

Carbon Paste Electrodes for Electroanalysis in Nonaqueous Media

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Abstract

The aim of this special study was to find out the relationship between the composition of carbon pastes and their stability in purely organic solvents and aqueous-organic mixtures. Scanning electron microscopy and cyclic voltammetry of 1 mmol L⁻¹ ferrocenium/ferrocene redox couple served as the tools of choice for this purpose. The results obtained suggest one that it is not possible to prepare a universal carbon paste electrode that would be applicable in voltammetric measurements independently of the character and composition of the working medium.

Key words: Carbon paste electrode; Organic solvent; Surfactant; Ferrocene

Introduction

Carbon paste electrodes (CPEs) belong to a special group of heterogeneous carbon electrodes which are generally prepared by combining a carbonaceous material and an organic binder¹. Their utilization in voltammetric measurements performed in purely organic solvents or aqueous-organic mixtures depends on the choice of both main components and eventual modifiers/stabilizers, especially surfactants². Thus, the actual composition of carbon pastes has a fundamental influence upon their final mechanical and electrochemical properties³. The simplified classification of the type of CPEs according to their composition and possibilities of use is described below in the individual paragraphs. This work is devoted to the detailed characterization of CPEs for measurements in nonaqueous media.

Assuming an optimal ratio between the two main components, the mechanical stability of CPEs prepared from commercially marketed graphite powders depends only on the type of organic binder. If one considers that mineral (paraffin) or silicone oils represents the most frequently used organic binders, the properties and electrochemical performance of conventional CPEs are being tailored to measurements in purely aqueous media. Unfortunately, it is well known that a content of water-miscible organic solvents higher than *ca.* 5% (v/v) causes irreversible disintegration of the carbon paste electrode material⁴.

The required stability of CPEs in the working media can be achieved by simply replacing the sheets (almost planar particles) of natural or spectroscopic graphite powder with glassy carbon powder (spherical particles). Generally, glassy carbon paste electrodes (GCPEs) made of the latter type can be used for voltammetric measurements even in media with a high content of organic solvent (e.g., methanol) up to 90% (v/v)⁵.

Carbon pastes prepared by dispersion of multi-walled carbon nanotubes (MWCNTs) or single-walled nanotubes (SWCNTs) in mineral oil represent yet another type of heterogeneous electrode material which resembles a glassy carbon paste in its consistence and mechanical properties⁶. Such carbon nanotubes paste electrodes (CNTPEs) exhibit an excellent electrocatalytic activity toward clinically important compounds due unique properties of the nanomaterials present, which includes high conductivity and specific surface area⁷. However, their mechanical and electrochemical properties in aqueous-organic mixtures and pure organic solvents have not been yet investigated in detail.

Electrodes obtained by homogenization of reduced graphene oxide with an organic binder (GrPEs) are characterised with similar mechanical and electrochemical properties like the previously introduced analogues with nanotubes. In general, it can be noted that conventional CPEs modified with a low content of these nanomaterials (usually ranging from 10 to

50%, w/w) are more preferred due to a relatively high acquisition cost of nanomaterials⁸. As deduced, all the above-mentioned types of CPEs cannot be selected for voltammetric measurements in purely organic solvents. In the mid-1960s, a research team around Adams published a pioneering paper² describing a bulk-modification of conventional carbon pastes with high amount of sodium dodecyl sulphate (SDS) as a practical way to achieve the required stability and favourable electrochemical properties in pure organic solvents, such as acetonitrile, nitromethane, and propylene carbonate. Since then, however, other works of this focus have not appeared and these so-called nonaqueous carbon paste electrodes have been forgotten for a long time^{3,9}.

Experimental part

Ferrocene, pure acetonitrile (MeCN) for HPLC, anhydrous lithium perchlorate, SDS, and sodium dodecylbenzenesulfonate (SDBS), and mineral oil (MO) were purchased from Merck KGaA (Darmstadt, Germany). Glassy carbon powder with particle size of 5–20 μm from HTW Hochttemperatur Werkstoffe (Thierhaupten, Germany) and graphite powder with particle sizes of $\geq 5 \mu\text{m}$ from Graphite Týn, (Týn nad Vltavou, Czech Republic) were chosen for preparation of CPEs. A deionized water of resistivity 18.3 $\text{M}\Omega \text{ cm}$ was obtained from Millipore Milli-Q[®] purification unit purchased also from Merck KGaA.

A set of carbon paste electrodes, differing in the type of carbon materials, organic binder, surfactants, and their contents, were prepared by homogenisation in a ceramic mortar for 15 min. The resulting nonaqueous pastes were manually pushed into cavities of the corresponding Teflon[®]-piston holders. The surfaces of obtained CPEs were renewed by wiping with a dry filter paper.

Scanning electron microscopy (SEM) for imaging the microstructures of nonaqueous CPEs was carried out using Vega3 SBU from TESCAN Brno (Brno, Czech Republic). A conventional three-electrode cell, consisting of a glassy carbon electrode (GCE) or nonaqueous CPE (both of surface diameter 3 mm) (working), saturated calomel electrode (SCE) with 0.1 mol L^{-1} LiClO_4 in MeCN as salt bridge (reference) and platinum sheet (auxiliary), were connected to the AUTOLAB PGSTAT101 potentiostat/galvanostat from Metrohm Česká republika s.r.o. (Prague, Czech Republic), which was operated through NOVA 1.11 software.

All voltammetric measurements were performed in pure MeCN and its mixtures with water, both containing 0.1 mol L^{-1} LiClO_4 . A linear sweep voltammetry (LSV) with a scan rate (ν) of 50 mV s^{-1} and potential step (E_{step}) of 5 mV was employed for the determination of limiting values of the anodic ($E_{\text{lim}}^{\text{a}}$) and cathodic potentials ($E_{\text{lim}}^{\text{c}}$). Cyclic voltammetry of 1 mmol^{-1} ferrocenium/ferrocene redox couple was carried out in a potential range from -0.4 to $+1.0$ V vs. SCE at a scan rate varying from 200 to 2000 mV s^{-1} and the E_{step} of 5 mV.

Results and discussion

As shown in Fig. 1, no difference in the structures of glassy carbon pastes containing only 20% (w/w) MO and 20% (w/w) MO with 10% (w/w) SDS was observed, when the individual carbon particles remained in intimate contact. Unlike the paste with a high SDS content (see Fig. 1c), where the particles were evidently more scattered, which resulted in a low electrical resistance ($R = 41 \Omega$) and high stability in organic solvents due to the presence of the surfactant.

For comparison, a nearly identical resistance value of about 40 Ω was measured for a carbon paste prepared from natural (chemically purified) graphite⁴, 20% (w/w) MO and 30% (w/w) SDS. It is well-known from the literature that the limiting amount of organic binder in carbon pastes depends only on the type of carbon material used^{6,10}. Because the surfactants dissolve in

the organic binder, it should be clear that their amount is in close relation with the choice of carbon material.

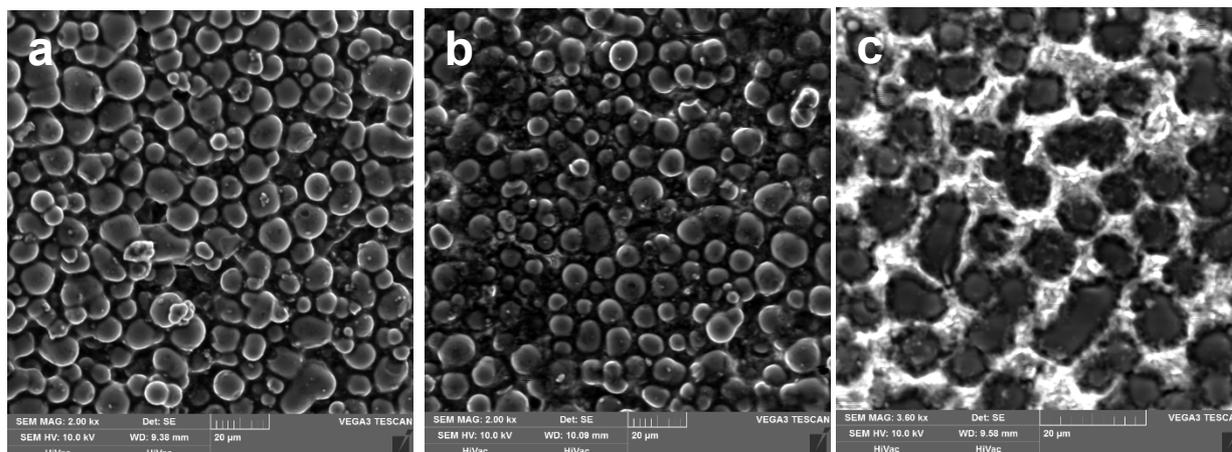


Fig. 1. SEM images of bare GCPE (a), GCPE modified with 10% (w/w) SDS (b), and GCPE modified with 30% (w/w) SDS, all containing the same amount of MO (20% w/w).

As evident from polarization curves in Fig. 2a, nonaqueous CPEs could be used for voltammetric measurements in a wide potential range, as well as commercially available GCE. In addition to the preferred SDS^{2,3}, other surfactants can also be used as suitable modifiers (Fig. 2b). Generally, electrochemical inertness in the required potential range can be considered as the main criteria for the selection of a surfactant³.

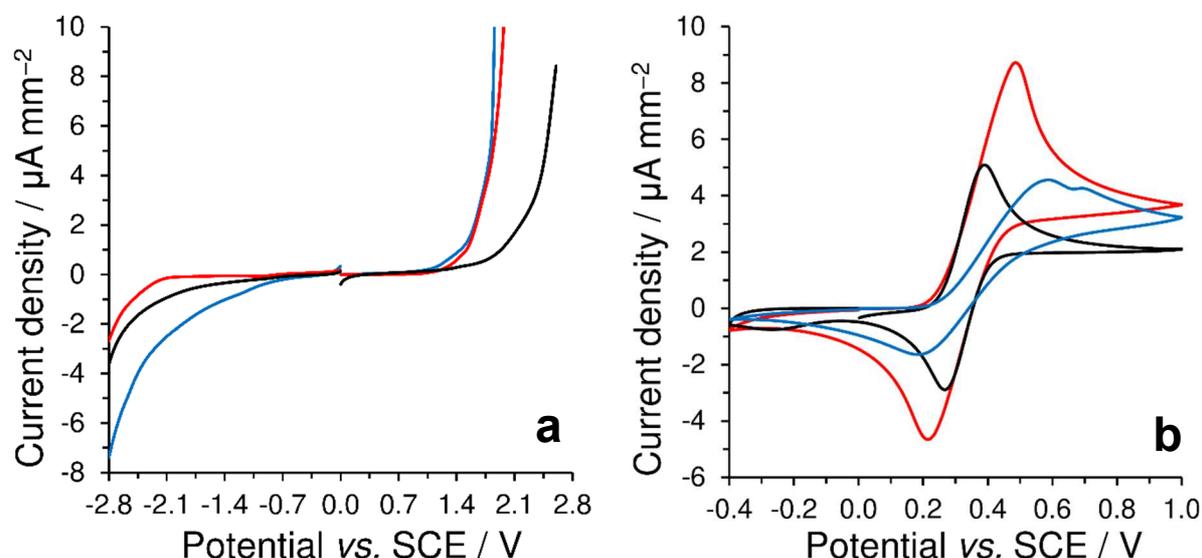


Fig. 2a. Polarization curves obtained for GCE (black), GCPE modified with 15% (w/w) SDS (red), and CPE modified with 30% SDBS (blue curves), both paste-based electrodes contained 20% (w/w) MO, in pure MeCN containing 0.1 mol L⁻¹ LiClO₄ at scan rate of 50 mV s⁻¹ and potential step of 5 mV.

Fig. 2b. Cyclic voltammograms of 1 mmol L⁻¹ ferrocenium/ferrocene redox couple recorded on GCE (black), GCPE modified with 15% (w/w) SDS (red), and CPE modified with 30% SDBS (blue curves), both paste-based electrodes contained 20% (w/w) MO, in pure MeCN containing 0.1 mol L⁻¹ LiClO₄ at scan rate of 50 mV s⁻¹ and potential step of 5 mV.

To achieve optimum peak separation ($\Delta E_p \leq 80$ mV) of ferrocenium/ferrocene redox couple³,

different nonaqueous CPEs with constant content of MO (20% w/w) have to the following composition: 20% SDS for spectroscopic graphite, 10% SDS for glassy carbon powder, and 10% SDS for MWCNTs, all in w/w. Comparable electrochemical properties of nonaqueous CPEs with solid GCE was obtained for voltammetric measurements in purely pure organic solvents with a maximum water content up to 10% (□/□). An illustrative diagram of CPEs utilization according to the content of organic solvent in the working medium / electrolyte is shown in Fig. 3.

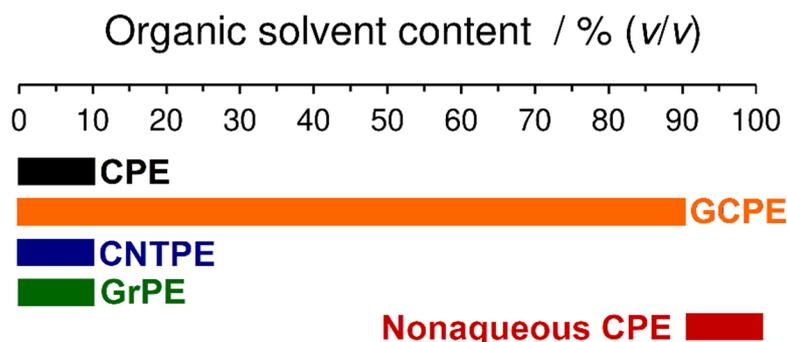


Fig. 3. Utilization of various carbon paste electrodes according to the content of organic solvent.

Conclusion

Based on the observation and results presented above, it can be laconically stated that there is no (universal) carbon paste electrode that could be used simultaneously in both purely aqueous and non-aqueous environments.

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