

SELECTION OF SUITABLE POLYMERIC MATERIAL FOR LABORATORY PREPARATION OF CARBON INKS

VÝBĚR VHODNÉHO POLYMERICKÉHO MATERIÁLU PRO LABORATORNÍ PŘÍPRAVU UHLÍKOVÝCH INKOUSTŮ

Jan Šrámek, Milan Sýs, and Karel Vytřas

Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, CZ-53210 Czech Republic

E-mail milan.sys@upce.cz

Abstract

The aim of this work was to find out which of the selected polymeric materials has optimal properties and can be considered the most suitable for the preparation of carbon inks, from which the printed carbon electrodes can be prepared. The theoretic part describes in details the main components of carbon inks and their laboratory preparation. There are shown also information about screen-printed carbon electrodes, respectively their laboratory preparation and applications in electrochemical analyses. Unlike this, the experimental part was focused on description of laboratory preparation and testing of screen-printed carbon electrodes differing in their composition. Ohmic resistance, electrochemical properties, and mechanical stability in organic solvents were tested. Results obtained herein were compared with the properties characterized chosen conventional electrode.

Souhrn

Cílem této práce bylo zjistit, který z vybraných polymerních materiálů vykazuje optimální vlastnosti a lze jej považovat za nejvhodnější k přípravě uhlíkových inkoustů, z nichž lze následně připravit tištěné uhlíkové elektrody. V teoretické části jsou detailně popsány hlavní komponenty uhlíkového inkoustu a s tím spojená jeho laboratorní příprava. Nedílnou součástí jsou informace týkající se tištěných uhlíkových elektrod, respektive seznámení s laboratorní přípravou, komerčními elektrodami a aplikací v elektrochemických analýzách. Experimentální část se věnuje popisu přípravy a následnému testování elektrod lišících se svým složením. Obdržené ohmické odpory, mechanické a elektrochemické vlastnosti a mechanická stabilita elektrod v organických rozpouštědlech jsou konfrontovány s komerční tištěnou elektrodou.

1. Introduction

Laboratory preparation of screen-printed carbon electrodes (SPCE) is gaining popularity every day. The main reason is possibility of selecting individual components as well as their relative ratio. Unfortunately, the high price of disposable commercial SPCEs in many cases can be considered a serious deficiency [1]. In this respect, laboratory-prepared SPCEs in the comparison with commercial ones represent significant benefits because commercial SPCEs are not familiar with the characteristics of the individual components.

This information is often subject to well-known business secrets. With custom choices, analysts can predict the electrochemical and physical properties of the resulting SPCEs. They can then decide which type of prepared SPCEs is optimum for certain type of electroanalysis [2]. SPCEs belong to group of heterogeneous sensors basically they are composite materials of graphite powders and appropriate polymers representing suitable binders [3]. Thus, carbon ink used for working electrodes must contain a binder, solvent, and graphite particles. In this contribution, several common polymers (polyvinyl chloride, polystyrene, polydimethylsiloxane, paraffin wax, and parafilm) were tested for preparation of home-made carbon inks and SPCEs prepared from them. Electrochemical properties of these SPCEs and commercial one from DropSens company towards $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ redox couple were compared.

2. Experimental

2.1. Reagents and Chemicals

Polyvinyl chloride (PVC), polystyrene (PST), parafilm (PF), polydimethylsiloxane (PDMS), and paraffin wax (PW) as polymer substances, and potassium hexacyanoferrate(II) trihydrate of p.a. grade were purchased from Sigma Aldrich (Prague, Czech Republic). For demonstration, 3D structures of common polymer material are shown in Fig. 1. Graphite powder “CR-2“ type (2 μm average of particle diameter) obtained from Maziva Týn nad

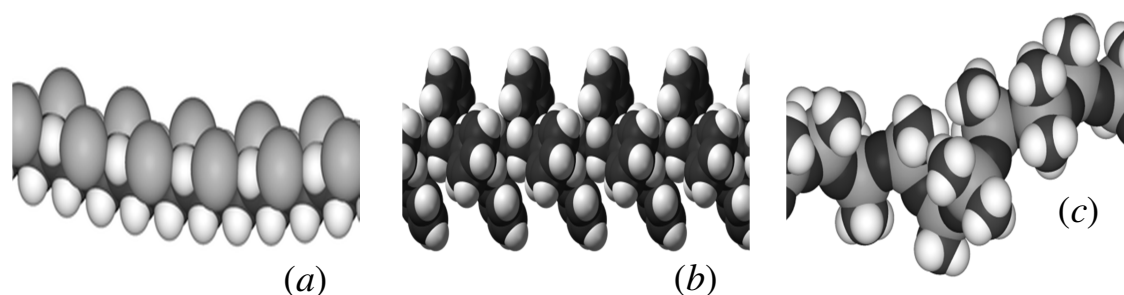


Figure 1. 3D chemical structures of PVC (a), PST (b), and PDMS (c).

Vltavou (Czech Republic) was used for preparation of corresponding carbon inks. Organic solvents such as cyclohexanone, xylene (mixture of isomers), dimethylformamide (DMF), acetonitrile (ACN), tetrahydrofuran (THF), and acetone from Lach-Ner (Neratovice, Czech Republic) were used for dissolving of polymers and testing electrodes mechanical stability. Potassium chloride and hydrochloric acid (35%) for preparation of 0.01 M HCl with content of 0.1 M KCl as supporting electrolyte were also provided by Lach-Ner. Demineralized water

with electric resistivity $\sim 18.3 \text{ M}\Omega \text{ cm}$ prepared using Milli-Q system from Merck Millipore (Burlington, USA) was used to prepare supporting electrolyte solutions as well as a 0.01 M stock solution of $\text{K}_4\text{Fe}(\text{CN})_6$.

2.2. Carbon Ink Preparation

Individual carbon inks were prepared in the same way, namely by dispersing the carbon powder in the organic solvents mixture containing tested polymer. At first, each polymer (0.15 g) had to be dissolved in the appropriate solvent (4.85 g) in a closed vial at constant stirring speed 150 rpm of Teflon[®] magnetic stir bar. Closure of the vial is necessary to prevent excessive evaporation of the organic solvent used. Setting low value of stirring speed ensure a continuous mixing for a better homogenization of viscous carbon ink.

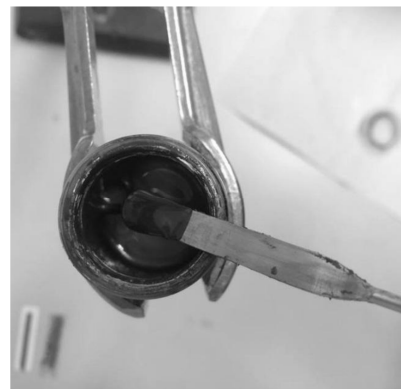


Figure 2. Prepared carbon ink.

Initially, graphite powder (3 g) was successively added at high doses to the dissolved polymer. At a time when the resulting mixture had an oil consistency and the carbon powder was poorly dispersed, these doses were reduced and stirring speed had to be set to 100 rpm because the entire mixture is only blurred at higher values. Picture of vial with freshly prepared carbon ink is shown in Fig. 2.

2.3. Manual Printing and Curing of Layer

Fig. 3. shows individual steps necessary for manual printing of corresponding SPCEs.

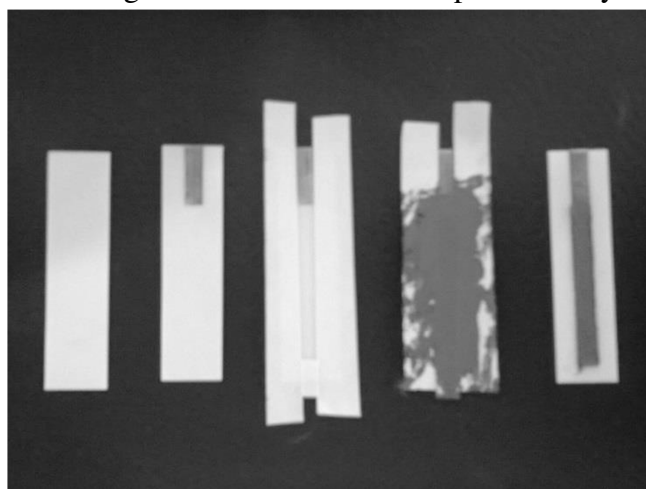


Figure 3. Individual steps in the manual printing.

In the first step, a standard ceramic platform or elastic plastic foil (1×4 cm) was provided with small copper plate due to avoiding damage of electrode layer by crocodile contact. After that, electrode area was set using paper adhesive tape, freshly prepared carbon ink was applied onto surface of the ceramic platform using a metal spatula, and the printed layer was cured in an

oven at 60°C for 2 hours. During the last mentioned process, used organic solvent evaporates and the bond between the substrate and the carbon ink is reinforced.

2.4. Electrochemical Instrumentation

All electrochemical measurements were carried out at conventional three electrodes arrangement consisting always one of prepared SPCEs (working), together with the Ag/AgCl/3.0 M KCl (reference), and Pt-wire (auxiliary electrode). For comparison, commercial SPCE type DRP-150 from DropSens (Llanera, Spain) was chosen also as working electrode. Mentioned electrochemical setup was connected to PalmSens potentiostat (Ivium Technologies, Netherland) operating with software PSTtrace version 4.6.

2.5. Methods

All electrochemical experiments were performed at room temperature using 0.01 M HCl with 0.1 M KCl (pH 2.05) as a supporting electrolyte. As chosen electrochemical technique, cyclic voltammetry (CV) of 0.5 mM $K_4Fe(CN)_6$ from -0.5 to +1.0 V at potential step 5 mV and scan rate 50 mV s⁻¹ was used.

3. Results and Discussion

3.1. Selection of Suitable Organic Solvents

Generally, selecting a suitable organic solvent is a key parameter in the preparation of carbon inks but also in the printing itself. Two basic conditions are decisive. Namely, used polymer must be soluble in the organic solvent which cannot be too volatile. Unlike parafilm soluble only in the xylene, all other tested polymers were easily dissolved in commonly used cyclohexanone [4]. It was also observed that acetone and THF are not a suitable organic solvent due to its relatively high volatility.

3.2. Mechanical Stability of Printed Layers

Within this study, it was found that printed electrode layers composed of PVC or PST are characterized by great mechanical stability. These types of layers cannot even be removed from the ceramic platform by manual wiping. Other types rather resembled carbon pastes that blotted out even with slight manipulation. The comparison of SPCEs prepared onto plastic foils is shown in Fig. 4.

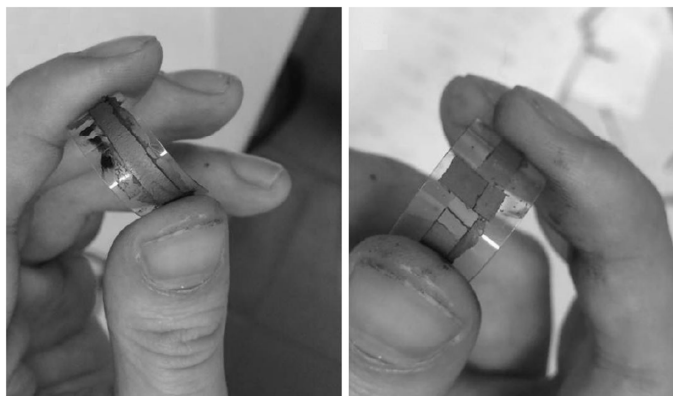


Figure 4. Comparison of using of PVC and PDMS.

3.3. Stability of Printed Layers in Various Water-Organic Mixtures

Fundamentally, the necessity of each electro-analyser is the knowledge of the SPCEs stability in different electrolytes. The stability in the presence of organic solvents (ethanol, ACN, acetone, and DMF) and their aqueous mixtures was therefore tested for a certain duration of action. According to obtained results, it can be concluded that SPCE containing PVC was the most stable as in the case of commercial DRP-150. Its surface was more sticky only after the acetone action more than one hour. Other electrodes were not stable because they were dissolved even in the presence of ethanol.

3.4. Electrochemical Properties of Prepared Screen-Printed Carbon Electrodes

Surprisingly, relatively high value of ohmic resistance (R) 220Ω for commercial DRP-150 electrode was measured. SPCEs prepared from polymers like PDMS (viscous silicone oil with molecular weight of 8000 g mol^{-1}), PW, and PF rather resembled carbon pastes. Values higher than 550Ω were obtained for these electrodes. Average values of 533Ω and 322Ω were obtained for SPCEs containing PVC and PST, respectively.

Cyclic voltammetry is perhaps the most versatile electroanalytical technique for study of electroactive species. However, can be used to characterize and compare individual electrode materials using standard redox couples [2,5,6] like $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Ru}(\text{NH}_3)_6]^{2+} / [\text{Ru}(\text{NH}_3)_6]^{3+}$, $\text{Ce}^{3+} / \text{Ce}^{4+}$, quinone / hydroquinone, etc. According to equation 1, number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between anodic (E_p^a) and cathodic (E_p^c) peak potentials.

$$\Delta E_p = E_p^a - E_p^c \cong 0.059 / n \quad (1)$$

Consequently, a one-electron process such as the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ exhibits a ΔE_p , of 0.059 V. Slow electron transfer typical for surfaces of carbon electrodes, "irreversibility," causes the peak separation to increase. The relationship to concentration (c) is particularly important in analytical applications but also in studies of electrode mechanisms. The values of anodic peak (I_p^a) and cathodic peak (I_p^c) currents should be identical for used simple reversible redox couple. Evidently, the ratio between cathodic and anodic peak current responses $|I_p^a / I_p^c|$ has to be always close to 1 [7].

From results shown in Table 1, SPCE based on PST provided the most suitable electrochemical properties from all prepared ones. In comparison with commercial DRP-150, a minor increase in the irreversibility was found. It seems that PST represents the sufficient polymer material for preparation of SPCEs usable for work in the aqueous electrolytes.

Table 1. Comparison of individual SPCE types using $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ redox couple.

SPCE	E_p^a / mV	E_p^c / mV	$\Delta E_p / \text{mV}$	$I_p^a / \mu\text{A}$	$I_p^c / \mu\text{A}$	$ I_p^a / I_p^c $
PST	325	215	110	8.5	-7.8	0.92
PVC	351	200	151	7.7	-7.2	0.94
PW	415	130	285	4.5	-4.4	0.98
PF	375	150	225	6.5	-6.0	0.92
PDMS	460	50	410	7.9	-7.9	1.00
DRP-150	205	125	80	10.2	-13.0	1.27

4. Conclusion

This work should be understood as the initial step in the development of carbon inks and electrodes formed therefrom. It seems to be clear that the polymer content and combination of polymers have not been optimized. SPCEs based on PVC and PST had the most similar electrochemical properties with commercially available DRP-150 electrode. Both SPCEs can be characterized as solid, glossy, hard, and conductive materials that well adhered to the substrate surface such as ceramic platform or plastic foil. Unlike 220 Ω for DRP-150, average values of 533 Ω and 322 Ω were obtained for SPCEs containing PVC and PST, respectively. Anyway, sufficient electrochemical properties have been achieved at these types of SPCEs towards $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ redox couple.

Acknowledgment

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