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]

$$D = 2 + [\log 2/(\log f_m)], \tag{1}$$

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]

$$Z = Aw^{-\beta} \tag{2}$$

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

$$\beta = 3 - D; \quad (2 < D < 3) \tag{3}$$

Thus a log Z *vs* log w plot gives β, 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

$$Z = Af^{-\alpha} \tag{4}$$

$$\text{where} \quad \alpha = (D_{HD} - 1)^{-1} \tag{5}$$

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]

$$C = 1/(Z''w) \qquad = 1/ [Z(\text{im})\, w] \tag{6}$$

where $Z'' = Z(\text{im})$ 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_o. 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_o.

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 voltammetery, k_o 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_o.

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_o. 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(re) – Z(im) (Z$^{'}$-Z$^{''}$; Nyquist) plot - 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(re) – Z(im) plot straight lines were not the low frequency Warblerg 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_o [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(im) and frequency w

(eq.6). These values for platinum electrodes, r = 600, 100, 75 μm are collected in Tables-1 to 3.
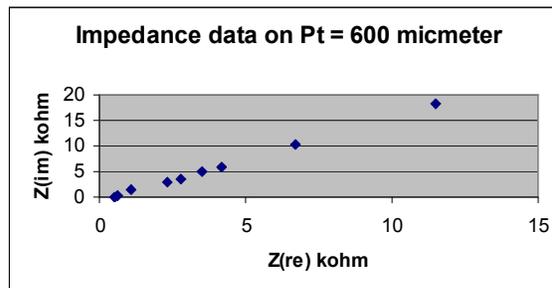
Fig. 1: Z(re) – Z(im) plot for platinum electrode 0f radius = 600 μm (0.1M TBAP, MeCN solvent).
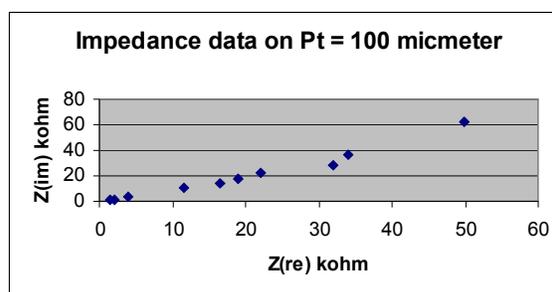
Fig. 2: Z(re) – Z(im) plot for platinum electrode 0f radius = 100 μm (0.1M TBAP, MeCN solvent).
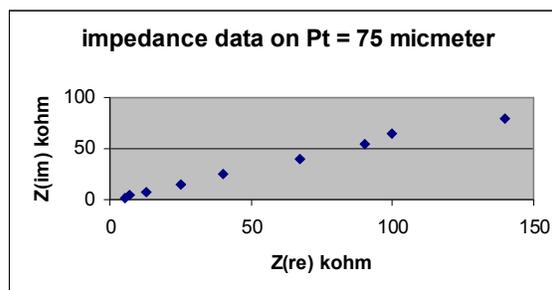
Fig. 3: Z(re) – Z(im) plot for platinum electrode 0f radius = 75 μm (0.1M TBAP, MeCN solvent).

Table-1: Impedance data for platinum electrode r = 600 μm; 0.1 TBAP in MeCN.

f (Hz)	w = 2πf (rad/s)	Z (im) (kohm)	Z (re) (kohm)	(wZ (im))$^{-1}$ ×10^6 = Cs (μ F)
80	502	18.2	11.5	0.109
100	628	10.4	6.70	0.150
300	1, 884	6.00	4.20	0.088
400	2, 512	4.90	3.50	0.081
500	3, 140	3.60	2.80	0.088
700	4, 396	3.00	2.30	0.076
1, 000	6, 280	1.50	1.10	0.106
5, 000	31, 400	0.44	0.60	0.072
10, 000	62, 800	0.25	0.60	0.064
16, 000	100, 480	0.11	0.06	0.090
				Ave 0.083

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

f (Hz)	w = 2πf (rad/s)	Z (im) (kohm)	Z (re) (kohm)	(wZ (im))$^{-1}$ ×10^6 = Cs (μF)
100	628	62.3	50.0	0.026
200	1256	36.9	34.0	0.022
300	1884	28.6	32.0	0.019
400	2512	22.9	22.0	0.014
500	3140	17.8	19.0	0.018
700	4396	14.6	16.5	0.016
1, 000	6280	10.8	11.5	0.015
5, 000	31400	3.0	4.0	0.011
10, 000	62800	1.10	2.0	0.015
16, 000	100, 480	0.60	1.5	0.016
				Ave 0.017

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

F (Hz)	W = 2πf (rad)/s	Z (im) (kohm)	Z (re) (kohm)	(wZ (im))$^{-1}$ ×10^6 = Cs (μf)
100	628	80	140	0.011
300	1, 884	65	100	0.008
400	2, 512	55	90	0.007
500	3, 140	40	67	0.008
700	4, 396	25	40	0.009
1, 000	6, 280	15	25	0.011
3, 000	18, 840	8.0	13	0.007
5, 000	31, 400	4.0	6.7	0.008
10, 000	62, 800	0.9	5.2	0.008
				Ave 0.009

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.

S. No	Electrode	r(μm)	D^a	D$_{HD}$^{b}	C×10^6 F
1.	Pt	600	2.25	2.33	0.083
2.	Pt	100	2.33	2.49	0.017
3.	Pt	75	2.28	2.39	0.009
4.	Au	600	2.50	2.67	0.460
5.	Au	10	2.29	2.41	0.470
6.	G.P^c	600	2.85	7-10	0.026
7.	G.P^c	50	2.18	2.22	0.018
8.	UMA^d	10×10 μm	2.95	22-24	4.51
9.	G.P. Membrane	-	2.60	3.64	20
10.	G. Pellet Membrane	-	2.58	3.41	250

(*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_0'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].
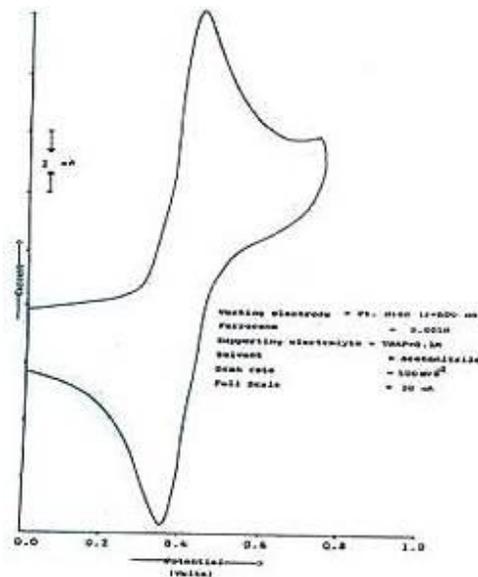
Fig. 4: Cyclic voltammogram of 0.001M ferrocene in 0.1M TBAP – MeCN platinum electrode, radius 600 μm, scan rate 500mV/s.
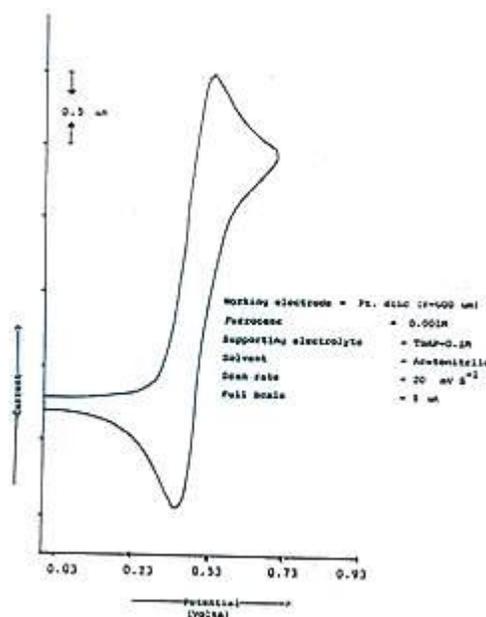
Fig. 5: Cyclic voltammogram of 0.001M ferrocene in 0.1M tBAP – MeCN platinum electrode, radius 600 μm , scan rate 20mV/s.
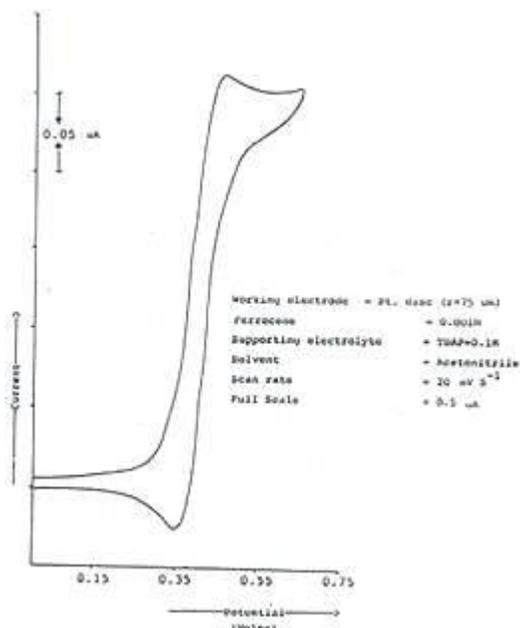
Fig. 6: Cyclic voltammogram of 0.001M ferrocene in 0.1M TBAP – MeCN platinum electrode, radius 75 μm, scan rate 25 mV/s.

Table-5: Electro chemical data of ferrocene (0.001M), Platinum working electrodes, 0.1M TBAP in acetonitrile; ref. electrode SCE.

Scan rate : (V/s)	0.02	0.1	0.5	2	10
Electrodes : (μm)	600; 100; 75	600; 100; 75	600; 100; 75	600; 100; 75	600; 100; 75
$(Ep)_a$ mv	437; 463; 455	435; 437; 437	442; 437; 440	485; 489; 483	509; 498; 570
$(Ep)_c$ mv	355; 353; 350	370; 363; 373	367; 365; 370	363; 386; 393	333; 360; 373
ΔEp mv	82; 110; 105	65; 74; 64	75; 72; 70	112; 103; 90	170; 138; 137
$\dfrac{(Ep)_c + (Ep)_a}{2}$	396; 408; 403	403; 400; 405	405; 401; 405	424; 438; 438	421; 429; 472

Table-6^a: Heterogeneous electron transfer rate constants and magnification factors for ferrocene at various electrodes.

S. No	Electrode	r(μm)	k° (cm/s)	f_m^b
1.	Pt	600	0.1	16.6
2.	Pt	100	0.1	8.16
3.	Pt	70	0.1	11.9
4.	Au	600	0.08	4.0
5.	Au	10	0.10	10.9
6.	G.P	600	0.08	2.26
7.	G.P	50	0.20	46.9
8.	UMA	-	0.07	4.08
9.	G.P. Membrane	-	c	1.52
10.	G. Pellet Membrane	-	c	1.63

(a) See Table IV for foot notes (b); from eq. (1) (c) not measured

There are mainly two subject matters for discussions: (i) how the various fractal parameters and capacitance values are related to ko, if they do correlate (in other words, are these parameter quantitatively or qualitatively reflected in k_o), and (ii) how the dimension / nature of electrode surface is reflected in D or D_{HD} or f_m or C?

Then we can ask the question what conclusion(s) can be drawn.

k_o, fractal parameters, capacitance and the surface of the electrode

The various parameters, in Tables-4 and 6 were plotted against k_o. Except for f_m, none gave a reasonable linear relationship; f_m vs k_o (Excel) plot gave a reasonable linear plot with $r^2 = 0.92$ (Fig. 7). Even D from which f_m was calculated did not give a good linear relationship with k_o ($r^2 < 0.5$). Fractal parameters D_{HD} and D which are manifestation of the nature of the surface, do not relate to k_o, (electrode kinetics) linearly hence it may mean that the surface structure (D_{HD} or D) does not affect the heterogeneous electron transfer process as much. The magnification parameter f_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_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_{HD} = 2) nor pure 3-dimensional character (*i.e.* D or D_{HD} = 3), rather in-between values, which means that though the surface is rough (D, D_{HD} > 2), but having no linear relationship with ko, the nature of surface (roughness) does not show profound effect on electrode kinetics.
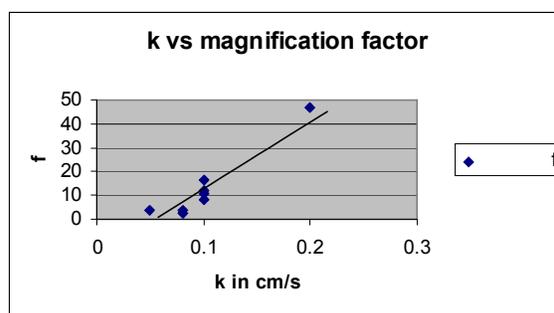
Fig. 7: Standard heterogeneous electron transfer rate constant k_o *vs* f_m (magnification factor). The correlation factor r^2 = 0.92.

While it is shown that C and D_{HD} have no linear relationship with k_o, even then some comments on these two factors are worthwhile. Except for platinum electrodes (r = 600 μm, 100 μm, 75 μm), 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 defies 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 (ΔE_p) [5] was used for electrodes of dimension r = 600 μm. The solution resistance was accounted for. The corrected ΔE_p'$_s$ was then used to evaluate ψ and hence k_o [4-5]

$$\psi = k_o / (a\ D_o)^{1/2} \qquad (7)$$

where D_o, the diffusion coefficient of ferrocene, was taken [8] as 2.53×10^{-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]

$$1 - \exp\ [nF\ (E_{1/2} - E_h)/(RT\ )]\ =\ 2D_o/(k_o a) \quad (8)$$

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

$$E_h = E° + (RT/nF)\ \log\ (D/D_o) \qquad (9)$$

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)

$$\Delta E_k = \Delta E_p - \Delta E_{rev} \qquad (10)$$

ΔE_k is additional peak separation due to finite electrode kinetics. ΔE_p is observed peak separation and ΔE_{rev} is the reversible value obtained when $k°$ approaches infinity and

$$\Delta E_{res} = \Delta E_p' - \Delta E_k - \Delta E_{rev} \qquad (11)$$

where $\Delta E_p'$ is the total cathodic-anodic peak separation obtained in the presence of both finite kinetics and solution resistance effects. ΔE_{res} is the peak separation component "attributable" to solution resistance effect [10] . ΔE_{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

1. F. Marken, S. Kumbhat, G. H. W. Sanders, and R. G Compton, *Journal of Electroanalytical Chemistry*, **414**, 95 (1996).

2. K. S. Birdi, "Fractals in Chemistry, Geo-chemistry, and Biophysics, An Introduction", Plenum Press (1992).

3. W. H. Mulder, Ph. D. Thesis, Rijksuniversiteitte, Ultrecht, the Netherlands (1989).

4. M. Mohammad, *Journal of the Chemical Society of Pakistan*, **31**, 964 (2009).

5. (a) A. J. Bard, and L. R. Faulkner, "Electro-chemical Methods, Fundamentals and Applications". John Wiley (1980) (b) J. Heinz, *Berichte der Bunsen-Gesellschaft für Physikalische Chemie*, 85, 1096(1981)

6. R. S. Nicholson, *Analytical Chemistry*, **37**, 135 (1965).

7. E. Gilladi, and U. Kisner, *Journal of Electroanalytical Chemistry*, **28**, 82 (1970); See also C. Russel, and W. Jaenicke, *Electrochimica Acta*, **27**, 1745 (1982).

8. R. J. Killinger, and J. K. Kochi, *Journal of Physical Chemistry*, **85**, 1731 (1981).

9. (a) M. Mohammad, A. Y. Khan, M. S. Subhani, N. Murtaza, R. Wahab, and S. Malik, *Journal of Electrochemical Society of India*, **47**, 207 (1998), (b). M. Mohammad, R. Qureshi, A. Y. Khan, N. Ashraf, W. Begum, and. M. S. Subhani, *Bulletin of Electrochemistry*, **10**, 218 (1994).

10. K. B. Oldham, C. G. Zoski, and A. Bond, *Journal of Electroanalytical Chemistry*, **248**, 467 (1988)

11. L. K. Safford, and M. J Weaver, *Journal of Electroanalytical Chemistry*, **261**, 241(1989).

12. D. O. Wipf, E. W. Kristensen, M. R. Deakin, and R. Mark Wrightman, *Analytical Chemistry*, **60**, 306 (1988).

13. A. M. Bond, S. W. Feldberg, H. B. Greenhill, and P. J. Mahan, *Analytical Chemistry*, **64**, 1014 (1992).

14. C. P. Andrieux, P. Hapiot, and J. M. Saveant, *Electroanalysis*, **2**, 183 (1990).

15. M. Mohammad, A. Y. Khan., M. S. Subhani, N. Murtaza, R. Wahab, and S. Malik, *Journal of the Electrochemical Society of India*, **47**, 214 (1998).

16. M. Mohammad, A. Y. Khan, M. S. Subhani, N. Murtaza, R. Wahab, S. Malik, and A. Nseer, *Journal of the Electrochemical Society of India*, **49**, 21 (2000).

17. M. Mohammad, A. Y. Khan, U. Akhtar, S. Malik, M. S. Subhani, and R. Wahab, *"Impedance Spectroscopic Studies on High Tc Superconductors",* Second International Symposium on Electrochemical Impedance Spectroscopy, Santa Barbara, California, July 12-17 (1992) and references therein.

18. M. Mohammad, A. Y. Khan, M. S. Subhani, S. Malik, and U. Akhtar, *Bulletin of Electro-chemistry*, **10**, 180 (1994).

19. U. Akhtar, M. Phil. Thesis, *Impedance studies on high T_C Superconductors*, Quaid-i-Azam University, Islamabad, Pakistan (1995).

20. R. Wahab, M. Phil. Thesis, *Capacitance and Electrochemical measurements on some Superconducting Ceramics*, Quaid-i-Azam University, Islamabad, Pakistan (1992).

21. R. Wahab, N. Murtaza, M. Mohammad, A. Y. Khan, and M. S. Subhani, *Science. International. Pakistan,* 6, 117(1994).

22. M. Mohammad, Viqar un Nisa, A. Y. Khan, and R. Iqbal, *Pakistan Journal of Science and Industrial Research*, **30**, 258 (1987).