



SUPPLEMENTARY MATERIAL TO

Electrochemical characterisation of novel screen-printed carbon paste electrodes for voltammetric measurements

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Selection of suitable organic solvent

Tetrahydrofuran (THF), a traditional solvent commonly used when hand-made membranes are prepared, evaporates rapidly and thus, it cannot be used for screen-printing. The result is that viscosity of the ink rapidly changes during the printing process, which causes inhomogeneity of the ink composition. Several solvents exhibiting relatively high boiling point (*e.g.*, cyclohexanone, cyclohexanone–acetone mixtures or commercial thinner) were used to substitute THF. Purely cyclohexanone was found as the most suitable solvent.

Although many commercial carbon ink formulations are commonly used for printing the working electrodes, these formulations are rather unknown and may contain different additives which may interfere in the potentiometric measurements.¹ Therefore, we have decided to develop our own homemade carbon-based ink which is composed of graphite powder and a suitable binder dissolved in a proper organic solvent.

Different binding materials are usually used for the preparation of organic solvents-based inks including, cellulose triacetate (CTA), PVC, polyacrylic and epoxy resin.² In the present work, different inks containing the aforementioned binding polymers were used for printing of the working electrodes. While the printed electrodes containing CTA as a binding material showed the lowest electrical resistance (210, 700, 2200 and 1800 Ω for CTA, PVC, polyacrylic and epoxy resin, respectively), the application of such electrodes in the potentiometric measurements can be unreliable because of the serious interference with metal ions, probably caused by the complexation of these ions with CTA. On the other hand, PVC is known to be inert and usually used for fabrication of PVC mem-

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brane electrodes and hence SPEs prepared using this type of binder will not make such interferences.

Effects of used carbon powders

Two types of carbon powders were used for the preparation of carbon inks. Both of them (CR-2 and Sigradur-G) were identical for the preparation of conventional CPE and GCPE. The prepared carbon ink based on dissolved PVC in pure cyclohexanone, containing glassy carbon powder, is more sensitive to drying, than its analogue with graphite powder, due to its different shape and size. Unfortunately, the sedimentation of the used carbon powders was observed during the storage of the prepared carbon inks at laboratory conditions. Due to this negative phenomenon, the carbon inks had to be mixed before each printing.

Selection of suitable paste liquid

Based on the different solubility of the used binders in cyclohexanone, the preparation of carbon inks based on PVC is much more complicated than the mixing of carbon paste in a ceramic mortar. Carbon graphite or glassy carbon powders are covered by the thin film of cyclohexanone with the dissolved PVC in the corresponding carbon inks, therefore it is impossible to link the individual particles together by a binder, as it is in the case of conventional paste electrodes. Due to low boiling point of cyclohexanone, it is evident that only paste liquids soluble in this solvent can be used at laboratory conditions.

In comparison with PW and PO, which are completely soluble in cyclohexanone, pasting liquids like VA, PP and SO create unspecific emulsions. It was observed that PW dissolves more slowly than PO. It should be mentioned that when CPEs are prepared, PO is more often used than PW. It turned out that PO is the best choice because it is totally soluble in cyclohexanone and the resulting carbon ink does not dry out too quickly during mechanical printing, unlike the bare carbon ink containing only the organic solvent and PVC.

Effect of paraffin oil content

The possibility of characterization of CPEs using the ohmic resistance measurements was already studied by our group.³ As reported, CPEs are suitable for electrochemical measurements if they contain less than 30 % PO, because the higher amount of the binder causes an extreme increase of ohmic resistance. In the opposite situations, very low amount of the binder usually causes negative disintegration of carbon paste from an electrode holder. Nevertheless, in our case, the screen-printed carbon layer is still stable, due to the presence of PVC.

Several carbon inks containing different amounts of PO were printed onto ceramic platforms. After drying, their ohmic resistances were measured and the cyclic voltammograms measurements of $0.1 \text{ mmol dm}^{-3} \text{ K}_4[\text{Fe}(\text{CN})_6]$ at each electrode were recorded. Carbon inks containing more than 20 % PO usually

looked more like black liquids than like viscous inks. Therefore, the printing of these kinds of carbon inks was difficult. Moreover, the freshly printed carbon inks did not hold the desired shape. This negative effect was more evident for carbon inks based on glassy carbon powder. Values of the ohmic resistance lower than 500 Ω were found for the screen-printed electrodes with 10 % PO. Higher content of the used pasting liquid dramatically increased the ohmic resistance; values higher than 2.0 k Ω were measured at the screen-printed glassy carbon paste electrodes (SPGCPEs) with 20 % of PO. According to the observed facts, it can be assumed that these kinds of screen printed electrodes must not contain more than 10 mass % PO.

Selection of suitable isolation

At the beginning of printing, it was necessary to paste a copper plate on one end of ceramic platform, with conductive glue to protect the carbon layer damage caused by the repeating of the electric connection. Only then, the carbon ink could be printed and dried, where the part of the printed carbon ink had to cover also the copper plate partially.

The place between electrode active site and the copper plate had to be electrically isolated. This could be done in several ways, *e.g.*, by using hot wax, solution of PVC in tetrahydrofuran (2 mg cm⁻³), commercial nail polish, or the universal polyester resin (Lamit 109, Czech Republic).

Searching of suitable electrical insulation of the electric contact, realized by the identical electrode material, is complicated due to the physical properties of the participating components. The negative infiltration of the dissolved PVC in tetrahydrofuran, nail polish, and resin was observed during the covering of a carbon layer by a small brush. It caused an increase of ohmic resistance up to 1.0 k Ω . When very thin layers of these isolations were applied, the values of ohmic resistance were lower (about 400–600 Ω). Because of the rapid evaporation of organic solvents, the optimum is when the surface of the electrode material is covered by very thin layers of insulator repeatedly.

Fortunately, no increase of ohmic resistance was observed when hot wax was deposited. However, it should be mentioned that the SPCPE, covered by the thin film of PW, could not be used for extractions of lipophilic compounds into PO, which is a part of the sensor, because such compounds could be extracted into PW as well.

Effect of carbon layer thickness

Manually prepared SPGCEs without any content of PO provide usually lower ohmic resistance (~250 Ω) than electrodes printed mechanically at a machine (~800 Ω). This phenomenon was also observed for SPCEs. An explanation can be found in the differences of carbon layer thickness – with increasing thick-

ness, the values of ohmic resistance decrease. Unlike electrodes printed by the machine having the thickness of carbon layer 100 μm , the size of the carbon layer thickness was about 250 μm in the case of the handmade electrodes.

It is assumed, that an evaporation of cyclohexanone can cause the creation of small gaps between particles of carbon powder, therefore conductivity of carbon paste layer decreases. These gaps are probably filled with an indefinable amount of PVC and PO, both characterized by the extremely low electric conductivity. For that reason, the electrodes without PVC or PO are more conductive than SPCPEs because there is greater probability of contact between the conductive carbon particles.

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