

Relation Between the Composition and Properties of Carbon Nanotubes Paste Electrodes (CNTPEs)

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Abstract: Two types of carbon pastes were prepared, examined and characterized. Particular attention has been paid to the changes of the ohmic resistance, relative to the dependence on the composition of a carbon nanotubes paste electrode (CNTPE) and the respective constituents used. The results were compared with those of "classic" carbon paste electrode (CPE) based on graphite powder and the differences in physical as well as electrochemical properties were discussed and explained. As found, the most evident difference was in the optimal (applicable, employable) carbon-to-binder ratio of the paste. Whereas the CPE could be used only up to 20% (m/m) of the oil, the CNTPE allowed us to go up to 60% (m/m) of the same binding liquid. Finally, some problems connected with homogeneity and stability of carbon paste mixtures as such are also discussed.

Keywords: Carbon nanotube paste electrode; Carbon paste electrode; Characterisation, Cyclic voltammetry, Resistance measurements.

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Introduction

The area of carbon paste electrodes (CPEs) is still in centre of research focus even in the new millennium. Since 1958, when the first publication about CPE had been introduced by Adams [1], many other publications and reviews appeared and, from today's point of view, CPE have become one of the traditional types of solid electrodes [2-4].

Heterogeneous character of such electrode material, specific influence of liquid binder and especially variability in the composition makes this type of solid electrodes even more attractive for various areas of electrochemical research and analysis [5-7]. However, a good physicochemical characterisation of every paste composition is inevitable. In the past, some basic features to be defined *extra* were introduced [8,10]; later their number being extended [9]. Recently, the advantages of the resistance measurements in dependence of the carbon paste composition have been reported with some practical advices given [11].

Characterisation procedures still belong to one of the actual topics because new carbonaceous materials for carbon paste electrodes are appearing, hand in hand with new types of binders. The introduction of carbon nanotubes [12] opened a new and attractive space in the electroanalysis at solid electrodes and, a few years later, carbon nanotubes became the most frequently used alternative material for construction of paste-like electrodes usually presented as "carbon nanotubes paste electrodes" (CNTPEs). However, some types contain two graphite materials in the same mixture – namely, spectroscopic graphite and CNTs; the latter serving as a special CP-modifier. In these cases, the respective electrodes are often being classified as "carbon nanotubes-modified carbon paste electrodes" (CNT-CPEs). To date, both CNTPE and CNT-CPE configurations have appeared in almost 80 original reports with a very diverse applicability (see [3,13] and refs. therein). The flexibility of carbon nanotubes-containing paste electrodes can then be illustrated on the fact that both variants are expanding to different areas of electroanalysis or even beyond, which is the case of clinical analysis with the new types of biosensors [14,15].

More recently, two contributions about CNTPE have appeared [16,17], focused on the task of purity of carbon nanotubes, optimal paste composition; both in close association with the later use. In addition to this, a comparison between CNTPE and other solid electrodes (made of glassy carbon or platinum) was also presented being based on some physicochemical parameters and electrochemical properties, and tested on various typical redox probes (e.g.: ferricyanide, ferrocene and its derivatives, dopamine, etc.).

In this paper, a newly made study is presented dealing with physical properties and resistance measurements of CNTPEs varying in the systematically adjusted "carbon nanotubes-to-pasting liquid" ratio. The series of electrodes investigated has demonstrated not only change(s) in physico-chemical parameters, but also the effect of the liquid binder upon the resultant electrochemical properties. Last but not least, the observations and results obtained were compared to those obtained recently with a set of traditional CPEs [11].

Experimental

Chemicals and Reagents

Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ (p.a. grade), and potassium chloride, KCl (Suprapur), were used as received (both from Merck). Throughout the experimental work, all solutions were prepared from doubly deionized water obtained by passing through a laboratory purification system (model "Milli-Q"; Millipore, USA).

Apparatus and Other Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT-30 (Metrohm Autolab B.V., Utrecht, The Netherlands) was used in combination with a control by GPES 4.9 software (from the same manufacturer). The three-electrode cell compartment was an integral part. All the measurements were carried out in the cyclic voltammetric (CV) mode.

The ohmic resistance of the individual carbon pastes was measured with a Voltcraft® multimeter (model "VC 404", Conrad Electronics, Germany).

Electrodes and Accessories

Carbon nanotube paste electrodes (CNTPE) were prepared by intimately hand-mixing single-walled nanotubes (type: L.SWNTs, diameter < 2 nm; Shenzhen Nanotech Port Co. Ltd., China) with different amount of silicone oil (SO; LUKOIL MV 8000; Lučební závody, Kolín, Czech Republic) in order to obtain various electrodes with different ratio of carbon and binder, using a pestle and mortar. Freshly made carbon nanotube pastes were packed into specially designed electrode holders [18] of the uniform design and size. The electrode surface was renewed by smoothing on wet filter paper or by cutting using a sharp edge before starting a new set of experiments.

A classic carbon paste electrode (CPE) was prepared in the same way as described above, the only difference was the use of spectroscopic graphite powder ("CR-5"; Maziva, Týn nad Vltavou, Czech Republic). An Ag/AgCl / 3 M KCl as the reference and a Pt counter as the auxiliary electrode completed the cell.

Results and Discussion

The presented study binds up to the previous characterisation [11] performed with bare carbon paste electrodes. The first part of experiments was focused on the ohmic resistance measurement. According to the "close-packing" model, the resistivity of electrodes with increasing amount of binder in carbon paste mixture is not dramatically changing until the "break-point" is reached when the resistivity starts to increase very strongly – see Fig. 1, plot "A"). This effect was found for the classic CPE as well as for the CNTPE configuration tested. However, whereas the break point in CPE is around 20% (m/m) (30 % v/v) of the binder, in CNTPE it is about 60% (m/m).

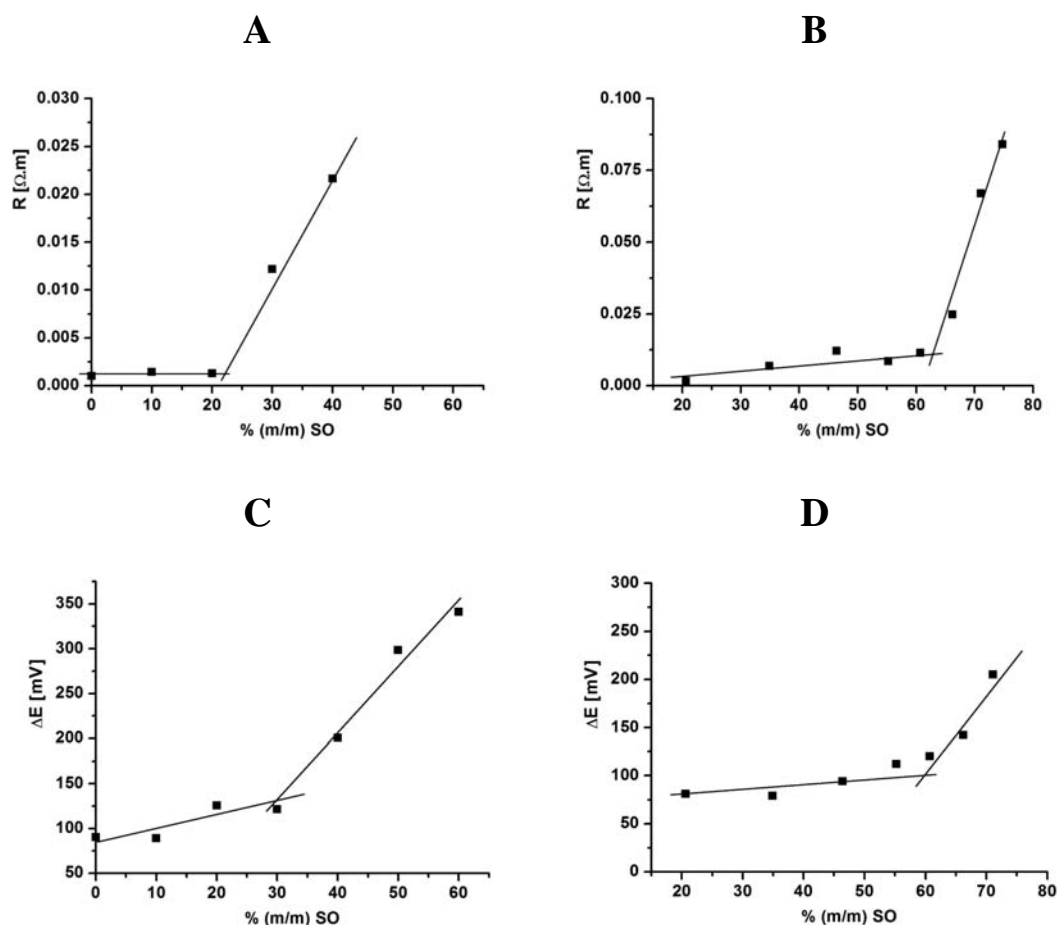


Figure 1. Dependence of resistivity on the amount of binder (silicone oil) present in the paste mixture for CPE (A) and CNTPE (B). Dependence of cathodic-anodic peak separation (from CV) on the amount of binder present in the paste mixture for CPE (C) and CNTPE (D). Experimental conditions: CV; CPE and CNTPE; 0.1 M KCl + 0.005 M $K_3Fe(CN)_6$. Potential range, from +1.0 V vs Ag/AgCl, to -0.7 V and backward; scan rate, 50 mV/s.

This fact can be qualitatively explained by the above-mentioned simple model: in the case of CPE, during addition of the first 20-30% of the oil, the binding liquid fills the external space between the particles being in a permanent contact. Since the penetration of oil into the structure of the carbon particles is not substantial, the additional amount of the oil (above those 20-30%) causes that the particles start to float in the oil, therefore the multiple contact between the particles is interrupted and the resistance sharply increases (see again Fig. 1A).

In the case of CNTPE, the remarkable shift of the break point on the resistivity graph (Fig. 1B) is most probably caused by ability of carbon nanotubes to intercept (entrap) a relatively large amount of binder either by its adsorption on the lipophilic surface of nanotubes, either by penetration of the oil into the carbon nanotubes of all diameters or *via* the allowance by the size of polydimethylsiloxane molecules (about 1 nm [19]). In addition to this, the fibrous microstructure of the nanotubes behaves like a felt providing better mechanical properties of the electrode and preventing the leakage of the oil.

For the electrochemical characterisation of the paste electrodes, data of the cyclic voltammetry experiments have been employed using a well known system of $[\text{Fe}(\text{CN})_6]^{3-}$ / $[\text{Fe}(\text{CN})_6]^{4-}$ (specifically: 5 mM in 1 M KCl), which behaves reversible at most of usual electrodes. The theoretical separation between the cathodic and anodic peak is $\Delta E_p = 59$ mV, however, on the paste electrodes the experimentally observed difference is usually between 100 and 150mV. The described increase of the resistance (= drop of conductivity) caused by excess of the binder manifests itself in electrochemical properties as an enormous increase of the ΔE_p behind the break point.

The "electrochemical" break point of CNTPE (Fig. 1D) corresponds perfectly to the "resistivity" one (Fig. 1B), similarly like in the case of CPE (Figs. 1A and 1C). It is possible to figure out that the nanotubes and their bundles in the paste serve as nanowires enabling better conductivity than mutually touching carbon particles in CPE. This is most probably the reason for the remarkable observation, that the peak separation on the cyclic voltammogram of the reversible system at carbon nanotube paste electrodes (CNTPE) is substantially lower (under 100 mV) than the peak separation in the case of a good CPE (100-150 mV).

The measurement of ohmic resistance and the anodic / cathodic peak separation offers thus the fundamental information about the paste quality, helping to find the optimal ratio between the carbonaceous material and the pasting liquid used. This is especially useful in the case of CNTPEs, when the proper paste has rather "sticky" consistency, suggesting one that the ultimate mixture would require even higher amount of the carbon component; i.e., already behind the optimal content ascertained with the aid of the objective measurement.

Conclusions

The results presented in the previous sections demonstrate that the measurements of ohmic resistance and the diagnostic analysis by means of the cyclic voltammetry can aid in the advanced specification of paste electrodes of various compositions, thus extending the present day's knowledge about carbon nanotube paste electrodes, CNTPEs (see e.g. [20]).

It has been confirmed that the preparation of a paste of good quality requires not only some experience, but also suitable methods for its characterisation. From the data presented, it can be concluded that the optimal ratio of tested materials for CPE is approx. 80% (m/m) of graphite and 20% (m/m) of silicone oil, for CNTPE about 50% (m/m) of carbon nanotubes with the same amount of binder (silicone oil). When the content of liquid binder in the paste is higher than the break-point, the oil starts to leak from the electrode. On the other hand, too low proportion of the binder gives rise to a powder-like consistency of the electrode material with evident tendencies to disintegrate.

The characterisation reported herein does not give priority to any of the electrode tested, because both have their pros and cons [3,13] and their final use depends on the system of choice, in which the electrode is to be employed.

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