carbon. Our approach utilises the localised electrodeposition of suitable polymers on the surface of needle-type Pt microelectrodes followed by pyrolysis. Similar attempts had been previously employed to deposit carbon films on inter-digitated microarray electrodes [25].

In order to extend the scope of application of carbon-based materials to the ultramicroelectrode level, we report the preparation of Pt electrodes whose surfaces are modified with a layer of pyrolytic carbon (carbonised Pt electrodes). The local modification of the surface of Pt microelectrodes with pyrolytic carbon will allow the development of sensors specifically designed for addressing the processes occurring at biological membranes with a high resolution.

2. Experimental

2.1. Chemicals

Acetonitrile, HCl and KCl were purchased from J.T. Baker (Griesheim, Germany) while $K_2HPO_4{\cdot}3H_2O$, KH_2PO_4 were from Merck (Darmstadt, Germany). Dopamine, tetraethylammonium-*p*-toluenesulfonate, tetrabutylammonium-*p*-toluenesulfonate, pyrrole, aniline and *p*-phenylenediamine were obtained from Sigma-Aldrich (Steinheim, Germany). HEPES buffer was from Merck, Darmstadt, Germany. Triply distilled water was used to prepare all aqueous solutions. Polyacrylic resins were synthesised as reported recently [26]. Pyrrole was cleaned by passing it through a short column filled with aluminium oxide (Riedel-de Haën, Seelze, Germany) prior to the experiments.

2.2. Electrochemical methods

All electrochemical experiments were performed in a conventional three-electrode cell configuration consisting of a Ag|AgCl (3 M KCl) reference electrode, a Pt wire counter electrode and either a Pt microelectrode or a Pt microelectrode modified with a carbon film (carbonised Pt microelectrode) as working electrode. Experiments were performed with a CHI 1030 eight-fold potentiostat (CH Instruments, Austin, USA) or an Autolab PGSTAT12 potentiostat (Eco Chemie, Utrecht, The Netherlands). Characterisation of the electrodes in phosphate buffer solution (pH 7.0) was performed after exclusion of oxygen with argon if not otherwise stated.

2.3. Preparation of Pt microelectrodes

Three different types of Pt electrodes were used to investigate possibilities and limitations for the formation of carbonised electrode surfaces. A Pt wire electrode (300 μm long, 125 μm diameter) was prepared by gluing a Pt wire (Goodfellow, Bad Nauheim, Germany) by means of a silver epoxy glue (EPO-TEK H20S, Polytec, Waldbronn, Germany) to a copper wire. Pt/W (95/5) electrodes (20 μm diameter, 300 μm long) were supplied by Thomas Recording GmbH (Gießen, Germany). The preparation of disk-shaped Pt microelectrodes was based on a method described previously [10]. The procedure consisted of inserting a short piece (≈20 mm) of Pt wire with a diameter of 25 μm into a 100 mm long quartz glass capillary (Hilgenberg, Malsfeld, Germany) having an outer diameter of 0.9 mm and an inner diameter of 0.3 mm. The glass capillary was mounted on the holders of a laser puller (P-2000, Sutter Instrument Company, Novato, CA, USA). The two ends of the capillary were connected to a vacuum pump with the aid of flexible silicone tubes. The laser puller was used to seal the Pt in the glass capillary and both capillary and Pt was pulled to obtain two Pt electrodes tightly sealed in glass. Electrical contact was established with Cu wires and silver epoxy. The size of the electrode was adjusted by successive polishing on a polishing cloth (Technotron, Wehrheim, Germany) covered with suspensions of polycrystalline diamond (Pace Technologies, AZ, USA) and alumina suspensions of decreasing particle size (1.0, 0.3, 0.05 μm; Leco, Kirchheim, Germany).

2.4. Deposition of polymers on electrode surface

Electrodeposition of different polymers was carried out in a three-electrode electrochemical cell. A Ag/AgCl (3 M KCl) electrode was used as reference electrode in aqueous solution and a chloridised silver wire as a quasi reference electrode in organic solution (CH_3CN, pyrrole). In all cases, a Pt wire was used as counter electrode.

Polypyrrole was deposited either from a solution of 0.4 M of pyrrole in water containing 0.1 M KCl as supporting electrolyte, 0.3 or 1 M pyrrole in CH_3CN containing 0.3 M tetraethylammonium-*p*-toluenesulfonate as supporting electrolyte, or solvent-free pyrrole containing 0.3 M tetraethylammonium-*p*-toluenesulfonate using repetitive cyclic voltammetry (potential range from −600 to +750 mV) and pulse amperometry (polymerisation potential of +800 mV for 0.2 s followed by a resting potential of 0 mV for 5 s). Polyaniline was deposited from an acidic solu-