

Carbonaceous Materials for Single-Use Metal Ion Sensors . Quality Assessment by Electrochemical Impedance Spectrometry

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Abstract: An overview of achievements and prospects of electrochemical impedance spectrometry (EIS) application for characterizing the surface of the carbon paste electrode (CPE) is emphasized. Several guidelines are pointed out and illustrated by preliminary experimental results.

Keywords: Metal ion sensors; Carbon paste electrodes; Electrochemical impedance spectrometry.

Introduction

Carbon pastes (i.e., intimate mixtures of carbon powder and a hydrophobic liquid binder) are widely used in electroanalytical chemistry and bioelectrochemistry [1,2,3] for preparing electrochemical sensors with a more or less degree of alteration by suitable additives (such as catalysts, biocatalysts, metal-ion binding reagents). The additive imparts as a rule the most typical characteristics of the sensor, but the properties of the paste itself also play an important role in deciding the sensor performance. That is why various methods for testing the

carbon paste have been proposed, as emphasized in comprehensive review [4]. As expected, most of the proposed testing procedures address empirical macroscopic parameters with direct relevance to the electroanalytical applications, such as limits of the potential window, background current, electric resistance and, more particularly, specific interactions between the analyte and paste components (adsorption and extraction).

Surface topography and heterogeneity at the microscopic scale may exert a considerable impact on the surface macroscopic behavior. Accordingly, scanning tunneling microscopy (STM) [5] and scanning electron microscopy (SEM) [6] have been employed to explore the surface of the carbon paste. STM investigations revealed the distribution of electroconductive and insulating regions whereas SEM put into evidence topographical features that substantiate the voltammetric behavior of the pastes. Scanning electrochemical microscopy may provide complementary information in regard to the local properties at the μm scale.

A different approach in CPE characterization lies on the determination of macroscopic properties that are connected with microscopic characteristics. Among various methods, EIS holds a particular position due to the wealth of available information. The electric impedance (i.e. "the apparent opposition in an electrical circuit to the flow of an alternating current that is analogous to the actual electrical resistance to a direct current and that is the ratio of effective electromotive force to the effective current"[7]) provides an exhaustive description of the charge transfer process by mean of two parameters: the impedance absolute value and the relative phase shift between the AC current and applied AC voltage. Often, the reciprocal quantity (termed as admittance) is used instead. For practical purposes the charge transfer at the electrode-solution interface is described by an equivalent circuit which takes into account the physical processes that exert an effect on the charge flow rate (mass transport, ion migration, electron-transfer reaction at the interface, charge redistribution within the electric double layer). In the absence of an electron transfer reaction, the equivalent circuit consists of the solution resistance (R_e) in series with a capacitor that represents the electric double layer. This simple representation applies to perfectly flat electrodes (like liquid mercury). For any solid electrode, the capacitor should be replaced by a constant phase element (*cpe*, Q in Fig. 1a) with the impedance Z_Q defined as follows [8]:

$$Z_Q = (j \omega Y_0)^{-n} \quad (1)$$

where Y_0 (the admittance modulus) and n are frequency independent parameters ($0 \leq n \leq 1$). A pure capacitor is characterized by $n = 1$ whereas a pure resistor results when $n = 0$.

The deviation of the solid electrode from the pure capacitor behaviour was assigned to the microscopic heterogeneity of the surface. An attempt at using this approach to the investigation of glassy carbon electrodes [9] demonstrated that a more elaborated model (Fig. 1b) is required in order to take into account the occurrence of both basal planes and edge planes of the carbon particles. Investigations of CPE by impedance measurement with no charge transfer reaction were first attempted in this work. As an important detail, the occurrence of adsorbed oxygen in the carbon paste should be taken into account and the applied DC potential should be selected so as to avoid the interference of oxygen reduction.

If a charge transfer reaction takes place at the interface, the equivalent circuit (Randles circuit, Fig. 1c) will include elements that account for the electron-transfer at the interface (charge-transfer resistance, R_c) and mass transport by diffusion (the Warburg impedance, Z_w). The last element represents processes occurring in the solution phase and does not provide direct information about the surface state. This kind of information can be expected to arise from R_c (which is inversely proportional to the standard rate constant) and the CPE parameters. Unfortunately, a straightforward interpretation of these parameters is not possible and the investigation output may appear not informative enough even if very large amount of experimental data are collected. However this approach (which was amply exploited in ref. [10]) deserves further attention. A sensitive point (which complicates the data interpretation) is represented by possible interactions of the redox probe with the surface. As an alternative, a metal can be plated on the active surface sites so as to make the redox probe reaction depending on the geometric parameters of that site only (i.e. average diameter and spacing). This approach is attempted in our laboratory.

On the other hand, one can resort to an investigation of the geometric parameters by an approach, which is based on the assumption that the CPE surface behaves as a microelectrode array. This model was developed to account for the behavior of partially blocked electrodes [11] and was adopted for EIS investigation of metal electrodes covered by self-assembled monolayers [12]. It is our goal to perform such investigations in the near future. Our preliminary results are presented in this paper.

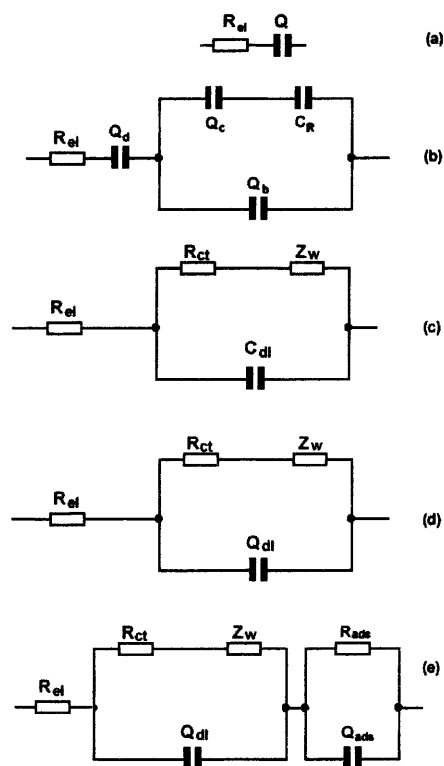


Figure 1. Equivalent circuits employed in this paper.

Experimental

Potassium ferrocyanide, potassium ferricyanide (p.a degree) and potassium chloride (Suprapur) were supplied by Merck. Spectrographic graphite powder RW-B (with microcrystalline structure and the particle diameter of 5-10 μm [13]) was obtained from Ringsdorff-Werke GmbH, Germany. The silicon oil (Lukoil MV8000) was provided by Lučební závody Kolín, Czech Republic. Filter paper for CPE surface renewing was a Schleicher & Schuell GmbH product (595-Rundfilter, red brand). The water was produced by a Milipore purification system. Dissolved oxygen was removed by a stream of nitrogen (99,99%, AGA AS, Oslo, Norway) which was directed over the solution surface during each run.

Carbon paste was prepared by adding 0.5 g of graphite and 0.25 g silicon oil into a laboratory mortar and homogenized by hand-mixing for 30 min, then tightly packed into the

electrode holder (3 mm inner diameter). The surface was renewed using manually smoothing by filter paper or paper towel.

In some experiments the unmodified (bare) CPE was subjected to an electrochemical pre-treatment in a solution containing 0.01 M Na_2HPO_4 , and NaH_2PO_4 , 0.1 M KNO_3 , and 0.01 M HNO_3 . The pre-treatment consisted of two steps: anodic polarisation of the CPE at +1.75 V for 120s and cathodic polarisation at -1 V for 15 s.

EIS experiments were carried out in a conventional electrochemical cell a CPE as working electrode, $\text{Ag}/\text{AgCl}/3\text{ M KCl}$ as reference and a Pt plate as counter electrode. Determinations in the absence of redox probe have been performed in 1 M KCl at 0.30 V. In determinations with $\text{Fe}(\text{CN})_6^{3-/4-}$ the test solution contained 1 M KCl and 5 mM of each redox couple member. EIS runs in this case were performed at the equilibrium DC potential (measured as the open circuit potential). The superimposed AC voltage was always of 10 mV. All measurements were performed with a PGSTAT 30 (Ecochemie, Utrecht, Netherlands) instrument. Fitting and simulation was done with Autolab FRA 4.8 software. Additional data processing operations have been carried out by the Origin 7.0 software (OriginLab Corporation).

Results and Discussion

CPE surface was investigated by EIS either in the absence or in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$. The results are further presented as the average of five replicate runs and are accompanied by the standard deviation of the mean (in percent).

Electrolyte resistance (R_e) has no connection with surface properties, but it was also considered because it provides additional information about the reproducibility, particularly in the case when the CPE position was not changed between replicate runs.

The results obtained with a bare paste in the absence of the redox couple are shown in Table 1. The best fitting was obtained with the equivalent circuit (a) in Fig. 1. Attempts at fitting by the more elaborate circuit (b) were unsuccessful. Probably the carbon material in the paste does not display the heterogeneous features that are accounted for by the circuit (b). We can infer that only the edge planes (that are partially oxidized and more hydrophilic) are exposed to the solution. Conversely, the basal planes are supposed to be covered and insulated by the binder oil.

The values of n in Table 1 are very close to 1, proving that Y_0 represents with a fair accuracy the capacitance of the double layer. Reproducibility of both n and Y_0 was good if the surface was not renewed before each run. Conversely a higher variability of Y_0 occurs if each

Table 1. CPE investigation by EIS in the 1 M KCl. Results of data fitting by the equivalent circuit (a) in Fig. 1. (1) Surface renewed before each run (filter paper); (2) surface renewed only before the first of 5 replicate runs; (3) Data collected after subjecting the electrode to an electrochemical pretreatment; (4) same electrode, after being soaked in distilled water for 24 hours.

	(1)		(2)		(3)		(4)	
	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.
R_{el} [Ω]	54.9	5.8	55.0	1.2	55.2	1	57.8	1.2
Y_0 [$10^{-6} \Omega^{-1/2} s$]	0.12	3.7	0.12	2.9	0.30	2.8	0.87	5.2
n	0.94	0.53	0.98	0.1	0.79	0.4	0.81	0.9

run is proceeded by surface renewal, most probably because of Y_0 dependence on the real (i.e. active) surface area. Y_0 appears therefore as suitable for testing the surface renewing procedure.

Column (3) in Table 1 demonstrates the effect of the electrochemical pre-treatment described in Experimental Part. An increase in Y_0 and a decrease of n resulted, proving a higher degree of heterogeneity. After prolonged soaking in distilled water, a further increase in Y_0 occurred, whereas n increased also. Slow penetration of water to the polar groups produced by the electrochemical pre-treatment may be the reason of these changes.

EIS data obtained with the redox couple have been fitted by equivalent circuits (c), (d) and (e) in Fig. 1. The last one proved to be not suitable, probably because no electron reaction in the adsorbed state occurs. Only fitting results obtained with circuits (c) and (d) are therefore reported.

Table 2 presents results that illustrate the reproducibility of the surface renewing procedure as determined by means of the redox probe. Both equivalent circuits (c) and (d) have been checked. For the equivalent circuit (c), $n = 1$ (by definition) and Y_0 represents the double layer capacity (in F; $1 F = 1 \Omega^{-1} s$). As shown in this Table, the quality of the fit (expressed by standard deviation values) is almost the same with both circuits, as can be expected if one take

into account that n values for the circuit (d) are very close to 1. Surface smoothing by towel paper resulted in a higher dispersion of R_{ct} values, although Y_0 variability was slightly lower in this case as compared with that resulted when filter paper was used to do surface smoothing. Also, R_{ct} was higher when paper towel was used as smoothing material. These results may be due to towel paper roughness but also to some impurity that adhere to the CPE surface in a random manner and inhibit the electron transfer reaction. It is clear that filter paper, a material with well controlled texture and purity is more convenient from the viewpoint of surface renewing reproducibility.

The Warburg impedance, which depends to a high degree on the diffusion process, shows a low dependence on the smoothing material and also a low variability.

Table 2. Effect of surface renewal procedure on the reproducibility of the EIS data obtained in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$. 5 replicate runs with the surface renewed before each of them.

Smoothing material	Filter paper				Paper Towel			
	(d)		(c)		(d)		(c)	
	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.
R_{el} [Ω]	49	12	58	5.2	61.6	3.5	66.4	3.8
R_{ct} [$\text{K}\Omega$]	0.27	3.1	0.26	5.3	0.8	14	0.7	14
Y_w [$10^{-2}\Omega^{-1}\text{s}^{1/2}$]	0.17	1.1	0.17	0.5	0.19	2.5	0.2	2.5
Y_0 [$10^{-6}\Omega^{-1/n}\text{s}$]	0.05	12	0.11	11	0.09	6.2	0.12	4.9
n	0.94	0.9	1		0.95	0.9	1	

The high standard errors of Y_0 for filter paper smoothing arise from the imprecision in Y_0 fitting operation. It appears therefore that R_{ct} is more reliable than Y_0 when assessing the reproducibility of surface renewal procedure.

Table 3 demonstrates an excellent reproducibility of the fitting parameters for replicate runs with no intermediate surface smoothing, with the exception of Y_0 values obtained when filter paper was used. This proves that the low reproducibility of Y_0 is not due to the smoothing procedure itself but to the low accuracy of the fitting operation. Y_0 shows a much better

reproducibility if paper towel was employed to do the initial surface renewal. Anyway, data in Table 3 prove that no surface alteration occurs during the EIS runs in the presence of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple. Such an alteration may be expected when performing cyclic voltammetry because, under high overpotential conditions, traces of Prussian blue can form and contaminate the surface [14].

Table 3. Reproducibility of the EIS parameter for 5 replicate runs in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$ with no intermediate surface renewal.

Smoothing material	Filter paper				Paper Towel			
	(d)		(c)		(d)		(c)	
Equivalent circuit (Fig. 1)	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.	Aver.	Dev.
R_{ct} [Ω]	44	2	57	1.2	56.2	0.3	61.9	0.4
R_{ct} [$\text{K}\Omega$]	0.232	0.2	0.21	3.3	0.70	4	0.7	4
Y_w [$10^{-2} \Omega^{-1} \text{s}^{1/2}$]	0.163	0.2	0.16	0.3	0.20	0.2	0.2	0.2
Y_0 [$10^{-6} \Omega^{-1/n} \text{s}$]	0.04	10	0.11	6	0.11	3	0.14	2
n	0.84	0.8	1		0.93	0.2	1	

Conclusions

Our preliminary investigations demonstrate that EIS data fit best the circuit (a) when no redox probe is present, whereas the data obtained in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$ are fairly well fitted by both circuits (c) and (d) but not by the circuit (e). The last one was assumed as most suitable by another group [10]. The discrepancy between our results and the previous ones [10] may result from the difference in the characteristics of the material employed to prepare the carbon paste. As no sufficient details on carbon paste characteristics are available in ref. [10], it was not possible to reproduce the paste composition investigated in that paper.

Further investigations will be done with different redox probes in order to assess the effect of probe charge and hydrophobicity. Also, data processing in the frame of the microarray model is in progress and results will be reported in a near future.

Acknowledgement

NATO financial support under the project PST.EAP.CLG 980619 is gratefully acknowledged.

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