

Surface Topography and Impedance of Metal-Electrolyte Interfaces

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The small-signal impedance of chemical cells with "blocking" electrodes is dominated at low frequencies ($f \lesssim 100$ Hz) by the impedance of the metal-electrolyte interfaces which is accurately represented by $Z_i = A(j\omega)^{-n}$. The frequency exponent n , $n < 1$, is sensitive to the texture of the interface, and several recent theories have been proposed that relate n with the fractal dimension \bar{d} of the rough interface. We find no correlation between n and \bar{d} from experiments using aqueous electrolytes and metal and semiconductor electrodes.

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The impedance of a cell consisting of an electrolyte sandwiched between two electrodes should ideally be represented by a series RC circuit provided no charge passes between the electrolyte and the electrodes. In this case, $Z(\omega) = R - j/\omega C$, where R represents the ionic resistance of the electrolyte, and C represents the capacitance of the two "blocking" (ideally polarizable) electrode-electrolyte interfaces. However, to the best of our knowledge, this ideal response has never been observed. The impedance of real cells of this type can be accurately represented by

$$Z(\omega) = R + A(j\omega)^{-n} \quad (1)$$

at frequencies below ≈ 50 kHz. The interface impedance Z_i is given by the second term, the so-called constant-phase-angle (CPA) impedance,¹ where $j = \sqrt{-1}$, and A and n are constants with $n < 1$. A typical example of this behavior is shown in Fig. 1. Note that Z_i contributes a frequency-dependent term to $\text{Re}(Z)$, $A\omega^{-n}\cos(n\pi/2)$, which has the same slope as $-\text{Im}(Z) = A\omega^{-n}\sin(n\pi/2)$ at low frequencies. Although the values of A and n depend on the electrolyte and electrode, the CPA behavior is a general characteristic observed for both liquid and solid ionic conductors.

The origin of the CPA impedance has remained an unsolved puzzle in electrochemistry for many years. For example, more than sixty years ago, Wolff reported² an unusual frequency-dependent capacitance from measurements on one of the same kinds of cells we investigated: aqueous sulfuric acid in contact with platinum electrodes. Following observations that the value of the frequency exponent n depends on the roughness of the electrode surface, de Levie³ proposed a model of a mechanically polished electrode assumed to contain parallel V-shaped grooves in which the impedance of the grooves was represented by tapered transmission lines. While this model gives a CPA impedance over several decades in f , n is fixed at $\frac{1}{2}$. Wang and Bates⁴ showed that de Levie's result could be generalized to give values of n close to those observed experimentally (0.8 to 0.9) by use of position-dependent resistors and capacitors.

The subject of this Letter, however, deals with several recent theories that relate the frequency exponent n to the fractal dimension \bar{d} of the surface of a rough electrode. Le Mehaute and Crepy⁵ first suggested that n and \bar{d} are related. Later, Nyikos and Pajkossy⁶ proposed that $n = 1/(\bar{d} - 1)$ and claimed that impedance measurements on large self-similar electrodes support their theory. However, Keddah and Takenouti⁷ and Wang⁸ have raised serious doubts about the validity of this relationship between n and \bar{d} and about the supposed experimental verification as well. Liu⁹ showed analytically that, at low frequencies, the impedance of an equivalent circuit for a Cantor bar model of a grooved electrode-electrolyte interface is given exactly by the CPA expression and also that $n = 3 - \bar{d}$. Kaplan and Gray found¹⁰

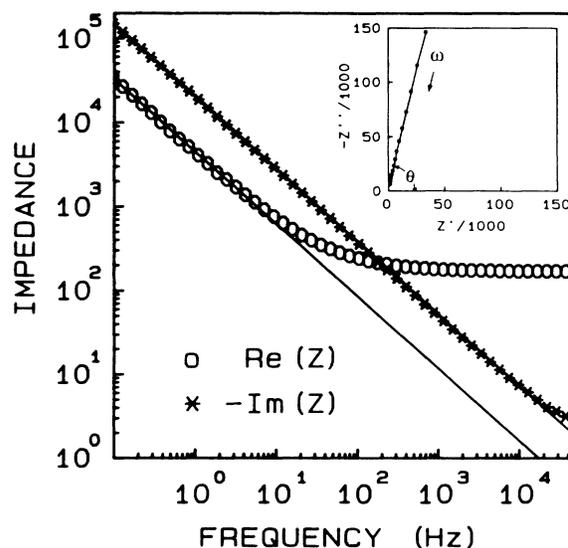


FIG. 1. Impedance spectra of a 0.1M H_2SO_4 solution at 25°C in contact with platinum electrodes polished on 600-grit emery paper. The solid lines are graphs of $Z_i' = A\omega^{-n} \times \cos(n\pi/2)$ and $Z_i'' = -A\omega^{-n} \sin(n\pi/2)$ with $n = 0.87$. Inset: Graph of $-\text{Im}(Z)$ vs $\text{Re}(Z)$; $\theta = n/2$ is the impedance phase angle.

that the CPA form of the impedance and the relationship $n=3-\bar{d}$ held when both random branching and random scaling of the resistors were introduced into the equivalent circuit model. Recently Kaplan, Gray, and Liu showed¹¹ from calculations on equivalent circuits of more general self-affine models of grooved interfaces that this relationship applies only to specific cases, whereas, for the most general case considered, $n < 3-\bar{d}$. Sapoval¹² calculated the response of electrodes with cross sections resembling a Sierpinski carpet. He reported that Liu's relation holds provided the electrode has a finite depth and that, for the surface, $\bar{d} < \frac{5}{2}$. These fractal models of the electrical response of a rough electrode-electrolyte interface are potentially very important since they imply that the dominant effect governing the electrical properties at interfaces is geometric scaling of the interface microstructure. In this Letter, we report the results of experiments aimed at establishing whether or not there is a correlation between the CPA impedance exponent and the fractal dimension of rough electrode surfaces.

The electrodes used in our studies included platinum and low-resistivity silicon with and without a thin gold coating. Square pieces, $\approx 0.25-1.0 \text{ cm}^2$, of platinum and silicon were polished with various grades of emery paper and alumina powder. The choice of grit size was based on our earlier experience¹³ with solid electrolytes and the correlation found between the value of n and the texture produced by polishing. When viewed at low magnification, the resulting surface finish had a definite lay. One-dimensional surface height profiles were measured with a profilometer equipped with an $0.5\text{-}\mu\text{m}$ diameter stylus. This instrument has a height resolution of $0.005 \mu\text{m}$ and a minimum horizontal step size of $0.04 \mu\text{m}$. For each electrode, several profiles of 80, 400, and 2000 μm length were measured in directions perpendicular to the lay at different positions near the center section to be used in the electrical measurements. For one of the

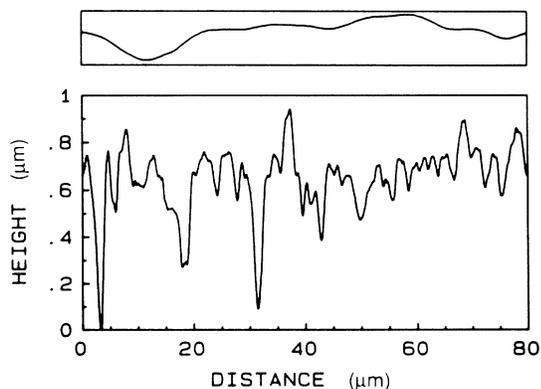


FIG. 2. Profile of a platinum electrode polished on 800-grit emery paper; top section shows the expanded segment between 30 and 40 μm plotted with equal horizontal and vertical scales.

platinum electrodes, profiles were measured at 45° and parallel to the lay. With a tracking force of 1 mg, no detectable damage tracks from the stylus were found in the platinum on microscopic examination before and after profiling. Also, within the limit of resolution, repeated measurements along the same track gave identical profiles. (Sputtered Au films on several silicon plates were prepared after profiling.) Several surface profiles were obtained by digitizing of scanning-electron micrographs of the edge of cross sections of electrodes that had been cut and the polished to remove damage from the cut.

An example of a profile obtained from a platinum electrode is shown in Fig. 2. The apparent large fluctuation in surface height is a somewhat misleading gauge of surface texture resulting from the different scales used for the vertical and horizontal axes (compare with the short segment plotted with the same scale for both axes). To test for their possible fractal properties, we assumed that the profiles behaved as fractional Brown curves¹⁴⁻¹⁶ and determined their structure function.^{15,17} The structure function for a one-dimensional record is given by

$$S(\delta) = \langle \Delta h^2(\delta) \rangle = K\delta^{2H}, \quad (2)$$

where $\Delta h(\delta) = h(x+\delta) - h(x)$ is the difference in the height h of the profile at x and $x+\delta$, K is a constant, H is a characteristic exponent, and the brackets mean that the average is taken over all increments of length δ . The fractal dimensions \bar{d}_p for a self-affine profile is then given^{16,17} by $\bar{d}_p = 2 - H$, so that for the electrode surface, $\bar{d} = \bar{d}_p + 1$. Examples of graphs of $\log S(\delta)$ vs $\log \delta$ determined from two profiles are shown in Fig. 3. Typically, Eq. (2) was satisfied over $\approx 1\frac{1}{2}$ decades in shift distance, from $\delta = 0.04 \mu\text{m}$ (limited by the horizontal resolution of the instrument) to a maximum δ of a few mi-

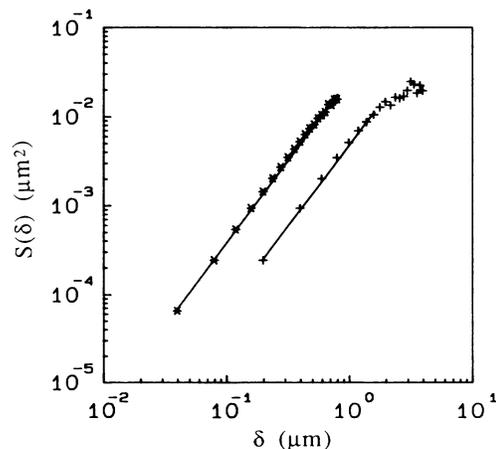


FIG. 3. Graphs of $\log S(\delta)$ vs $\log \delta$ for an 80- μm (asterisks) and 400- μm (plusses) profiles of a platinum electrode ground on 800-grit emery paper. The solid lines are graphs of $S = K\delta^{2H}$, where K and H are the best-fit parameters.

cons. The displacement of the two graphs in Fig. 3 along the $\log S$ axis is caused by the fact that the 80- and 400- μm profiles were measured from two different starting positions on the surface and, therefore, have different zero-level reference points. We verified that the value of H is independent of the choice of the level points and also of whether leveled or unleveled profiles are analyzed. (The parameter K does depend on the level points, but its value is not important to our final result.) Values of the exponent H and the fractal dimension \bar{d}_p are listed in Table I; the uncertainties listed for H are twice the standard deviations based on averages of two or more traces of length 80, 400, and 2000 μm measured at four different places on the electrode surface.

A second related test¹⁷ of the profiles was made by determining the distribution of Δh , $N(\Delta h(\delta))$, for several of the 80- μm traces at shift distances δ from 0.04 to 0.24 μm . The (unnormalized) distributions were fitted by a Gaussian function with three parameters: a preexponential, width $(\overline{\Delta h^2})^{1/2}$, and mean $\overline{\Delta h}$. For each of the profiles, the mean was $\overline{\Delta h} = 0.0 \pm 0.01$ (± 0.1 in the worst case), and the graph of $\log(\overline{\Delta h^2})$ vs $\log \delta$ was linear with a slope $2H$ equal to that obtained from the structure function within ± 0.01 . These are the properties expected of a fractional Brown curve,^{15,16} i.e., a Gaussian distribution with a zero mean $\overline{\Delta h}$ and a width proportional to H .

After the profiling of sets of platinum or silicon plates, electrodes were prepared by our fixing each plate to a glass substrate, attaching a wire lead to an edge of the plates with silver paint, and then sealing the plates and the wire leads to the substrate with waterproof epoxy. The electrodes were completed by the sealing of a short, 6-mm-diam glass cylinder to the plates so that a 0.3-cm^2

region was exposed to the electrolyte. The glass tubes served to define the exposed area of the electrodes and to eliminate fringing fields at the edges of the plates that often had a significant effect on the measured frequency exponent. The electrodes were immersed in aqueous H_2SO_4 , usually $0.1M$, and separated by ≈ 4 cm. The open-circuit potential of each electrode relative to a standard hydrogen electrode was measured while dissolved oxygen was removed from the acid solution by nitrogen stirring. After the electrode potentials reached a steady value (≈ 0.5 V for platinum and ≈ 0.3 V for gold on silicon), impedance measurements were made at frequencies from 0.1 Hz to 50 kHz with an ac peak-to-peak voltage of 50 mV or less applied to the cell. For several of the cells with platinum electrodes, these measurements were extended to 1 mHz. No change in the steady-state open-circuit potential of the electrodes was observed after the impedance measurements.

An example of the impedance spectra is shown in Fig. 1. The solid lines through the data points are graphs of $\text{Re}(Z_i)$ and $-\text{Im}(Z_i)$. As can be seen, the CPA impedance follows the data closely over about five decades in frequency. In the measurements made at lower frequencies with the platinum electrodes, the ideal CPA behavior was typically observed to ≈ 5 mHz. Below this frequency, the impedance of several of these electrodes indicated the presence of Faradaic process, probably the reduction of residual dissolved oxygen. This deviation from ideal blocking behavior at very low frequencies, which is always a potential problem with platinum electrodes, has no measurable effect on the impedance above 0.1 Hz provided the concentration of impurities in solution, especially oxygen, remains small. At $f \approx 200$ Hz, the resistance of the electrolyte dominates the impedance so that $\log Z'$ vs $\log f$ flattens at high frequencies, while the imaginary part of the impedance becomes so small that large relative errors occur in the recorded values. For a given set of electrodes, the low-frequency impedance remained unchanged as the concentration of the electrolyte was changed by a factor of 10^3 from $1M$ to $0.001M$. At high frequencies, of course, the frequency (f_c) at which the resistance dominates the impedance varies as R changes with concentration. Values of the exponent n reported in Table I were determined by least-squares fit of the CPA impedance [Eq. (1)] to $\text{Re}(Z)$ and $\text{Im}(Z)$ at frequencies well below f_c .

The results in Table I show that there is no obvious correlation between the CPA impedance exponent and the fractal dimension of the rough electrodes. The conclusion reached by Kaplan, Gray, and Liu¹¹ that n is not just a function of the fractal dimension of the electrode is consistent with our findings. Moreover, the general condition specified in their work, $n < 3 - \bar{d}$, is satisfied by our data. However, on the basis of our experimental results, we conclude that there is no correlation between the CPA exponent and the fractal dimension of a ran-

TABLE I. Values of the exponent H and average roughness R_a from the profiles of roughened electrodes and the CPA impedance exponent n determined from impedance measurements using these electrodes in $0.1M$ H_2SO_4 . Results are listed in order of decreasing H .

Electrode ^a	H	$\bar{d}_p = 2 - H$	n	R_a ^b (nm)
Au/Si/180	0.98 ^c	1.02	0.91 ^d	1345
Au/Si/600	0.96	1.04	0.96	210
Si/600	0.96	1.04	0.97	210
Pt/600	0.95	1.05	0.87	193
Pt/800	0.92	1.08	0.78	90
Au/Si/800	0.91	1.09	0.94	50
Pt/0.05	0.89	1.11	0.89	45

^aAu/Si/600: Gold-coated silicon ground on 600-grit paper, etc. (Note: The larger the grit size the smaller the particles on the emery paper.)

^b R_a , the average roughness, is the average deviation of a surface profile about its mean line. See Ref. 18.

^cUncertainty ± 0.01 from repeated measurements.

^dUncertainty ± 0.005 from least-squares fit.

domly rough electrode. The extended pore model⁴ and the results of computer simulations¹⁹ suggest that the shape of the protrusions on the surface of the electrode is one of the more important factors determining the value of n . A comparison of the scanning-electron micrographs and the high-resolution (80 μm) profiles with the impedance data indicates that rounded or flattened protrusions such as those produced on the silicon substrates give large exponents ($n > 0.9$), while sharp protrusions such as those formed by grinding of the soft platinum plates give small exponents ($n \approx 0.8$ to 0.9). This dependence of n on the shape of the protrusions can also help explain the lack of correlation between the frequency exponent and the average roughness¹⁸ R_a of the electrodes given in Table I and also the fact that n does not approach unity as R_a gets smaller. Although polishing the platinum electrodes with 800-grit emery paper or with 0.05- μm powder produces a surface with a small average roughness, the polishing material still leaves sharp sub-micron-sized protrusions on the surface of the electrodes that result in small frequency exponents. Only in the ideal case of $R_a = 0$ can we expect that $n = 1$.

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¹P. H. Bottleberghs and G. H. J. Broers, *J. Electroanal. Chem.* **67**, 155 (1976). See inset in Fig. 1.

²I. Wolff, *Phys. Rev.* **27**, 755 (1926).

³R. de Levie, *Electrochim. Acta* **10**, 113 (1965).

⁴J. C. Wang and J. B. Bates, *Solid State Ionics* **18 & 19**, 224 (1986).

⁵A. Le Mehaute and G. Crepy, *Solid State Ionics* **9 & 10**, 17 (1983).

⁶L. Nyikos and T. Pajkossy, *Electrochim. Acta* **30**, 1533 (1985); T. Pajkossy and L. Nyikos, *Proc. Electrochim. Soc.* **133**, 2061 (1986).

⁷M. Keddam and H. Takenouti, *C.R. Acad. Sci. Ser. 2* **302**, 281 (1986).

⁸J. C. Wang, "Impedance of a Fractal Electrolyte/Electrode Interface," *Electrochim. Acta* (to be published).

⁹S. H. Liu, *Phys. Rev. Lett.* **55**, 529 (1985).

¹⁰T. Kaplan and L. J. Gray, *Phys. Rev. B* **32**, 7360 (1985).

¹¹T. Kaplan, L. J. Gray, and S. H. Liu, *Phys. Rev. B* **35**, 5379 (1987).

¹²B. Sapoval, *Solid State Ionics* **23**, 253 (1987).

¹³J. B. Bates, J. C. Wang, and Y. T. Chu, *Solid State Ionics* **18 & 19**, 1045 (1986).

¹⁴B. B. Mandelbrot, *Phys. Scr.* **32**, 257 (1985).

¹⁵M. V. Berry, *J. Phys. A* **12**, 781 (1979).

¹⁶R. H. Voss, in *Fundamental Algorithms in Computer Graphics*, edited by R. A. Earnshaw, NATO Advanced Study Institute, Series F, Vol. 17 (Springer-Verlag, Berlin, 1985), p. 805.

¹⁷R. S. Sayles and T. R. Thomas, *Wear* **42**, 263 (1977).

¹⁸Y. Tamimura, E. C. Teague, F. E. Scire, R. D. Young, and T. V. Vorburger, *J. Lubr. Technol.* **104**, 533 (1982).

¹⁹Y. T. Chu and J. B. Bates, to be published.