On the origin of capacitance dispersion of rough electrodes

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Abstract

The interfacial impedance of polycrystalline solid electrodes in the absence of Faradaic reactions is never purely capacitive; the deviation from ideal capacitive behaviour is usually larger on rough electrodes than on smooth ones. We present qualitative experiments to demonstrate that the frequency dependence of capacitance on solid electrodes is due to the atomic scale inhomogeneities rather than to the geometry aspect of roughness. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

According to what is found in the electrochemical textbooks, the ideally polarizable electrode — that is, on which no Faradaic reactions proceed — should exhibit ideally capacitive impedance. This has been, in fact, observed with geometrically and atomically uniform electrodes (with liquid mercury or single crystalline solid electrodes). However, on polycrystalline solid electrodes (even on smooth ones) the impedance is not purely capacitive, but has a functional form as if the double-layer capacitance were frequency-dependent. This is referred to as 'frequency dispersion of capacitance' or simply 'capacitance dispersion' is observed. To characterize dispersion in a simple way, the interface is often approximated by a constant phase element (CPE)[1]; in other words the ('frequency dependent') capacitance, C, is a power-law function of frequency, ω, that is, $C(\omega) \propto (i\omega)^{\alpha - 1}$, where i is the imaginary

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[1] We define CPE by its admittance: $Y(\omega) = \sigma(i\omega)^{\alpha}$. For ideal capacitances $\alpha = 1$.

unit. Such behaviour with exponent α between 0.7 and 0.9 is often obtained with solid electrodes in the audio and sub-audio frequency range. The aim of the studies of this paper is to clarify the origin of this frequency dispersion.

The surface of the polycrystalline solids is never perfectly flat: on the atomic scale steps, kinks, dislocations; on a much larger scale corrugations, scratches, pits, grooves, etc. make them rough, or 'disordered' from geometric point of view. Disregarding the macroscopic (> 1 mm) features of the surface, we can distinguish between two types of geometrical irregularities: 'surface disorder' means atomic scale imperfections and the term 'roughness' will be used exclusively for geometric imperfections of characteristic size much larger than, say, 10 nm. Surface disorder and roughness are frequently interrelated: for example, a mechanically coarsened surface carries a great number of dislocations. Surface disorder means not only atomic scale non-uniformities but energetic inhomogeneities along the surface as well.

The connection between capacitance dispersion and surface roughness was recognized ∼ 50 years ago [1]; for early observations and theories see Ref. [2]. Gener-

ally, there are two approaches of explaining the connection:

1. The physical theories — the first of which appeared almost a half of a century ago — start with the assumption that the capacitance of the double layer is uniform along the rough surface and the only role of geometry is that the effective solution resistance is greater at the bottom of the hollows than at the top of the protrusions of the electrode. This yields that the overall impedance is some complicated function of the resistive and capacitive elements of the solution bulk and of the interface, respectively, appearing as if the interfacial capacitance had a frequency dependence. By assuming certain electrode geometry (e.g. porous [3–5] or fractal [6] geometry) one can calculate the impedance function — which is often of CPE form. However, as it was shown in [7], these models yield unrealistic results: the frequency range in which these models predict the capacitance dispersion of the usual electrochemical systems is much higher (kHz to GHz) than that at which the dispersion is observed[2], and therefore the models taking into account the geometry aspect of roughness only are not suitable for interpreting the de facto existing link between roughness and capacitance dispersion.

2. According to the other, physico-chemical, explanation [7] the origin of the capacitance dispersion can be allocated to the double layer; and it can be attributed to the presence of atomic scale inhomogeneities — 'disorder' — of the electrode surface, together with the presence of some kinetic process, most probably with specific anion adsorption. One can observe capacitance dispersion even with single crystalline electrodes (i.e. which have perfect surfaces) as a consequence of specific anion adsorption [8,9]; this dispersion with energetically non-uniform surfaces is enhanced, because on these surfaces the activation energies of the kinetic processes has a certain distribution. Due to the exponential connection between rate coefficient and activation energy, a relatively narrow distribution of the latter quantity causes a broad distribution of the rate coefficients (or time constants) — yielding a more pronounced frequency dependence.

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[2] This claim applies to electrodes of microscopic (micron scale) roughness with the usual aqueous electrolytes. Capacitive electrodes with macroscopic (mm or larger) irregularities can show frequency dependence capacitance in the audio–frequency range [17,18]. Due to the same reason, systems with electrolytes of very low conductivity (e.g. certain solid electrolytes) or with electrodes of extremely high interfacial capacitances might yield low frequency capacitance dispersion. These systems, however, are exceptional in the present electrochemical laboratory practice.

In this paper — just as in our preliminary report of this study [10] — we disregard specific anion adsorption and focus our attention on the role of the atomic scale non-uniformity of the surface. Atomic scale inhomogeneities can be introduced by mechanical treatment and can be decreased by annealing. We show a set of impedance measurements made on noble metals (Au, Pt, Ag) to demonstrate that the capacitance dispersion on rough electrodes is due to atomic scale non-uniformities rather than to roughness.

2. Methodological details of the impedance measurements

The electrochemical measurements were performed in an all-glass electrochemical cell and an impedance measurement system being very similar to the ones described in Refs. [7–9]; with very similar overall accuracy, i.e. for impedances, with better accuracies than 1% of the magnitude and 1% of the phase angle in the frequency range below 1 kHz. The following points need mentioning:

1. The overall purity of the cell, solutions, chemicals and procedures was similar to the ones described in Ref. [8,9]. Cleanliness was regularly tested by voltammetric measurements (not shown here). The extent of specific adsorption was diminished by applying pure, non-adsorbing electrolytes and cathodic potentials.

2. To avoid high frequency phase shifts due to the high reference electrode impedance, a double reference electrode [11] was applied: a platinum needle electrode, placed close to the saturated calomel electrode (SCE) tip, was connected capacitively (through a 4 μF capacitor) to the latter.

3. To emphasize the extent of capacitance dispersion, it is instructive to transform the $Z(\omega)$ impedance spectra to $C(\omega)$ complex capacitances by calculating the $C(\omega) = 1/([Z(\omega) - Z(\omega \rightarrow \infty)]i\omega)$ function. Being a complex quantity, $C(\omega)$ can be plotted also in Bode representation (as function of frequency, $f = \omega/2\pi$). There is no capacitance dispersion if the $\log(C_{abs})$ versus $\log(f)$ curve is a horizontal line and the phase angle, ϕ, is everywhere zero. Capacitance dispersion on this plot appears as tilted $\log(C_{abs})$ versus $\log(f)$ curve and non-zero ϕ values. (An ideal CPE appears as a straight line of slope $\alpha - 1$ on the $\log(C_{abs})$ versus $\log(f)$ plot, and the phase angle is constant, $\phi = 90*(1 - \alpha)$.) We note that the first step of the $Z(\omega) \rightarrow C(\omega)$ transformation is that solution resistance is subtracted from the measured impedance data. Any inaccuracy of the $R_s = Z(\omega \rightarrow \infty)$ value highly affects the accuracy of $C(\omega)$. This is the reason why the scatter of the high frequency points of the $C(\omega)$ spectra are rather high.
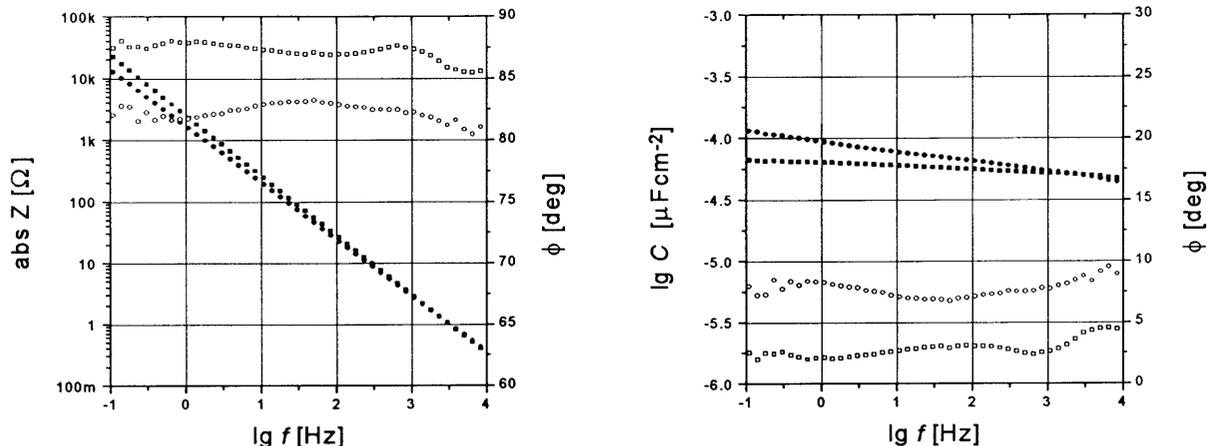
Fig. 1. Impedance (a) and capacitance (b) spectra of a polycrystalline gold electrode in 0.1 M $HClO_4$ solution at -0.25 V vs. SCE. Circles: original, roughened electrode; squares: after short annealing. Full and open symbols refer to absolute values and phase angles, respectively.

4. Reproducibility: the impedance measurements are highly reproducible on one and the same sample. However, the surface pretreatment procedure — roughening with a file or by emery paper and flame annealing — is not a standardized one (it was not aimed to be), and therefore the experiments are not 'point-by-point' reproducible. However, the tendency towards decreasing dispersion is clearly reproducible, for each potential.

3. The experiments

In general, to demonstrate the effect outlined in the Introduction, we need two electrodes of exactly identical shapes (roughness) but of different atomic scale homogeneities; the impedance spectra measured on these electrodes with identical conditions are to be compared. Instead of producing two electrodes of exactly the same roughnesses, we made the following sequence:
1. made one rough electrode with a high level of atomic scale inhomogeneity;
2. measured its impedance;
3. applied a mild annealing — this does not affect roughness but decreases the level of atomic scale inhomogeneity;
4. measured again its impedance.

Finally, we compared the spectra obtained in steps 2 and 4. We performed this sequence with noble metals (Au, Ag, Pt), for which ideally polarizable conditions can be assured. The details of the experiments are as follows:

Although the results with gold electrodes have already been published in Ref. [10], for the sake of completeness, we repeat here some of those measurement also here.

We prepared a hemispherical gold electrode, its flat face was roughened either by a steel file or by emery paper of grit 100 to yield a surface which is rough on microscopic, and disordered at atomic scale. Then this gold sample was cleaned by chemical means: it was soaked alternately for 10–10 min in freshly made Caroic acid ($\sim 10\%$ H_2O_2 in conc. H_2SO_4) and 10% KOH, in between and finally thoroughly rinsed by ultrapure water (obtained from a REWA water cleaning system). Because gold is insoluble in these solutions, its geometry remains unchanged during cleaning. Having cleaned, the impedance spectrum of the flat face of the gold was measured in a hanging meniscus configuration in 0.1 M $HClO_4$ solution at -0.25 V versus SCE; it is shown in Fig. 1a, as circles (with the series resistance subtracted). Were the interfacial impedance approximated by a CPE, the exponent α would be around 0.9 (note that the capacitance dispersion with single crystal gold electrodes, but otherwise identical conditions were much less, $\alpha \gg 0.99$, cf. Fig. 1 of Ref. [8,9]).

After this measurement, the electrode was flame-annealed for a short time (usually for several seconds only) in such a way that the red glow of the electrode was barely visible. We estimate that the temperature of the metal did not exceed 500°C, that is its temperature was much lower than the melting point[3]. After anneal-

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[3] Two comments are due here: first, a similar effect was observed when instead of flame annealing we annealed the sample in a furnace at 400°C for about an hour. (We preferred flame annealing to furnace heating, because the former — although not a well-controlled process — is a widely accepted practice of electrochemist.) Second, due to the flame annealing, roughness does not change — we have checked it using optical and scanning electron microscopes.
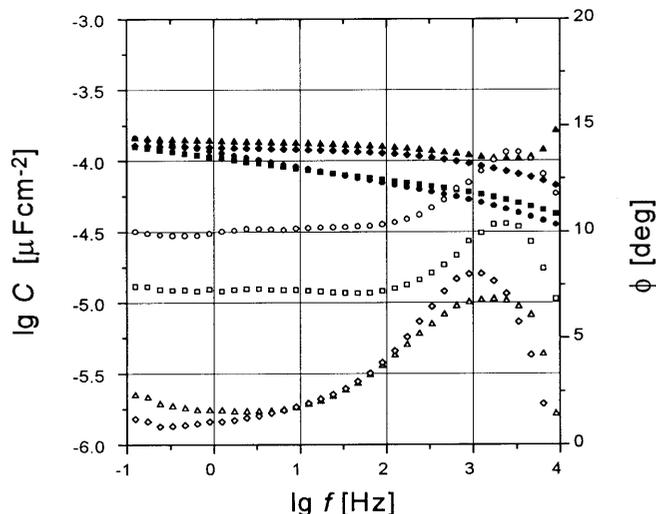
Fig. 2. Capacitance spectra of a polycrystalline silver electrode in 0.1 M $HClO_4$ solution at 0 V vs. SCE. Circles: original, roughened electrode; squares: after 1 min etching in 0.3 M KCN 20% H_2O_2; triangles: after annealing in Bunsen flame; diamonds: again etched for 1 min. Full and open symbols refer to $\log(Z_{abs})$ and to ϕ values, respectively.

ing we applied the very same chemical cleaning procedure, and measured the impedance spectrum again afterwards (Fig. 1a, squares). Comparison of the two spectra reveals that the latter spectrum shows a steeper frequency dependence and the phase angle values are closer to 90°. The difference between the two spectra is emphasized with the $Z(\omega) \rightarrow C(\omega)$ transformation (Fig. 1b). As it is seen in the figure, annealing yields a less frequency-dependent magnitude and a smaller phase angle (the average phase angle drops from ~ 7 to 2–3°.

As it is described in Ref. [10], the frequency dispersion can — to some extent — be further decreased by prolonged annealing. Anodic etching of the electrode in concentrated $CaCl_2$ solution — which procedure removes the scratched upper layer — significantly decreases capacitance dispersion.

Similar experiments have been made also with two other metals: silver and platinum. These are the metals for which one can find an ideally polarizable range, in which the metal surface is clean (oxide-free). This is true in 0.1 M $HClO_4$ solution at 0 V for silver, and in 0.1 M H_2SO_4 solution at $+0.2$ V for platinum.

For silver, the experiment was almost the same as of gold; we mention the following differences: the silver samples were cleaned by soaking into 0.3 M KCN in 20 vol.% H_2O_2 solution for 10 min and finally thoroughly rinsed with ultrapure water; to avoid oxidation, annealing was carried out at $\sim 500°$C in an electric furnace made of a quartz tube in nitrogen atmosphere; the impedances were recorded at 0 V. The effect of annealing on the capacitance dispersion is shown in Fig. 2. It is clear that both annealing and etching significantly decreases capacitance dispersion (~ 1 Hz the phase angle of capacitance drops by $\sim 8°$).

In the experiment with platinum we used a spherical platinum electrode, rather than a hemisphere, and the impedances were recorded in 0.1 M H_2SO_4 solution at $+0.2$ V, heat treatment was carried out again in the furnace — otherwise the conditions were the same as with gold. As it is shown in Fig. 3, by annealing dispersion decreases also with platinum, but in a much smaller extent than with gold or silver.

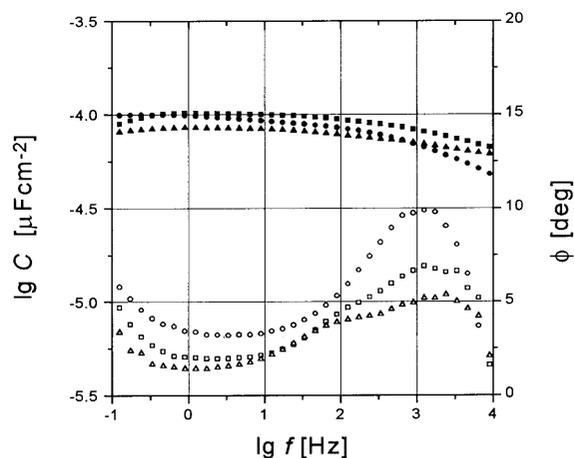We have also tried to extend the scope of the measurements for technical metals, e.g. copper and iron.

Fig. 3. Capacitance spectra of a polycrystalline platinum electrode in 0.1 M H_2SO_4 solution at 0.2 V vs. SCE. Circles: original, roughened electrode; squares: after 30 s annealing in Bunsen flame; triangles: after 10 min annealing in electric furnace. Full and open symbols refer to $\log(Z_{abs})$ and to ϕ values, respectively.
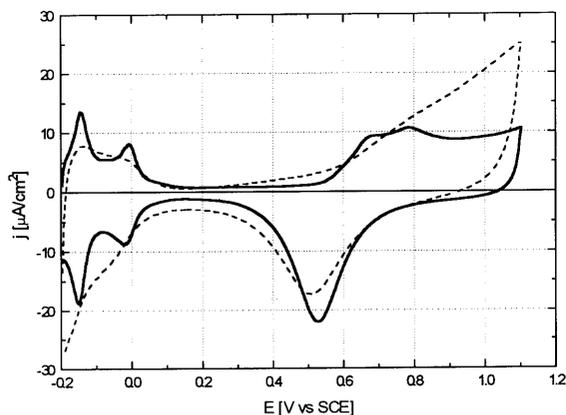
Fig. 4. Voltammograms of a polycrystalline platinum electrode in 0.1 M H_2SO_4 solution with sweep rate of 10 mV/s. Dotted line: original, roughened electrode; solid line: after 30 s annealing in Bunsen flame. The third cycles are shown.

Because in these metals the potential range of ideal polarizability is very narrow (if any) we measured the impedance at hydrogen evolution conditions. Preliminary experiments show that the interfacial impedance is a CPE-like element shunted by the Faradaic reaction's resistance, and the CPE exponent increases with annealing. This work is in progress.

Finally, to illustrate the connection to other areas of electrochemistry, we repeated the experiment with platinum with the only difference that instead of measuring impedances we recorded the voltammograms in the potential range between hydrogen and oxygen evolution potentials (Fig. 4). Whereas with scratched surface we get an ill-defined voltammogram, after the very mild annealing the voltammogram's shape becomes similar to that of a polycrystalline platinum electrode.

4. Comments and conclusion

1. Due to the annealing the frequency dependence of capacitance is markedly changed, though surface roughness remains the same. This means that irregular geometry (roughness) itself is not a sufficient condition for the appearance of the capacitance dispersion (for frequency limits, see Ref. [7]). The results of this series of experiments — in addition to those of Ref. [7] — proves that the almost fifty years old approach—theorizing capacitance dispersion by homogeneous interfacial capacitance and irregular geometry — is inappropriate.

2. Annealing can and does affect the atomic scale inhomogeneities, e.g. defects, thereby reducing the extent of surface energetic differences. One can achieve this goal also by etching — which removes the surface layer affected by the roughening — and by potential cycling [7].

3. Nowadays it is widely accepted that double layer capacitance of rough and porous solid electrodes is frequency dependent; this view is supported by the results of measurements which yielded rather large dispersions, e.g. Refs. [12–16]. All of these measurements have been made with unannealed rough or porous electrodes (there is no mention of annealing among the experimental procedures). We believe that at these experiments annealing would have diminished dispersion. So we re-formulate the old finding on the connection of roughness and capacitance dispersion in such a way that the extent of capacitance dispersion of electrodes of rough surfaces is larger than on smooth ones because the former ones are much less uniform on the atomic scale than are the latter ones.

4. A practical hint: in order to get 'well-behaved' impedance spectra with solid electrodes, apply some annealing procedure prior to the measurement, whenever possible.

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