Electrode Surface, Fractal and Heterogeneous Electron Transfer Rate Constants

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Summary: Impedance and cyclic voltammetric studies, were carried out on electrodes of various material, dimension and configuration. The substrate was ferrocene. This was done with the view to explore the relationship between heterogeneous electron transfer rate constants \( k_o \) of ferrocene and various fractal parameters. It was found that the best relationship was obtained between the magnification factor \( f_m \) and \( k_o \), implying that electrodes behave as cantor sets, and “grooves” in an electrode affect the electron transfer process.

Introduction

In cyclic voltammetric studies on solid electrodes, a highly polished electrode is used to obtain a good reproducible cyclic voltammogram. This means a very smooth surface of electrode is desired for obtaining good, reproducible voltammograms. If the surface of the electrode is not smooth or if it is filmed, a smooth cyclic voltammogram may not be obtained. Instead a dragged, an irreversible and even non-reproducible irregular shaped voltammogram may experimentally be recorded. The standard heterogeneous electron transfer rate constant \( k_o \), obtained from such voltammograms may thus be affected by the nature of the surface of the electrode [1-4].

The nature of the surface of the electrode as well as electrochemical reactions taking place at the surface may be analyzed by fractal theory [2, 3]. Thus exploration of effect of electrode surface as analyzed by fractal theory, on \( k_o \) as obtained by voltammetry, becomes an attractive target for studies.

According to fractal theory [2, 3] an electrode can be considered as a cantor set [2] with grooves and each groove having two branches. Each branch is self-similar to the whole groove with a magnification factor \( f_m \) given by [2]

\[
D = 2 + \log \frac{2}{\log f_m}
\]  

(1)

where \( D \) is the “Dimension of the electrode surface” [2], a fractal parameter obtained through impedance measurement [2]. The impedance \( Z \), of the electrode surface is related to the frequency \( w \) as (eq. (2)) [1, 2]

\[
Z = Aw^{-\beta}
\]  

(2)

where \( A \) is a frequency independent parameter and, [2]

\[
\beta = 3 - D; \quad (2 < D < 3)
\]  

(3)

Thus a log \( Z \) vs log \( w \) plot gives \( \beta \), hence \( D \) and \( f_m \). Mulder [3], on the other hand, has dealt in great detail the importance of:

(i) fractals-rough-electrochemical surface,

(ii) plane electrode with circular electro-active area, and

(iii) smooth electrodes with fractal carpet structure.

He and other workers [1-3] proposed relationship between impedance \( Z \) and the frequency \( f \), as

\[
Z = Af^{-\alpha}
\]  

(4)

where \( \alpha = (D_{HD} - 1)^{-1} \)  

(5)

\( A \) = frequency independent parameter

\( D_{HD} \) is called Hausdorff parameter. We note the similarity between eq.(2) and eq.(4) however, we also note \( D \) of eqs. (1-3) may not necessarily be the same as \( D_{HD} \) of eqs. (4-5). But both \( D \) and \( D_{HD} \) are in the range 2 – 3.

Another useful parameter to gauge the state of the surface of the electrode could be the capacitance, calculated from the relationship [4]

\[
C = 1/(Z''w) = 1/ [Z(im) w]
\]  

(6)

where \( Z'' = Z(im) \) is the imaginary part of impedance \( Z \).

The measurement of standard heterogeneous electron transfer rate constant \( k_o \), is of fundamental importance in electrochemistry. For the measurement of \( k_o \), voltammetry and impedance based methods [4] have been employed. Voltammetry, in particular, has been extensively used. Based upon the theory of stationery electrode
polarography [4], Nicholson [5], Gileadi [6], and Kochi [7], proposed methods for the determination of \( k_\alpha \). These methods have been used by many workers, for example [4, 8]. The peak separation method of Nicholson [5], for voltammetry at stationary microelectrode has been most popular [4, 8]. This method is most suitable for quasi-reversible case.

With the advent of “ultra-micro” electrodes of micrometer dimension and high-speed voltammetry, several workers [4, 8-15], made use of high-speed voltammetry at these micrometer dimension electrodes to evaluate \( k_\alpha \).

In the present study electrochemical impedance studies were carried out on electrodes of various dimension, material and configuration to determine Hausdorff parameter \( D_{HD} \), the “dimension of the electrode surface” parameter \( D \) and magnification of groove parameter \( f_m \). At the same time using cyclic voltammetry, \( k_\alpha \) for ferrocene was evaluated on these electrodes. An attempt is made to determine if there exists any correlation between these fractal parameters (\( D_{HD}, D \) or \( f_m \)) and \( k_\alpha \).

A related nevertheless interesting subject of interest is what would be the fractal parameters of an assembly of electrodes, how the fractal parameter(s) can be interpreted and correlated with \( k_\alpha \). This subject matter has also been made a part of this study. Attempt is also made to correlate capacitance (eq.(6)) with the radius of the electrodes as well as other fractal parameters.

**Results and Discussion**

\[ Z(\text{re}) - Z(\text{im}) \ (Z^{-2}; \text{Nyquist}) \text{ plot} - \text{a routine investigation of the electrochemical impedance relationship - gave linear plots,(Figs. 1-3). From our previous studies on superconducting ceramics [16] we had concluded that these } Z(\text{re}) - Z(\text{im}) \text{ plot straight lines were not the low frequency Warburg impedance lines. In the present case, there is practically no electroactive species (including impurities) undergoing faradaic process, hence mass transfer (of an electro active species), the manifestation of which is low frequency impedance (Warberg impedance) line, could not be the controlling factor.} \]

The electrode surface roughness may affect \( k_\alpha \) [1] whereas the electrode roughness can be studied through the fractal method and / or the capacitance measurements. Capacitance can be obtained as the reciprocal of the product of \( Z(\text{im}) \) and frequency \( w \) (eq.6). These values for platinum electrodes, \( r = 600, 100, 75 \mu m \) are collected in Tables-1 to 3.

### Table-1: Impedance data for platinum electrode \( r = 600 \mu m \); 0.1 TBAP in MeCN.

<table>
<thead>
<tr>
<th>( f ) (Hz)</th>
<th>( w = 2 \pi f ) (rad/s)</th>
<th>( Z(\text{im}) ) (kohm)</th>
<th>( Z(\text{re}) ) (kohm)</th>
<th>( (wZ(\text{im}))^{-1} \times 10^{10} - C_s \mu F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>502</td>
<td>18.2</td>
<td>11.5</td>
<td>0.109</td>
</tr>
<tr>
<td>100</td>
<td>628</td>
<td>10.4</td>
<td>6.70</td>
<td>0.150</td>
</tr>
<tr>
<td>300</td>
<td>1,884</td>
<td>6.00</td>
<td>4.20</td>
<td>0.088</td>
</tr>
<tr>
<td>400</td>
<td>2,512</td>
<td>4.90</td>
<td>3.50</td>
<td>0.081</td>
</tr>
<tr>
<td>500</td>
<td>3,140</td>
<td>3.60</td>
<td>2.80</td>
<td>0.088</td>
</tr>
<tr>
<td>700</td>
<td>4,396</td>
<td>3.00</td>
<td>2.30</td>
<td>0.076</td>
</tr>
<tr>
<td>1,000</td>
<td>6,280</td>
<td>1.50</td>
<td>1.10</td>
<td>0.106</td>
</tr>
<tr>
<td>5,000</td>
<td>31,400</td>
<td>0.44</td>
<td>0.60</td>
<td>0.072</td>
</tr>
<tr>
<td>10,000</td>
<td>62,800</td>
<td>0.25</td>
<td>0.60</td>
<td>0.064</td>
</tr>
<tr>
<td>16,000</td>
<td>100,480</td>
<td>0.11</td>
<td>0.06</td>
<td>0.090</td>
</tr>
</tbody>
</table>

**Ave 0.083**
Table-2: Impedance data for platinum electrode r = 100 µm; 0.1M TBAP in MeCN.

<table>
<thead>
<tr>
<th>f (Hz)</th>
<th>w = 2πf (rad/s)</th>
<th>Z (im) (kohm)</th>
<th>Z (re) (kohm)</th>
<th>(wZ (im))² × 10⁶</th>
<th>Cs (µF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>628</td>
<td>62.3</td>
<td>50.0</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1256</td>
<td>36.9</td>
<td>34.0</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1884</td>
<td>28.6</td>
<td>32.0</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2512</td>
<td>22.9</td>
<td>22.0</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3140</td>
<td>17.8</td>
<td>19.0</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>4396</td>
<td>14.6</td>
<td>16.5</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>6280</td>
<td>10.8</td>
<td>11.5</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td>31400</td>
<td>3.0</td>
<td>4.0</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>62,800</td>
<td>1.10</td>
<td>2.0</td>
<td>0.015</td>
<td></td>
</tr>
</tbody>
</table>

Ave 0.017

Table-3: Impedance data for platinum electrode r = 75 µm; 0.1M TBAP in MeCN.

<table>
<thead>
<tr>
<th>f (Hz)</th>
<th>W = 2πf (rad/s)</th>
<th>Z (im) (kohm)</th>
<th>Z (re) (kohm)</th>
<th>(wZ (im))² × 10⁶</th>
<th>Cs (µF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>628</td>
<td>80</td>
<td>140</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1,884</td>
<td>65</td>
<td>100</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2,512</td>
<td>55</td>
<td>90</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3,140</td>
<td>40</td>
<td>67</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>4,396</td>
<td>25</td>
<td>40</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>6,280</td>
<td>15</td>
<td>25</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td>18,840</td>
<td>8.0</td>
<td>13</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td>31,400</td>
<td>4.0</td>
<td>6.7</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>62,800</td>
<td>0.9</td>
<td>5.2</td>
<td>0.008</td>
<td></td>
</tr>
</tbody>
</table>

Ave 0.009

Ave 0.017

D (from eq. (3)), D_HD (from eq.(5)) and C (from eq. (6)) for various dimensions and configuration of electrodes are collected in Table-4. From Table-4 it is clear that except for GP (600 µm), micro-array- and membrane electrodes, both D and D_HD are within the range 2-3. Capacitances of various electrodes, except, again, array and membrane electrodes, are within one order of magnitude. However, surprisingly, capacitance C of ultramicro-array electrode is many fold larger than that of other electrodes. Such anomalies need explanation (see Discussion section).

Table-4: Fractal parameters and capacitance for various electrodes.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Electrode</th>
<th>r(µm)</th>
<th>D'</th>
<th>D_HD</th>
<th>Cs × 10^6 F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt</td>
<td>600</td>
<td>2.25</td>
<td>2.33</td>
<td>0.083</td>
</tr>
<tr>
<td>2</td>
<td>Pt</td>
<td>100</td>
<td>2.33</td>
<td>2.49</td>
<td>0.017</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>75</td>
<td>2.28</td>
<td>2.39</td>
<td>0.009</td>
</tr>
<tr>
<td>4</td>
<td>Au</td>
<td>600</td>
<td>2.50</td>
<td>2.67</td>
<td>0.460</td>
</tr>
<tr>
<td>5</td>
<td>Au</td>
<td>10</td>
<td>2.29</td>
<td>2.41</td>
<td>0.470</td>
</tr>
<tr>
<td>6</td>
<td>G.P</td>
<td>600</td>
<td>2.88</td>
<td>7.10</td>
<td>0.026</td>
</tr>
<tr>
<td>7</td>
<td>G.P</td>
<td>50</td>
<td>2.18</td>
<td>2.22</td>
<td>0.018</td>
</tr>
<tr>
<td>8</td>
<td>UMA'</td>
<td>10x10 µm</td>
<td>2.95</td>
<td>22-24</td>
<td>4.51</td>
</tr>
<tr>
<td>9</td>
<td>G.P. Membrane</td>
<td>-</td>
<td>2.60</td>
<td>3.64</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>G. Pellet Membrane</td>
<td>-</td>
<td>2.58</td>
<td>3.41</td>
<td>250</td>
</tr>
</tbody>
</table>

(a) From eqs (2,3) (b) from eqs (4,5), (c) G.P = Graphite Paste (d) UMA = ultramicro electrode.

k_o of ferrocene was obtained on micro- (Au, Pt and graphite paste (G.P) electrodes (all of radius 600 µm), sub-/ ultramicro electrodes (Pt, r = 100 µm, 75 µm; G.P, r = 50 µm, Au = 10 µm) and ultramicro-array electrodes. These k_o’s were obtained from C.V’s obtained for the above mentioned electrodes by the methods earlier described. Figs. 4-6 are representatives of C.V’s on platinum electrodes r = 600 and 75 µm and the data collected in Table-5. These k_o values along with the magnification factor f_m are collected in Table-6. These k_o values are lower than those reported by Wrightman [11]. The difference in k_o-values could be due to different fractal conditions of electrodes. Information regarding the surface condition through impedance studies is lacking in Wrightman’s work [11].

Fig. 4: Cyclic voltammogram of 0.001M ferrocene in 0.1M TBAP – MeCN platinum electrode, radius 600 µm, scan rate 500mV/s.

Fig. 5: Cyclic voltammogram of 0.001M ferrocene in 0.1M tBAP – MeCN platinum electrode, radius 600 µm, scan rate 20mV/s.
Then we can ask the question what conclusion(s) can be drawn.

\[ k_{\text{m}}, \text{fractal parameters, capacitance and the surface of the electrode} \]

The various parameters, in Tables-4 and 6 were plotted against \( k_{\text{m}} \). Except for \( f_{\text{m}} \) none gave a reasonable linear relationship; \( f_{\text{m}} \) vs \( k_{\text{m}} \) (Excel) plot gave a reasonable linear plot with \( r^2 = 0.92 \) (Fig. 7). Even D from which \( f_{\text{m}} \) was calculated did not give a good linear relationship with \( k_{\text{m}} \) (\( r^2 < 0.5 \)). Fractal parameters \( D_{\text{HD}} \) and D which are manifestation of the nature of the surface, do not relate to \( k_{\text{m}} \) (electrode kinetics) linearly hence it may mean that the surface structure (\( D_{\text{HD}} \) or D) does not affect the heterogeneous electron transfer process as much. The magnification parameter \( f_{\text{m}} \) does give a better linear relationship, as mentioned above. Magnification factor presents an electrode as cantor set with "grooves" \[2\]. This implies that the "grooves" in an electrode, their branches and magnification \( f_{\text{m}} \), are more relevant to the electrode kinetics compared to the roughness or the “dimensionality” of the surface of the electrode. None of the electrodes showed pure 2-dimensional character (i.e. D or \( D_{\text{HD}} = 2 \)) nor pure 3-dimensional character (i.e. D or \( D_{\text{HD}} = 3 \)), rather in-between values, which means that though the surface is rough (D, \( D_{\text{HD}} > 2 \)), but having no linear relationship with \( k_{\text{m}} \), the nature of surface (roughness) does not show profound effect on electrode kinetics.

\[ k \text{ vs magnification factor} \]

![Fig. 7: Standard heterogeneous electron transfer rate constant \( k_{\text{m}} \) vs \( f_{\text{m}} \) (magnification factor). The correlation factor \( r^2 = 0.92 \).](image)

While it is shown that C and \( D_{\text{HD}} \) have no linear relationship with \( k_{\text{m}} \), even then some comments on these two factors are worthwhile. Except for platinum electrodes (\( r = 600 \mu m, 100 \mu m, 75 \mu m \)), which show a qualitative linear relationship between the geometrical area of the electrodes and capacitance C (Table-4), the same cannot be claimed for other electrodes (Table-4). Nevertheless, there are some
interesting observations. The UMA electrode’s capacitance is such as if ten 10–μm Au-electrodes each of which acting as a capacitor, are connected in parallel. Also the capacitance value at 10 μm electrode, instead of being small, is extraordinarily large: almost the same as for a 600 μm radius Au-electrode. One may be tempted to conclude that the material of electrodes does not affect the capacitance values as much as configuration and/or polishing the surface.

Carbon paste electrodes exhibit another interesting behavior: These electrodes are supposed to be quite porous - no smooth, bright, shining surface. The $D_{HD}$ of 600 μm G.P electrode is abnormally high and defy physical interpretation. Where as 50μm radius electrode, $D_{HD}$-wise, is normal (2 < $D_{HD}$ <3); capacitance values at the two electrodes are not much different. The magnification factor for 50 μm G.P electrode is very high implying too many branches. These branches have been smoothed out at 600 μm G.P. electrode.

$D_{HD}$-values for G. P electrodes have been mentioned above. The $D_{HD}$ for UMA electrode assembly is such that the array behaves as if ten 10 μm electrodes have been connected in series - $D_{HD}$ adding up. Qualitatively speaking the $D_{HD}$ of 600 μm Au electrode may be a manifestation of a combination of series and parallel cantor sets in such a way that the resultant is high $D_{HD}$.

**Experimental**

**Chemical and Materials**

Purification of acetonitrile (MeCN), tetra-$n$-butyl ammonium perchlorate (TBAP), ferrocene etc, and fabrication of electrodes have been described before [17-20] Electrochemical impedance (ECI) measurement technique employed has also been described earlier [17-20].

**Measurement**

For ECI measurements and hence evaluation of fractal parameters it was necessary to ascertain that there was no electro-active species (impurity) in 0.1 M TBAP(MeCN ) solution. Cyclic voltammetry was carried out: both the peak current and area under the curve analysis [21] established that any electro-active impurity, if present in these solutions, was less than $10^{-5}$ M. $Z'$ (the real part, $Z$(re)), $Z''$ (the imaginary part ($Z$(im))) and $Z$ (the total impedance) were obtained as usual [17-20].

For heterogeneous rate constant $k_o$. Nicholson peak separation ($\Delta E_p$) [5] was used for electrodes of dimension $r = 600 \mu m$. The solution resistance was accounted for. The corrected $\Delta E_p$ was then used to evaluate $\psi$ and hence $k_o$ [4-5]

$$\psi = k_o / (a D_o)^{1/2}$$

where $D_o$, the diffusion coefficient of ferrocene, was taken [8] as $2.53 \times 10^{-5}$ cm$^2$/s; $a = nFv/(RT)$, v being the scan rate and $T = 298K$. For the evaluation of $k_o$ on ultramicro electrode two methods were employed (i) the method of Oldham-Zoski-Bond (0-Z-B) [9]

$$1 - \exp \left[ nF (E_{1/2} - E_h)/(RT) \right] = 2D_o/(k_o a)$$

where $E_h$ is the reversible half wave potential given by

$$E_h = E^o + (RT/nF) \log (D/D^o)$$

And $E_{1/2}$ is the experimental half wave potential of a nearly reversible steady state voltammogram. Using $E_h = 0.400$ V (vs. SCE) [9], $RT/F = 25.69$ mV, $T = 298K$, $k_o$ was calculated from experimental $E_{1/2}$ at ultramicro electrodes.

(ii) Safford-Weaver (S-W) diagram in conjunction with S-W eq. (10)

$$\Delta E_k = \Delta E_p - \Delta E_{rev}$$

$\Delta E_k$ is additional peak separation due to finite electrode kinetics. $\Delta E_p$ is observed peak separation and $\Delta E_{rev}$ is the reversible value obtained when $k'$ approaches infinity and

$$\Delta E_{rev} = \Delta E_p' - \Delta E_k - \Delta E_{rev}$$

where $\Delta E_p'$ is the total cthododic-anodic peak separation obtained in the presence of both finite kinetics and solution resistance effects. $\Delta E_{rev}$ is the peak separation component “attributable” to solution resistance effect [10]. $\Delta E_{rev}$ is taken as 59 mV at 298 K. Diagram given by S-W may then be used for the calculation of $k_o$.

**Conclusion**

From the numerical values of $r$, $k_o$, $D_{HD}$, $D$, and $f_m$ and attempt to correlate these parameters, it looks like that the grooves and their branches as manifested in $f_m$ are more relevant to the electrode kinetics. Also it looks that the capacitances measured
at the various electrodes are the result of distribution of the individual capacitors, connected in series, parallel or random at microstate in a micro-electrode.

Reference