

Traditional vs. Non-Traditional Materials for Carbon Paste Electrode Preparation: On Relation between the Composition and Properties

Tomáš Mikysek^{1*}, Kamila Rosecká¹, Matěj Stočes¹, Kurt Kalcher², and Ivan Švancara¹

¹ *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-53210 Pardubice, Czech Republic.*

² *Institute of Chemistry-Analytical Chemistry, University of Graz, Universitätsplatz 1/I, AT-8010 Graz, Austria.*

Abstract: Several new types of carbon pastes were prepared as well as pastes made from various abrasive materials, examined and characterized. The main attention has been paid to the changes in their ohmic resistance, relative to the dependence on the composition of powder material to paraffin oil as pasting liquid. The results were compared with those of “traditional” carbon paste electrodes 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 carbon-to-binder ratio of the paste.

Keywords: Carbon paste electrode; Characterisation; Nanopowder; Abrasive materials, Resistance measurements; Cyclic voltammetry.

*) To whom correspondence should be addressed. E-mail: tomas.mikysek@upce.cz

Introduction

Carbon paste electrodes (CPEs) representing a heterogenous mixture of carbonaceous material and pasting liquid had been introduced by Adams in 1958 [1]. Since then, the electrodes became rather popular and joined the group of traditional solid electrodes suitable for electroanalysis [2-5].

The early period of these electrodes was in terms of characterisation where some basic procedures were introduced, mainly thorough physicochemical characterisation and optimisation of every paste composition which is inevitable. The first characterisation was performed again by Adams and his co-workers when having tested different graphite powders in combination with liquid hydrocarbons. They found connection between electrochemical behaviour of CPEs and properties of employed carbon and binder. [6]. Moreover, several other studies reporting on some characterisation of new CPEs appeared. More recently, a characterisation procedure based on the resistance measurements in dependence of the carbon paste composition was presented together with some practical advices [7-10].

As mentioned above, a characterisation of each new CPE is inevitable. The main reason is the choice of carbonaceous material. Whereas a binder (in most cases paraffin or silicone oil) plays a minor role – except some special cases [2,11,12] – the carbon is the main component responsible for the electrochemical behaviour and its brand is specific for each laboratory. Therefore, it is not possible to unify CPE composition and its properties.

When talking about different carbonaceous materials suitable for carbon paste electrodes, between traditional materials belong in most cases spectroscopic graphite powders and graphite gear lubricants [13] and recently also carbon nanotubes [14] which opened new attractive field in electroanalysis. Hence, *carbon nanotubes paste electrodes*, CNTPEs or *carbon nanotubes-modified carbon paste electrodes*, CNT-CPEs are now widely used [15,16] and belong to a group of *modern carbon (nano)materials*. Preparation of CPE also reflects growing popularity of employing modern carbon materials and utilization of their unique properties. Among these materials besides CNTs belongs: fullerene C-60, carbon nanohorns, carbon nanopowder, template carbon, porous carbon foam, porous carbon microspheres, ordered carbon, carbon nanofibers, graphene and graphene oxide [13,17-21]. Among others, *alternative carbon materials* can perhaps be mentioned representing only rarely used materials; namely: acetylene black, carbon black, colloidal graphite, soot, activated charcoal, natural coal and diamond powder, etc. [13].

In this paper, an investigation of physical properties and resistance of various types of CPEs is presented, proposed as a systematic variation of the actual “carbon-to-pasting liquid” ratio. The series of electrodes studied being prepared with various composition demonstrated not only change(s) in physicochemical parameters, but also the effect of the liquid binder upon the resultant electrochemical properties.

The observations and results reported below could also be compared to those obtained in the previous investigations carried out recently with a set of traditional CPEs and GCPE [10], CNTPEs [8,9], and lastly also with CILEs [7].

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 (model PGSTAT-128N; Metrohm Autolab B.V., Utrecht, The Netherlands) was used in combination with the three-electrode cell and controlled by software NOVA 1.10. All the measurements were carried out in the cyclic voltammetric mode (CV).

The ohmic resistance of the individual carbon paste mixtures was measured with a multimeter (model Voltcraft VC 404; Conrad Electronics, Germany) and with the aid of simple connection via two cables with stainless steel tips.

Electrodes and Accessories

For electrode preparation various materials were used: (i) two types of carbon powders - carbon black (CN500; carbon nanopowder < 500 nm; CAS: 699632, Sigma Aldrich) and activated charcoal (CN50; carbon nanopowder < 50 nm, CAS: 63310, Sigma Aldrich); (ii) abrasive materials – boron carbide (B_4C ; particle size < 10 μm ; CAS: 378119, Sigma Aldrich), titanium nitride (TiN; particle size < 3 μm ; CAS: 595063, Sigma Aldrich), titanium carbide (TiC; particle size < 4 μm ; CAS: 594849, Sigma Aldrich); titanium nitrido-carbide (TiNC; particle size 1-2 μm ; CAS: 518913, Sigma Aldrich), and tungsten carbide (WC; (particle size 2 μm ; CAS: 241881, Sigma Aldrich) together with paraffin oil (from Merck) as a binder. Hence, a series of seven different paste mixtures could be prepared; namely: CN50/PO, CN500/PO, B_4C /PO, TiN/PO, TiC/PO, TiCN/PO, WC/PO), each varying in the

carbon / abrasive material-to-binder ratio. All the pastes were hand-mixed using a pestle and mortar.

Freshly made pastes were packed into special electrode holders [22] of identical design and size. The electrode surface was renewed by smoothing on filter paper before starting a new set of experiments. For comparison, also carbon paste electrodes (CPEs), representing the two classical variants, were made: (i) mineral oil-based (C/PO type) and (ii) viscous silicone oil-containing analogue (C/SO); both being made from graphite powder (CR-5; originally, a natural form being chemically purified and then purchased as a gear lubricant; Maziva, Týn nad Vltavou, Czech Rep.) according to the above-described procedure. An Ag/AgCl electrode (containing 3M KCl as the inner electrolyte) as the reference and a Pt-sheet as the auxiliary electrode then completed the cell.

Results and Discussion

The presented study links up to the previous characterisations performed with traditional CPEs, CNTPEs, as well as with CILEs. The first part of experiments was focused on the ohmic resistance measurement. According to the closest-packing model (adopted from crystallography; see [10]), 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 [10]. This effect was found for the classic CPE, for CNTPE as well as for CILEs. However, whereas the break point in CPE is at around 25 % (w/w) (35 % v/v) of the binder, in CNTPE this threshold appears surprisingly at much higher proportion of the oil (at about 60 % w/w) and, in case of CILEs, the optimal amount of the ionic liquid is about 40-45 % (w/w). Materials presented herein could also be possibly examined in terms of resistance measurement and compared to those from previous studies. The break point of CN50/PO is about 30 % (w/w) and in case of CN500/PO is about 52 % (w/w). Such behaviour can be explained on a close-packing model basis described in previously published work [9,10]. Moreover it was found that the break point is influenced by a particle size as well as type of binder. One would expect its rise up with smaller particle size as in case of CNTPEs in comparison to CPEs, but in case of CN50/PO and CN500/PO it is exactly the opposite (see Fig.1). The only explanation can be found in differentness of microstructure of both materials. Whereas CN50 is activated charcoal, the CN500 is carbon black and most probably has higher active surface; therefore, the break point is at higher value (52 %) similar to CNTPEs. In order to confirm such claims it would be useful to provide some SEM pictures – this can be subject for future experiments.

This study also deals with non-traditional (alternative) materials such as abrasives which exhibit low ohmic resistance (and, oppositely, high electrical conductivity) in units (max. tens) of ohms such as TiN, TiC, TiCN or B₄C or WC. In fact, the initial idea was to develop a paste-electrode analogue to the B₄C solid electrode once propagated by Adams [3]. Thus, a series of electrodes was prepared; always with different ratio of abrasive material to binder and the results of ohmic resistance measurements were rather surprising. The break point for TiN/PO, TiC/PO, TiCN/PO mixtures was found to be at about 10 % (w/w) (see Fig.2) thus much smaller than in previous cases. When going back to the B₄C paste electrode, it was found out that its break point had been even lower at about 4 % (w/w); moreover, the surface seemed to be quite wet and, after inserting into aqueous solution, the B₄C/PO electrode material started to quickly disintegrate. The same problem was ascertained for WC/PO mixture and thus, both these pastes were excluded from other experimentation.

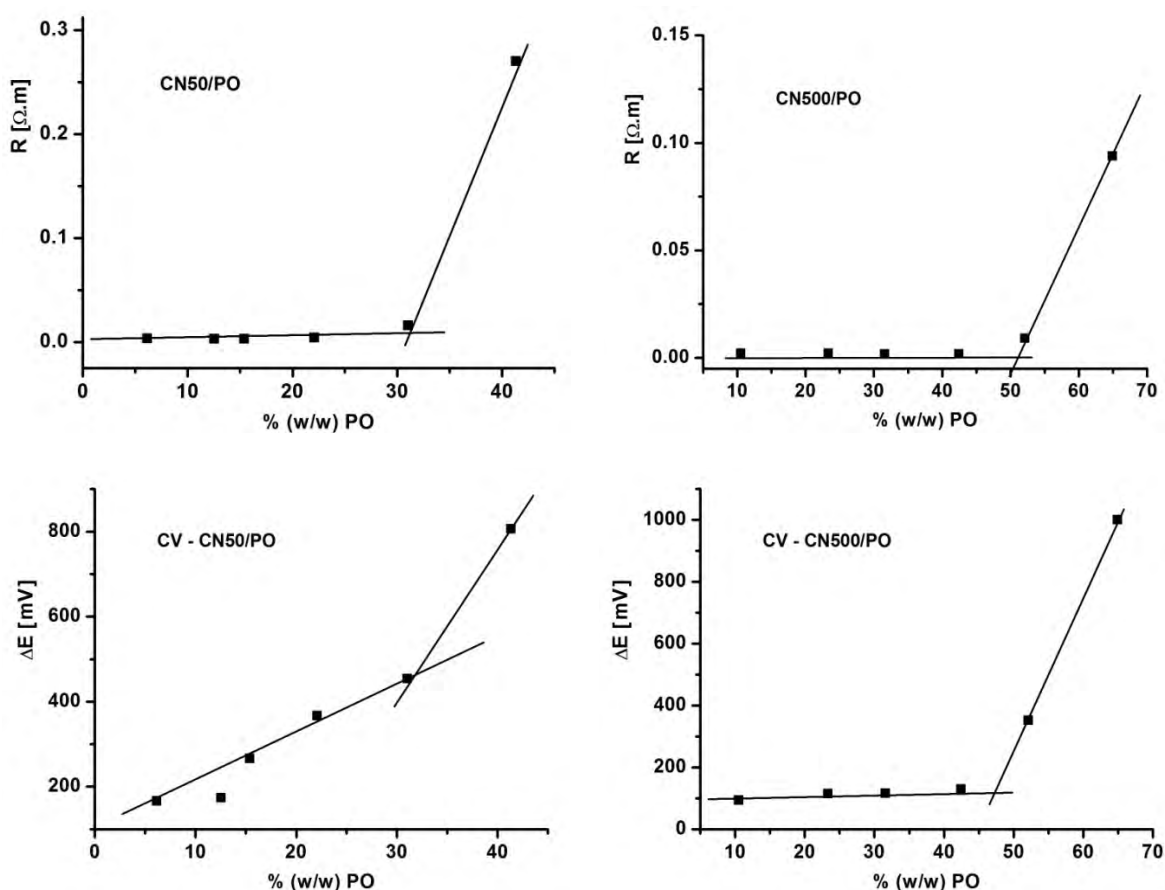


Fig. 1: Dependence of resistivity on the amount of binder (paraffin oil) present in the paste mixture for CN50/PO and CN500/PO (upper plots). Dependence of cathodic-anodic peak separation (from CV) on the amount of binder present in the paste mixture for CN50/PO and CN500/PO (lower plots). Experimental conditions: CV; CN/50/PO, CN500/PO; 0.1 M KCl + 0.005 M K₃Fe(CN)₆. Potential range: +1.0 V → -1 V vs. ref. and back; scan rate, 50 mV·s⁻¹.

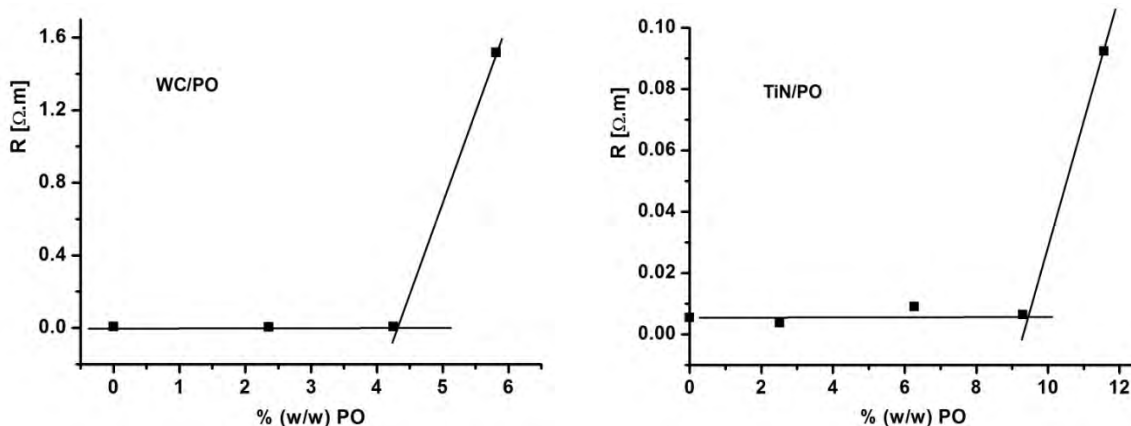


Fig. 2: Dependence of resistivity on the amount of binder (paraffin oil) present in the paste mixture for WC/PO (left) and for TiN/PO (right).

The second and also important part is an 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 0.1 M KCl) that behaves reversibly 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 150 mV. The described increase of the resistance (*i.e.*, 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 CPE [10] follows the “resistivity” one, similarly like in the case of CNTPE [9]. It is possible to figure out that the nanotubes and their bundles in the paste serve rather as nanowires enabling better conductivity than mutually touching carbon particles in CPE. Within the testing of CILEs, the situation is completely different and the binder/electrolyte represents a liquid-liquid interface and the electrochemical process can be considered as a charge-transfer across the boundary of two immiscible electrolytes [7].

In case of the above mentioned carbon nanopowders and the corresponding CN50/PO, CN500/PO mixtures is the electrochemical break point that can be attributed to the resistivity as shown in Fig. 1. Moreover it has to be stated that again it is opposite than one would expect according to particle size. Most probably the microstructure of CN500 represented by carbon black is able to entrap larger amount of binder (paraffin oil) rather than CN50 with smaller particles of activated charcoal.

Concerning the titanium-based abrasives tested for the first time in the carbon paste configuration, their electrochemical behaviour was very poor and only TiN/PO and TiC/PO

exhibited somehow identifiable signal during redox transformations of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ model system. Within the study, yet another testing procedure dealing with the response of the electrode toward hydrogen peroxide has been added. This could be important for future investigations of possible construction of some biosensors.

It can be stated that carbonaceous materials tested herein did not exhibit any “special” behaviour in comparison with the bare CPEs, but TiCN/PO mixture exhibited some response to hydrogen peroxide in both anodic and cathodic regions at rather low potential of +200 mV and -200mV vs. ref.

Thus, we had modified the TiCN/PO mixture with glucose-oxidase enzyme and performed the respective measurements in the FIA regime, but the system did not show good stability of the response toward glucose. This was, however, a first preliminary assay and the challenging problem still remains open for further studies.

Conclusions

The measurement of ohmic resistance and the anodic / cathodic peak separation offers the basic information on the paste quality, consistence, and stability, which helps to find the optimal ratio between the carbonaceous material and the pasting liquid used.

The data presented have shown that optimal ratio of components in paste mixture can be substantially different for each type of carbon paste-based electrodes. The main attention has been paid to recently studied carbonaceous and, newly, to abrasive materials and it can be concluded that the optimal consistence and composition of CN50/PO is at about 30 % (w/w) and CN500/PO at about 50 % (w/w) of the paraffin oil moiety. Concerning the employment of abrasive materials in paste electrodes, one can then conclude that TiN/PO, TiC/PO, TiCN/PO mixtures show a break point at about 10 % (w/w), whereas $\text{B}_4\text{C}/\text{PO}$ and WC/PO mixtures at about 4 % (w/w). If the content of liquid binder in the paste is higher than that for the break-point, the oily binder 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 disintegration.

Finally, the characterisation reported in this article is thought to serve also as a comparison of various traditional and non-traditional (alternative) pastes as the electrode materials, revealing that the classic carbonaceous materials exhibit better properties than alternative ones, but — maybe, in future — some new materials of better and satisfactory properties will be found.

Acknowledgements

The authors acknowledge that the Ministry of Education, Youth and Sports of the Czech Republic, project CZ.1.07/2.3.00/30.0021 “Enhancement of R&D Pools of Excellence at the University of Pardubice”, has financially supported this work.

References

1. R.N. Adams: “Carbon paste electrodes” *Anal. Chem.* 30 (1958) 1576-1576.
2. I. Švancara, K. Kalcher, A. Walcarius, K. Vytřas, in: *Electroanalysis with Carbon Paste Electrodes*, CRC Press, (2012).
3. R.N. Adams, in: *Electrochemistry at Solid Electrodes*, Marcel Dekker, Inc., (1969).
4. K. Kalcher, I. Švancara, R. Metelka, K. Vytřas, A. Walcarius: “Heterogenous carbon based sensors”; in: *The Encyclopedia of Sensors*, Vol. 4 (C.A. Grimes, E.C. Dickey, M.V. Pishko, eds.), pp. 283-430. ASP, Stevenson Ranch, (2006).
5. I. Švancara, A. Walcarius, K. Kalcher, K. Vytřas: “Carbon paste electrodes in the new millennium”. *CEJC – Centr. Eur. J. Chem.* 7 (2009) 598–656.
6. J. Lindquist: “A study of seven different carbon paste electrodes” *J Electroanal. Chem.* 52 (1974) 37-46.
7. T. Mikysek, M. Stočes, V. Jovanovski, H. Sopha, I. Švancara, J. Ludvík: “Relation between the composition and properties of carbon ionic liquid electrodes (CILEs)” in: K. Kalcher, R. Metelka, I. Švancara, K. Vytřas (Eds.), *Sensing in Electroanalysis*, pp. 157-166. University of Pardubice, Pardubice, 2011.
8. T. Mikysek, M. Stočes, I. Švancara, and J. Ludvík: “Relation between the composition and properties of carbon nanotubes paste electrodes (CNTPEs)” in: K. Vytřas and K. Kalcher, I. Švancara (Eds.), *Sensing in Electroanalysis*, pp. 69-75. University of Pardubice, Pardubice, 2010.
9. T. Mikysek, M. Stočes, I. Švancara, J. Ludvík: “The ohmic resistance effect for characterisation of carbon nanotube paste electrodes (CNTPEs)” *RSC Advances* 2 (2012) 3684-3690.
10. T. Mikysek, I. Švancara, K. Kalcher, M. Bartoš, K. Vytřas, J. Ludvík: “New approaches to the characterization of carbon paste electrodes using the ohmic resistance effect and qualitative carbon paste indexes” *Anal. Chem.* (2009) 6327-6333.

11. Q. He, J. Fei, S. Hu: "Voltammetric method based on an ion-pairing reaction for the determination of trace amount of iodide at carbon-paste electrodes" *Anal. Sci.* 19 (2003) 681-686.
12. C.A.H. Chambers, J.K. Lee: "Studies of the extraction of organic molecules into the carbon-paste electrode" *J. Electroanal. Chem.* 14 (1967) 309-314.
13. I. Švancara, T. Mikysek, M. Stočes, J. Ludvík, in: *Graphite Powder and Related Material as the Principal Components of Carbon Paste Electrodes*, Q. Campbell, C. (Ed.) Graphite: Properties, Occurrences and Uses, Nova Science Publishers, 2013, pp. 163-188.
14. S. Iijima: "Helical microtubules of graphitic carbon" *Nature* 354 (1991) 56-58.
15. G.A. Rivas, M.D. Rubianes, M.L. Pedano, N.F. Ferreyra, G.L. Luque, M.C. Rodríguez, S.A. Miscoria: "Carbon nanotubes paste electrodes. A new alternative for the development of electrochemical sensors" *Electroanalysis* 19 (2007) 823-831.
16. F. Valentini, A. Amine, S. Orlanducci, M.L. Terranova, G. Palleschi: "Carbon Nanotube Purification: Preparation and characterization of carbon nanotube paste electrodes" *Anal. Chem.* 75 (2003) 5413-5421.
17. D. Lowinsohn, P. Gan, K. Tschulik, J.S. Foord, R.G. Compton: "Nanocarbon paste electrodes" *Electroanalysis* 25 (2013) 2435-2444.
18. E. Nossol, A.J.G. Zarbin: "Carbon paste electrodes made from novel carbonaceous materials: Preparation and electrochemical characterization" *Electrochim. Acta* 54 (2008) 582-589.
19. Y. Wu, X. Mao, X. Cui, L. Zhu: "Electroanalytical application of graphite nanofibers paste electrode" *Sens. Actuators, B* 145 (2010) 749-755.
20. L. Xu, J. Du, Y. Deng, Z. Li, C. Xu, N. He: "Fabrication and characterization of nanoporous pseudo-carbon paste electrode" *Adv. Sci. Lett.* 4 (2011) 104-107.
21. S.A. Zaidi: "Graphene: a comprehensive review on its utilization in carbon paste electrodes for improved sensor performances" *Int. J. Electrochem. Sci.* 8 (2013) 11337-11355.
22. I. Švancara, K. Vytřas, R. Metelka, Czech Pat. Appl. PV 3939, (2002).