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Relation Between the Composition and Properties of Carbon Ionic Liquid Electrodes (CILEs)

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Abstract: Several 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 carbon ionic liquid electrodes (CILEs) and the proportions of 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 carbon-to-binder ratio of the paste. Finally, some problems connected with homogeneity and stability of carbon paste mixtures are also discussed.

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

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Introduction

Carbon paste electrodes (CPEs) as the mixture powdered spectroscopic graphite and a water-insoluble and electrically insulating pasting liquid belong to one of the traditional types of solid electrodes. Since 1958, when the first paper from Adams about CPE had been introduced, the use of such electrode material became very popular in electroanalysis [1-4].

However, a thorough physicochemical characterisation and optimisation of every paste composition is inevitable. In the past, some basic rules were introduced [5-7] and with varying components the number of modes of characterisation was extended [2]. Recently, the advantages of the resistance measurements in dependence of the carbon paste composition have been reported with some practical advices [8,9].

Characterisation procedures still belong to one of the actual topics because new carbonaceous materials for carbon paste electrodes are appearing, as well as new types of binders. One of the steps forward in material chemistry was discovery and introduction of carbon nanotubes [10] which opened a new and attractive field in the electroanalysis and the carbon nanotubes were used also as a carbonaceous material for *carbon nanotubes paste electrodes*, CNTPEs [11,12]. Later, carbon nanotubes (CNTs) were also employed as a modifier of common CPEs, giving rise to another new type of carbon paste-based electrode: *carbon nanotubes-modified carbon paste electrodes*, CNT-CPEs [13].

More recently, when room temperature ionic liquids (RTILs) became popular in electrochemistry and electroanalysis [14,15], their properties were attractive also for construction of new types of paste electrodes [16]. The use of ionic liquids in CPEs was firstly studied by Liu [17] and followed by Maleki and Safavi, together with their co-workers [18]. Later on, the presence of RTILs in CPEs was studied by other groups and presented as yet other novel carbon paste electrodes – either *carbon ionic liquid electrodes*, CILEs or the-called *ionic-liquid-modified carbon paste electrodes*, IL-CPEs [13,16].

It is evident that other combinations of carbonaceous materials and ionic liquids (e.g. CNT-ILEs) offer more possibilities in applications [13]. The necessity of characterisation of various CILEs is obvious as well since the ionic liquids change properties of the electrode material (*e.g.*, changes in conductivity, electrocatalytic effects, high charging current, *etc.*). Therefore, several principal studies were performed involving a comparison with the traditional CPEs [16-20].

In this paper, an investigation of physical properties and resistance of CILEs is presented, varying systematically the "carbon to pasting liquid" ratio. The studied series of electrodes of 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 the previous investigations obtained recently with a set of CPEs and CNTPEs [8,9].

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-128"; Metrohm / Autolab B.V., Utrecht, The Netherlands) was used in combination with the three-electrode cell and controlled by a software ("NOVA 1.7" package; the same manufacturer). 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 the carbon ionic liquid electrodes (CILEs), two types of carbon powders were used: a spectroscopic graphite (product "CR-5", with average particle size of 5μm; Maziva Týn nad Vltavou, Czech Republic) and pulverised glassy carbon (GC) ("Sigradur-G", with spherical particles with meash at the low mm level; HTW Meitingen, Germany) together with two types of ionic liquids as a binder: (i) trihexyltetradecylphosphonium dicyanamide (denoted as "IL-1"; from Merck), and (ii) 1-butyl-3-methylimidazolium hexafluorophosphate ("IL-2"; Sigma-Aldrich). Hence, three series of different carbon paste mixtures (CR-5/IL-1, CR-5/IL-2, GC/IL-2) could be prepared, each varying in the carbon-to-binder ratio. All the pastes were hand-mixed using a pestle and mortar.

Freshly made carbon-nanotube pastes were packed into specially designed electrode holders [3] 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.

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 gear lubricant; Maziva, Týn nad Vltavou, Czech Rep.) according to the above-described procedure. A 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 with CILEs links up to the previous characterisations [8,9] performed with traditional CPEs as well as with CNTPEs . The first part of experiments was focused on the ohmic resistance measurement. According to the "close-packing" model [8], 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 [8,9] (see also Fig.1 and 2). This effect was found for the classic CPE, for CNTPE as well as for tested 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 the case of CILES (CR-5/IL-1, CR-5/IL-2) the optimal amount of the ionic liquid is about 40-45% (w/w) – see Fig 1A,B.

Such behaviour can be explained by the above-mentioned model of close-packing: 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 25-30%) causes that the particles start to float in the oil, therefore the multiple contact between the particles is interrupted and the resistance sharply increases. In the case of CNTPE, the remarkable shift of the break point on the resistivity graph is caused by ability of CNTs to retain relatively large amount of binder by its adsorption on their extensive lipophilic surface. 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.

The experiments with both types of CILEs (CR-5/IL-1, CR-5/IL-2) have shown the break-point at 40-45% (w/w); hence, between those of CPE and CNTPE, respectively. This corresponds to the fact that the break-point is related both to the structure of carbon (compare CPE and CNTPE), as well as to the type of binder (compare CPE and CILE). This result reflects the question how the molecules of binder interact with the carbonaceous material or are allowed to penetrate into its structure. In the case CNTPE, the situation is more complicated due to the above discussed bundle of nanotubes.

In addition to this as well as for verification of all these statements the third type of carbonaceous material (glassy carbon - Sigradur-G) has been employed in this study with RTILs. The glassy carbon particles are ideal spheres with relatively smooth ("glassy") surface and therefore the break-point on resistivity curves of the respective CILE is shifted to lower proportion of the binder (about 30%) – see Fig. 2A, analogously to the case of two other binders (silicone or paraffin oil) studied in ref. [8].

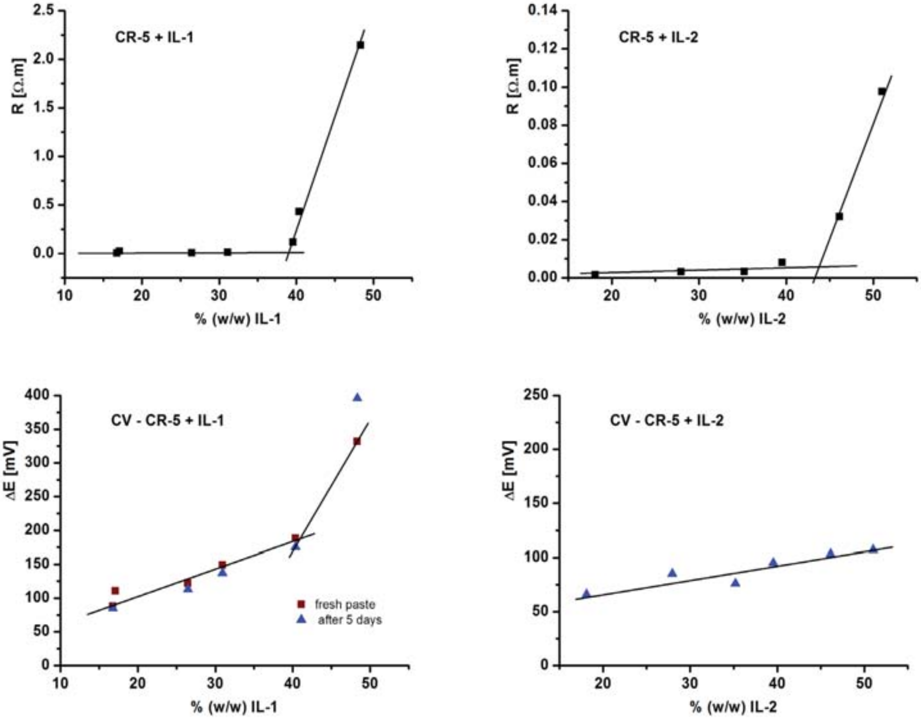

Fig. 1: *Dependence of resistivity on the amount of binder (ionic liquid) present in the paste mixture for CR-5/IL-1 and CR-5/IL-2* (**upper plots**). *Dependence of cathodic-anodic peak separation (from CV) on the amount of binder present in the paste mixture for CR-5/IL-1 and CR-5/IL-2* (**lower plots**). Experimental conditions: CV; CR-5/IL-1, CR-5/IL-2; 0.1 M KCl + 0.005 M $K_3Fe(CN)_6$. Potential range: +1.0 V → −1 V vs. ref. and back; scan rate, 100 $mV \cdot s^{-1}$.

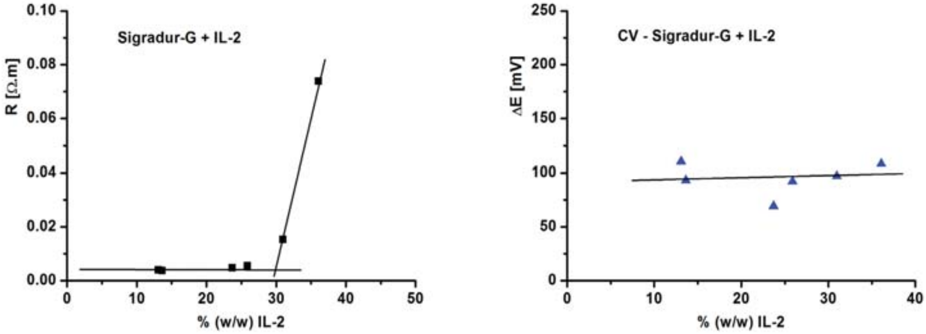

Fig. 2: *Dependence of resistivity on the amount of binder (ionic liquid) present in the paste mixture for GC/IL-2* (**left**). *Dependence of cathodic-anodic peak separation (from CV) on the amount of binder present in the paste mixture for GC/IL-2* (**right**). Experimental conditions: GC/IL-2; for other parameters, see Fig.1.

For the electrochemical characterisation of the paste electrodes, data of the cyclic voltammetry experiments have been employed using a well known system of $[Fe(CN)6]^{3-}$ / $[Fe(CN)6]^{4-}$ (specifically: 5 mM in 0.1 M KCl), which behaves reversible at most of usual electrodes. The theoretical separation between the cathodic and anodic peak is ΔEp = 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 ΔEp behind the break point.

The "electrochemical" break point of CPE [8] corresponds to 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 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).

Within the two RTILs being tested for CILEs the results show a different situation. Whereas in the case of CPEs, CNTPEs and also of CR-5/IL-1, the electrochemical break-point is corresponding to the resistivity one, in the case of CILEs prepared from the IL-2 this is not the rule as shown on Figs 1D and 2B and the drop in resistivity is not manifested itself as an increase of ΔEp. Fig. 3A shows that the cathodic (anodic) peak potential is not changing with the increasing amount of IL-2 whereas the peak current decreases. The precise explanation is not yet available, but it seems to be most probable that the surface of the CILE with IL-2 immersed into the $K_3[Fe(CN)_6]$ / KCl solution represents a liquid-liquid interface and the electrochemical process can be considered as a charge-transfer across the boundary of two immiscible electrolytes. The different behaviour of IL-1 and IL-2 therefore should originate from the structural/solubility difference of the two RTILs. This is, however, beyond the scope of this study and the challenging problem for further studies.

Yet another task – a limitation observed in our experiments and connected with CILEs is the presence of various capacitive currents. The intensity of charging current is probably dependent on the overall size of carbonaceous surface. In fact, there are two criteria: (i) The type of carbon being used – (i) glassy carbon has smaller surface than CR-5 and CNT at the same composition in mixture (see Fig. 3B); (ii) decrease of the carbon content in the actual mixture which results in diminishing of the total surface area of carbon particles, as well as in the drop of charging current (see Fig. 3A).

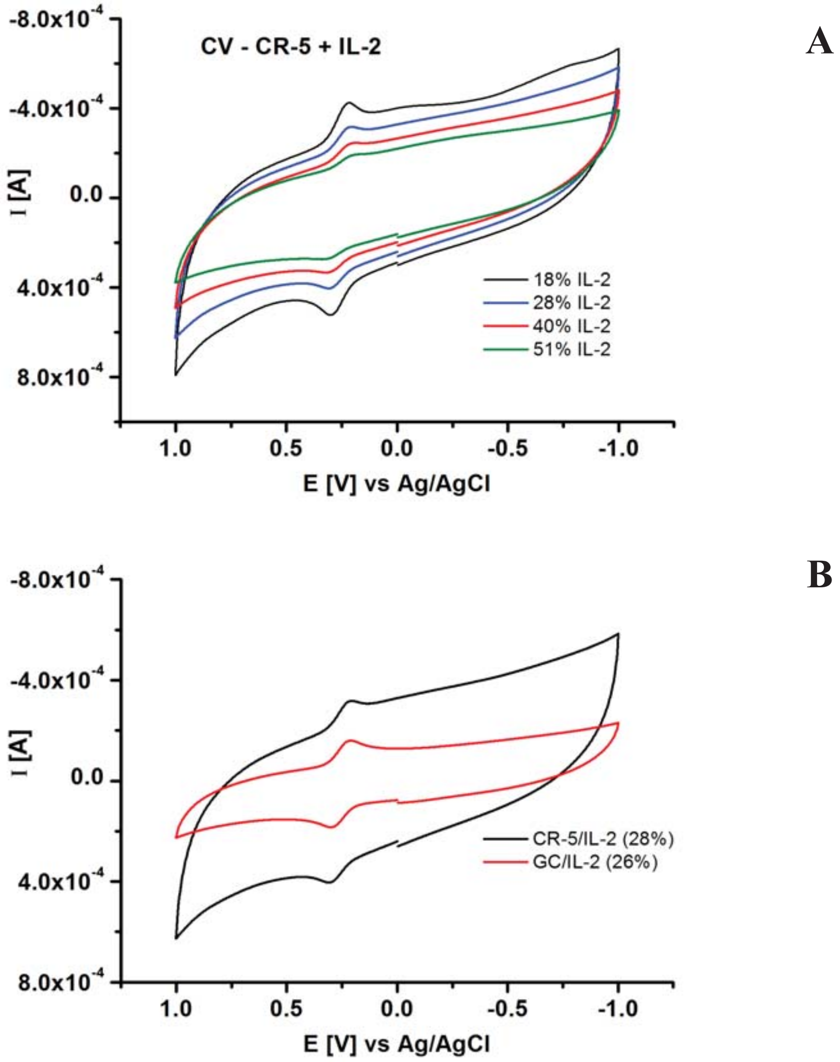

Fig. 3: *CV at various amount of binder (IL-2) present in the paste mixture for CR-5/IL-2* (**A**). *Comparison of CVs of different paste mixtures (GC/IL-2 and CR-5/IL-2) at the same type and approx. amount of IL-2* (**B**).

The replicate measurement of ohmic resistances (see again Fig. 1, the lower set of experiments) showed that the properties of the electrode are stable for at least 5 days, which is a finding important *e.g.* for CP-biosensing configurations employing such native pastes.

The next method potentially promising for characterisation of CILEs is the electrochemical impedance spectroscopy (EIS; see Fig. 4). However, for serious and more conclusive interpretation, it requires a wider palette of various RTILs.

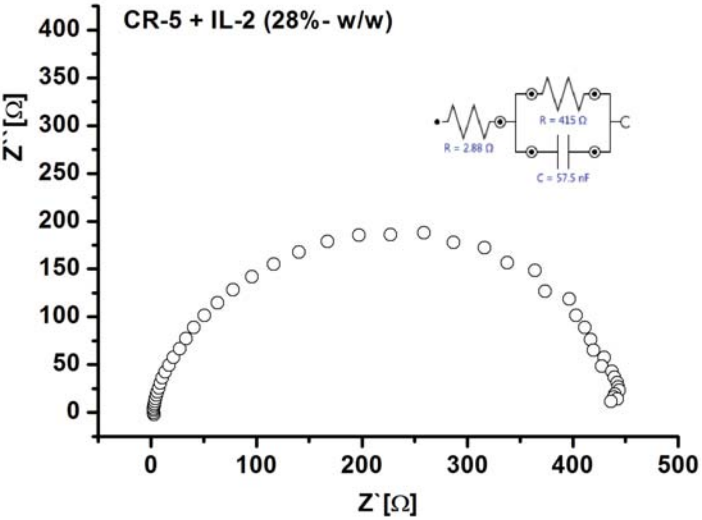

Fig. 4. *EIS of CR-5/IL-2 (28%) represented by Nyquist curve and equivalent circuit.*
Experimental conditions: E= 0 V, E_{ampl} = 0.01 V, frequency range: 100 Hz – 1 MHz.

Conclusions

As documented above, the measurement of ohmic resistance and the anodic / cathodic peak separation offers the fundamental information on the paste quality and stability helping to find the optimal ratio between the carbonaceous material and the pasting liquid used.

The presented data have shown that optimal ratio of components in carbon paste mixture can be substantially different for each type of carbon-based electrodes. The main attention has been paid to recently studied CILEs and it can be concluded that the optimal consistence and composition of CR-5/ IL-1 and CR-5/ IL-2 is at about 35-40% (w/w) of the ionic liquid whereas if the glassy carbon is used, the optimal proportion of the RTIL is lower (below 30% w/w), always before the "break-point" present on the composition dependence. 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 offers also comparison of various carbon pastes as electrode materials (CPE, CNTPE, and CILE). Some future prospects of fundamental characterisation can be found in the employment of new diagnostic techniques, such as electrochemical impedance spectroscopy (EIS).

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