



# Pyrolytic deposited graphite electrodes for voltammetric sensors: An alternative to nano structured electrodes



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## ABSTRACT

The paper presents optimized preparation conditions for a highly sensitive electrode material as an alternative to carbon nanotubes electrodes. Pyrolytic deposited graphite electrodes can be produced uniformly in high quality. They are suitable for voltammetric determinations of dissolved nitroaromatics and dopamine in concentrations of about 2 ppb. They have similar or better performances respecting sensitivity, cross sensitivity and reproducibility as electrodes made of carbon nanotubes. Such electrodes can be stored in water or in ambient air over at least years without any degradation of their sensor characteristics.

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## 1. Introduction

Active carbon surfaces of electrodes deposited from carbonaceous gases are known as an electrode material for voltammetric measurements since the 60ies [1]. But the prepared carbon layers contained often amorphous components. Therefore the adhesion on ceramic or metallic substrates was insufficient. Furthermore in many cases the preparation conditions were not well defined. That was the reason for a lack of reproducibility and sensitivity. Newly, the efforts are focused on electrodes with nano-materials like embedded gold particles or carbon nanotubes (CNT) [2]. The preparation of such electrodes is complex due to the risk of unwanted variations in their properties. Alternatively screen printed carbon electrodes (SPCE) are suitable for mass production [3]. But their properties depend on the kind of graphite paste.

The interest for production of pyrolytic graphite electrodes (PGE) is focused on precise control of the deposition of the active layer with more accuracy regarding a higher sensitivity and reproducibility. For this purpose, the parameters of the preparation have to be optimized with respect to partial pressure of the carbon containing gas, the deposition temperature and the time.

Pyrolytic graphite electrodes were fabricated to be applied for voltammetric measurements in aqueous solutions. They have been investigated for the simultaneous electrochemical determination of medical relevant substances such as dopamine (DA), ascorbic

acid (AA), and uric acid (UA) [4]. In addition in this paper the electro-chemical determination of nitroaromatics (NA) on pyrolytic deposited carbon electrodes is described.

## 2. Experimental

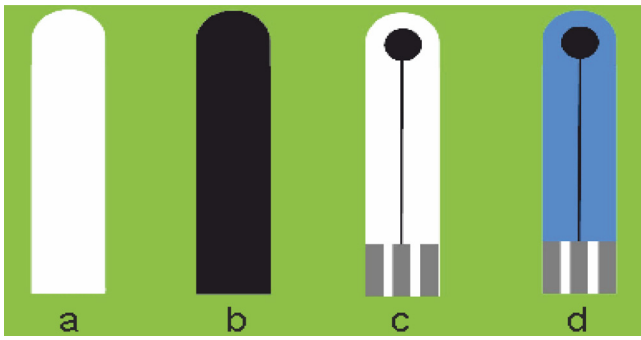
Pyrolytic graphite (PG) layers were prepared on alumina substrates ( $A=6.62\text{ cm}^2$ ) in a quartz tube furnace by chemical vapor deposition (CVD) of benzene. The ceramic used for the deposition is characterized by high mechanical strength, high thermal conductivity, good gas barrier properties and low surface roughness, respectively [5].

The source gas was a mixture of benzene and argon (purity: 99.999%) with the pressure bubbling method. Argon was used as carrier gas with a total molar flow rate of  $13.25\text{ g h}^{-1}$  with a 1.9 mass percentage amount of benzene. The flow rates were monitored by mass flow controllers and the two gases were mixed before entering the reactor tube ( $\varnothing 26\text{ mm}$ ). The carbon deposition was maintained at atmospheric pressure and at a deposition temperature of  $1050^\circ\text{C}$ . For the deposition the time was varied from 15 min to 120 min. The substrates were kept in a pure argon atmosphere during the heating (with the substrate oriented parallel to the gas flow) and were cooled slowly to ambient temperature under constant flow of the inert gas again.

The quantification of pyrocarbon deposition was carried out by weighing each preform before its insertion into the reactor and after pyrolysis, immediately after cooling down the reactor. The surfaces of PG layers were characterized concerning crystallinity and surface morphology by atomic force microscopy (AFM), X-ray photoelec-

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**Fig. 1.** Production procedure of PGE: (a) ceramic substrates ( $\text{Al}_2\text{O}_3$ ) as template, (b) deposition of pyrolytic graphite, (c) lasering of the pyrolytic graphite electrode (PGE) mask, (d) insulation with polymer ink or glass cover.

tron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Total resistance was determined on the top and bottom of the electrodes and on the areas ( $\varnothing$  3 mm), which act as working electrode.

Pyrolytic graphite electrodes (PGE) preparation was carried out as shown in Fig. 1. Electrochemical properties of PGEs were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). All voltammetric measurements were performed in a three-electrode cell arrangement. Micro crystalline PGE ( $\varnothing$  3 mm), platinum plate electrode, and a miniaturized  $\text{Ag}/\text{AgCl}/\text{Cl}(\text{sat.})$  electrode (SSE) were used as working-, counter- and reference electrode. The voltammetric measurements were carried out in aqueous electrolyte solutions consisting of 0.1 M  $\text{KNO}_3 + 0.1$  M  $\text{KCl}$  and in 0.1 M phosphate buffer (Phb, pH 7.4), respectively using an electrochemical sensor interface (PalmSens®).

Immediately before each measurement, the electrodes were conditioned in the same supporting electrolyte by CV and DPV.

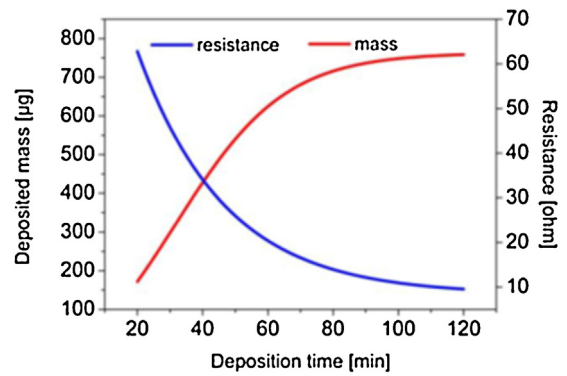
### 3. Results and discussion

#### 3.1. Characterization of the pyrolytic graphite layers

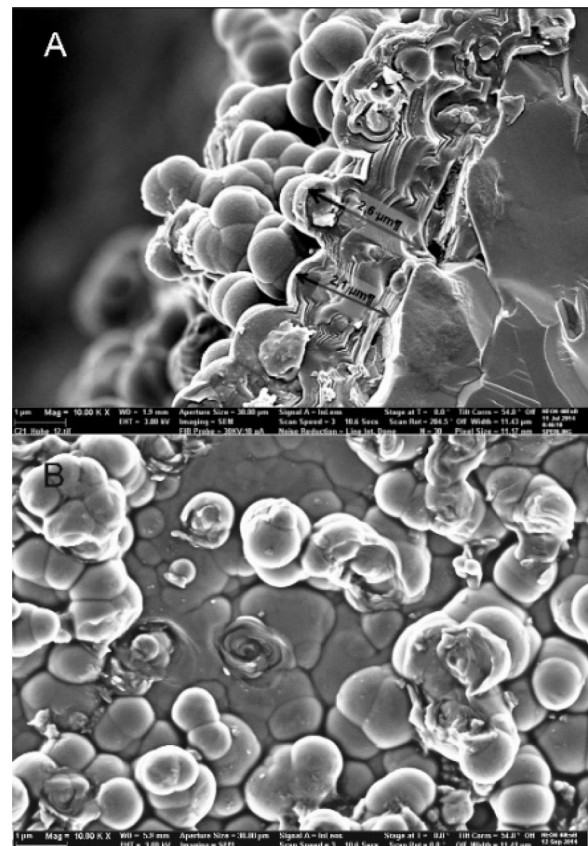
The preparation conditions could be improved respecting partial pressure of carbon containing gas and deposition time in that a way that homogeneous, crystalline and firmly adhering carbon layers could be obtained with laminar structure. The reproducibility of deposited pyrolytic layers was dependent on

- the dilution ratio of benzene-argon gas mixture
- and the use of a special sample holder in the quartz tube.

By variation of the deposition time different graphite layers were prepared with a defined increase of the mass and a reproducible total electrical resistance (bulk- and surface resistance). The best deposition results for the pyrolytic graphite layers were obtained by decomposition of benzene during 120 min in the quartz tube. The precipitated masses of the carbon layers and the measured resistances correlate with the deposition time as shown in Fig. 2. The relative standard deviations (RSD) were determined for the deposited pyrolytic masses and the measured total resistances as a function of deposition time [Table 1]. An extension of the deposition time from 20 min to 120 min increases the mass of deposited pyrolytic graphite from 172  $\mu\text{g}$  on the substrate surface (RSD = 25.7%) to 759  $\mu\text{g}$  (RSD = 5.7%). In contrast, the measured resistances of the layers decreased from 63  $\Omega$  (RSD = 9.1%) to 7  $\Omega$  (RSD = 4.7%).



**Fig. 2.** Relationship between mass and total resistance of the deposited pyrolytic carbon vs. deposition time at 1050 °C.



**Fig. 3.** SEM images of pyrolytic graphite—A: cross-section with height profile and laminar layer structure with nodular particles; B: surface with onion-like structure of concentric layers.

**Table 1**

Relative standard deviations (RSD/80 samples) for the deposited pyrolytic masses and the measured resistances as a function of deposition time.

deposition time: min	mass/ $A_0$ : $\mu\text{g}$	RSD: %	resistance: $\Omega$	RSD: %
20	172	25.7%	63	9.1%
40	427	9.0%	33	8.2%
60	624	8.3%	20	7.7%
80	709	7.3%	12	6.8%
120	759	5.7%	7	4.7%

The longer the pyrolytic deposition under these reaction conditions was executed, the more uniform and comparable were the properties of the samples. The PG crystallites are deposited preferably in ab- directions and parallel to the alumina surface. As a

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