Impedance Spectroscopy

A quick introduction

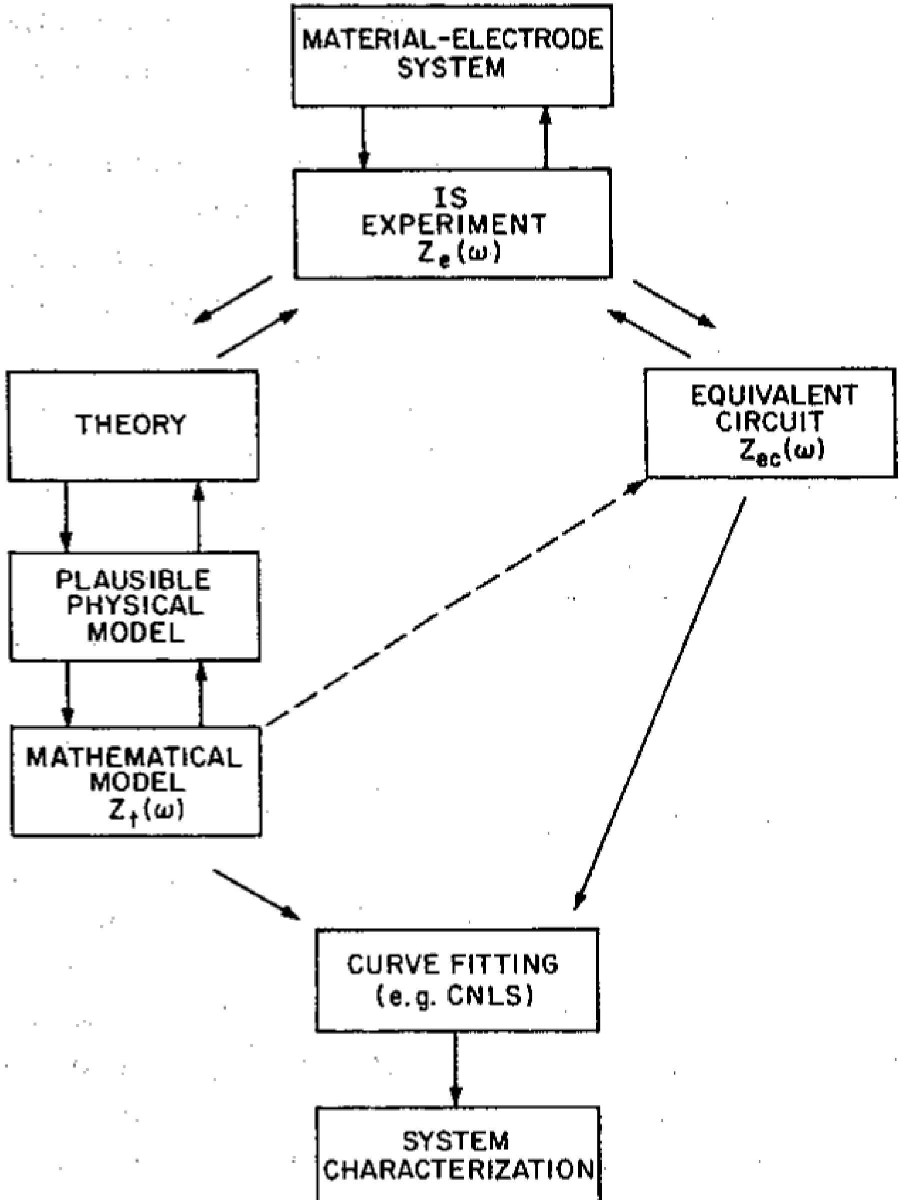

MATERIAL-ELECTRODE SYSTEM
IS EXPERIMENT $Z_e(\omega)$
THEORY
EQUIVALENT CIRCUIT $Z_{ec}(\omega)$
PLAUSIBLE PHYSICAL MODEL
MATHEMATICAL MODEL $Z_t(\omega)$
CURVE FITTING (e.g. CNLS)
SYSTEM CHARACTERIZATION

Table 1.1.1. Relations Between the Four Basic Immittance Functions[a]

	M	Z	Y	ε
M	M	μZ	μY^{-1}	ε^{-1}
Z	$\mu^{-1} M$	Z	Y^{-1}	$\mu^{-1}\varepsilon^{-1}$
Y	μM^{-1}	Z^{-1}	Y	$\mu\varepsilon$
ε	M^{-1}	$\mu^{-1} Z^{-1}$	$\mu^{-1} Y$	ε

[a] $\mu \equiv j\omega C_c$, where C_c is the capacitance of the empty cell.

The basic impedance spectroscopy experiment

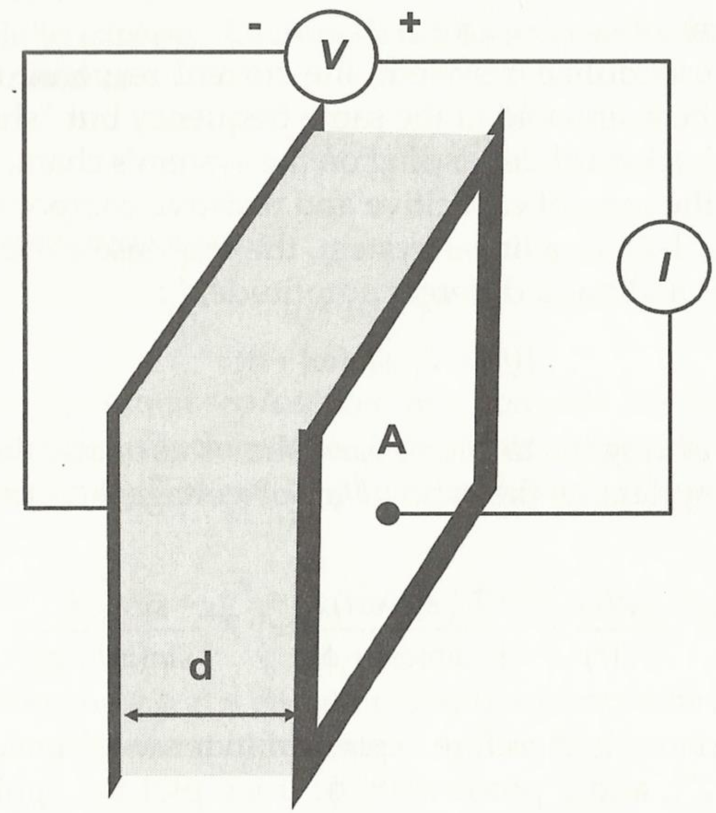


FIGURE 1-1 Fundamental impedance experiment

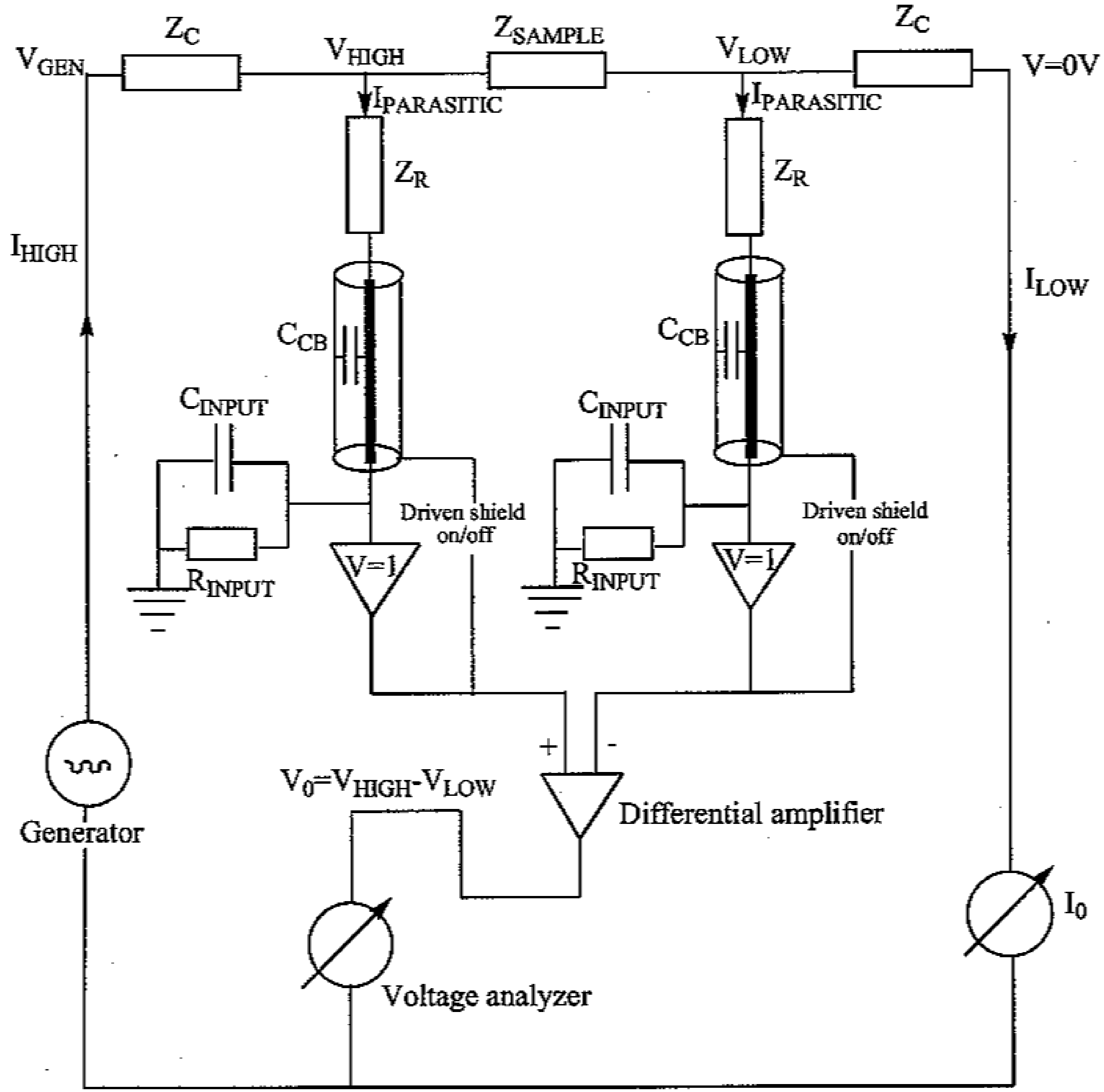


FIGURE 8-10 Four-electrode measurement schematic

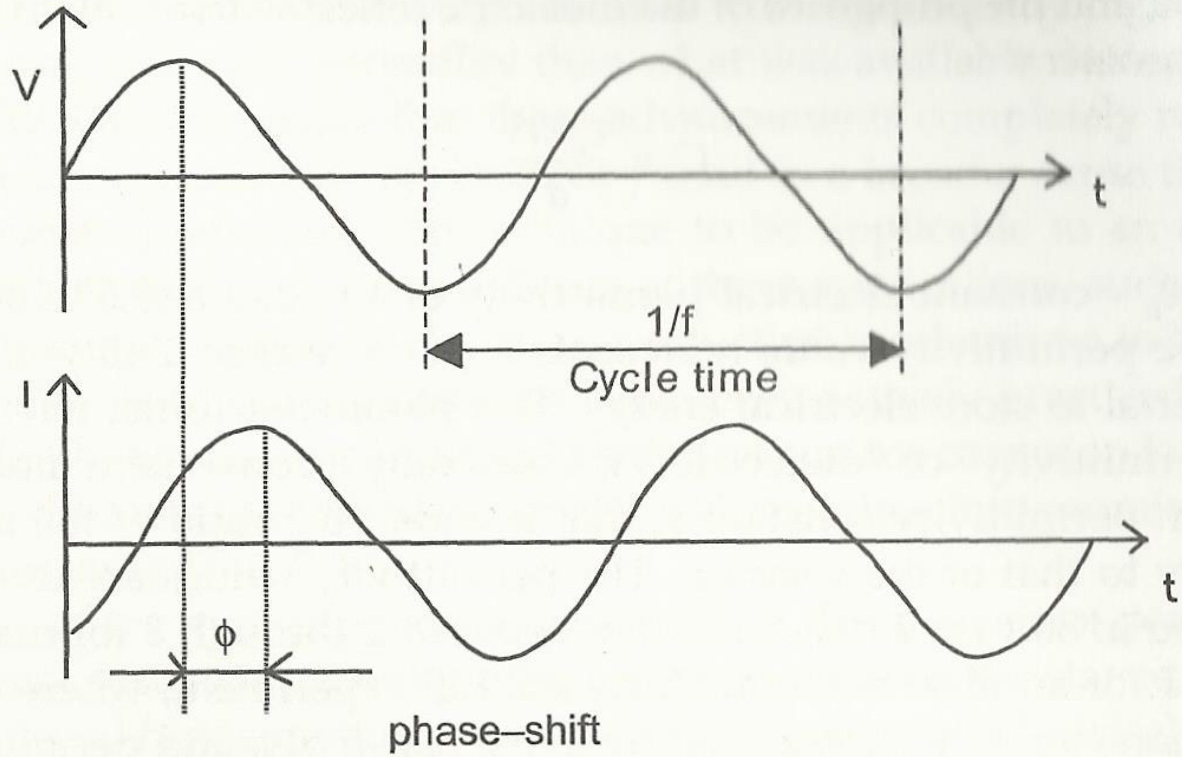


FIGURE 1-2 Impedance experiment: sinusoidal voltage input *V* at a single frequency *f* and current response *I*

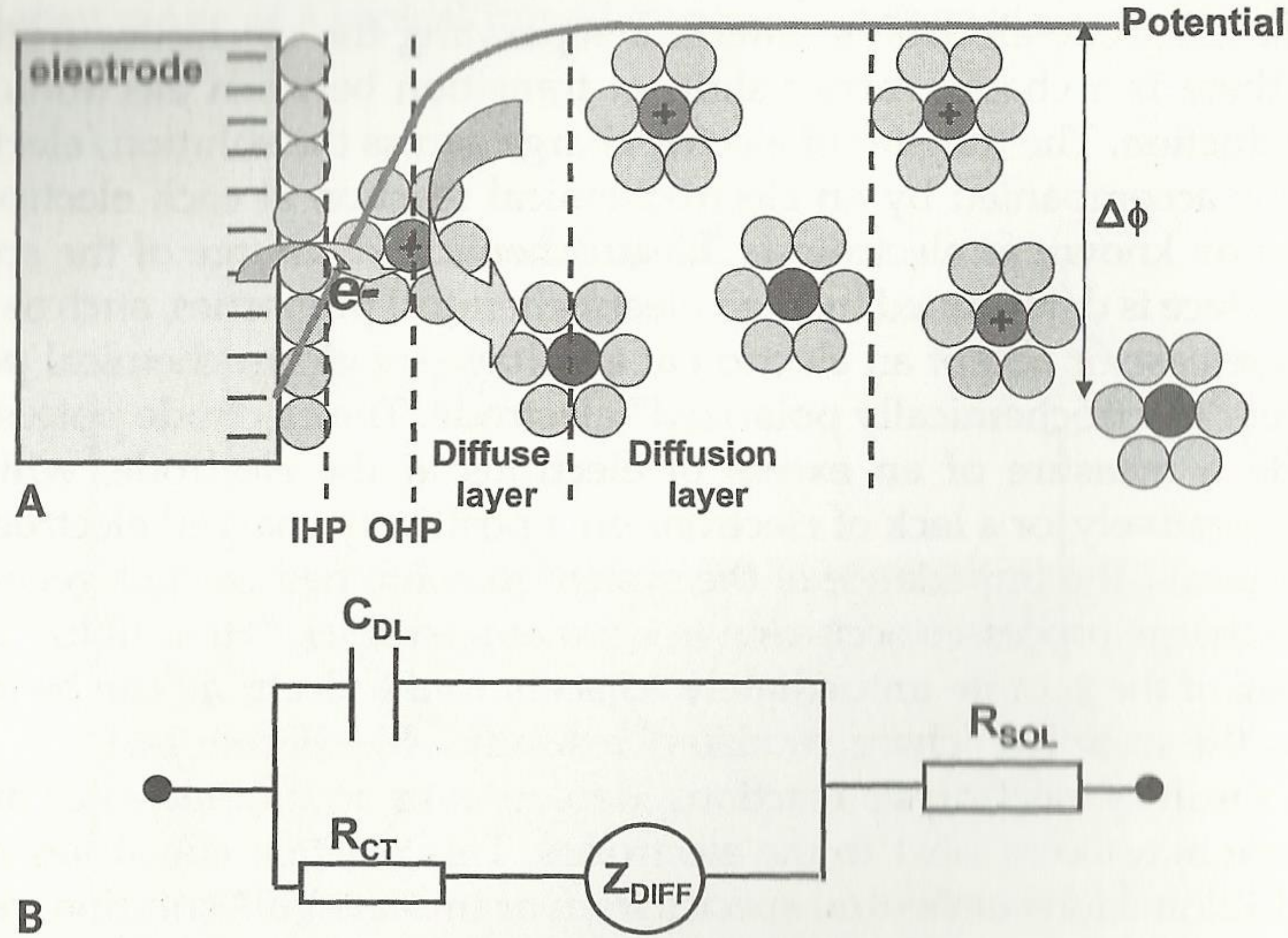
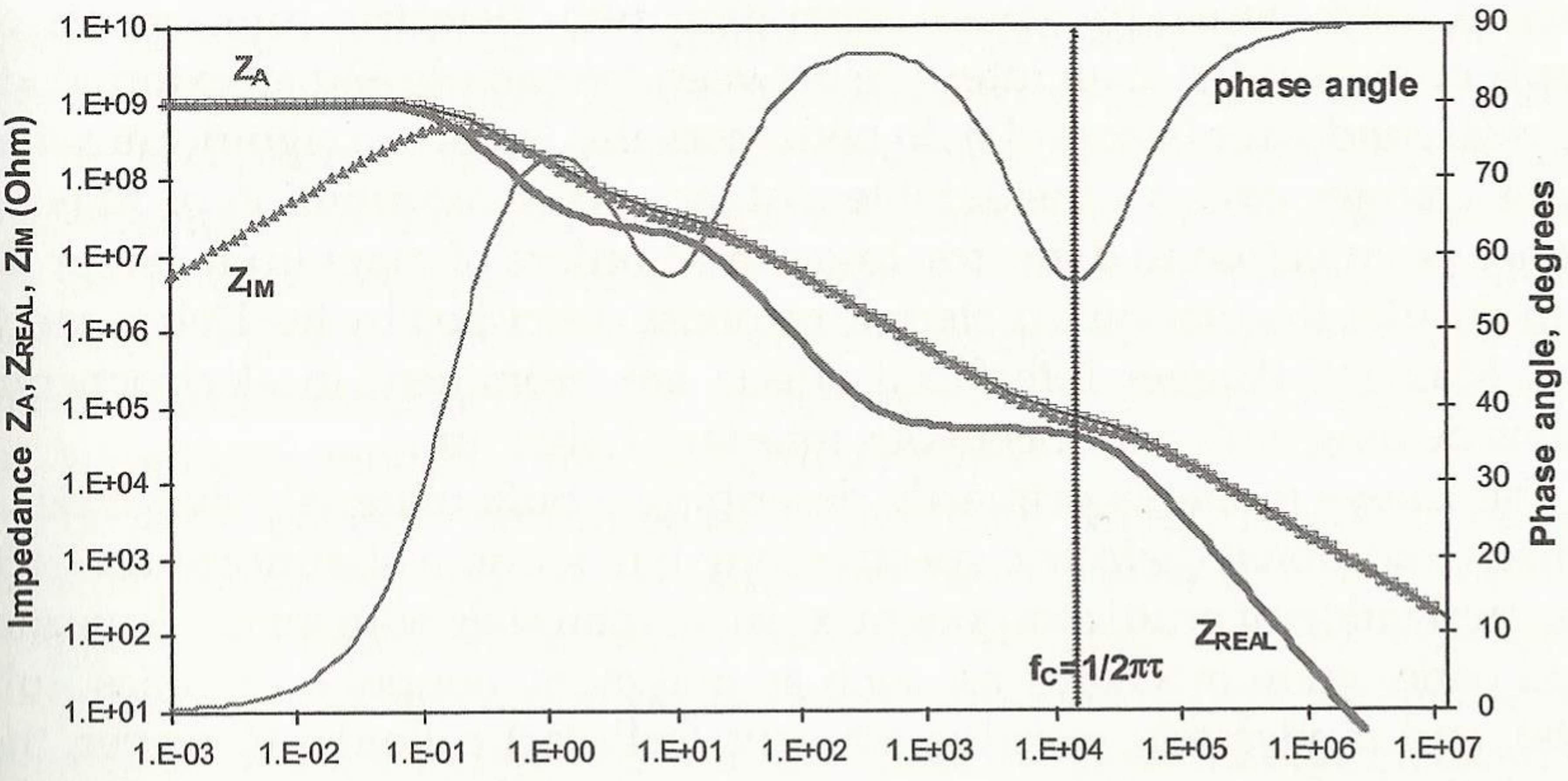
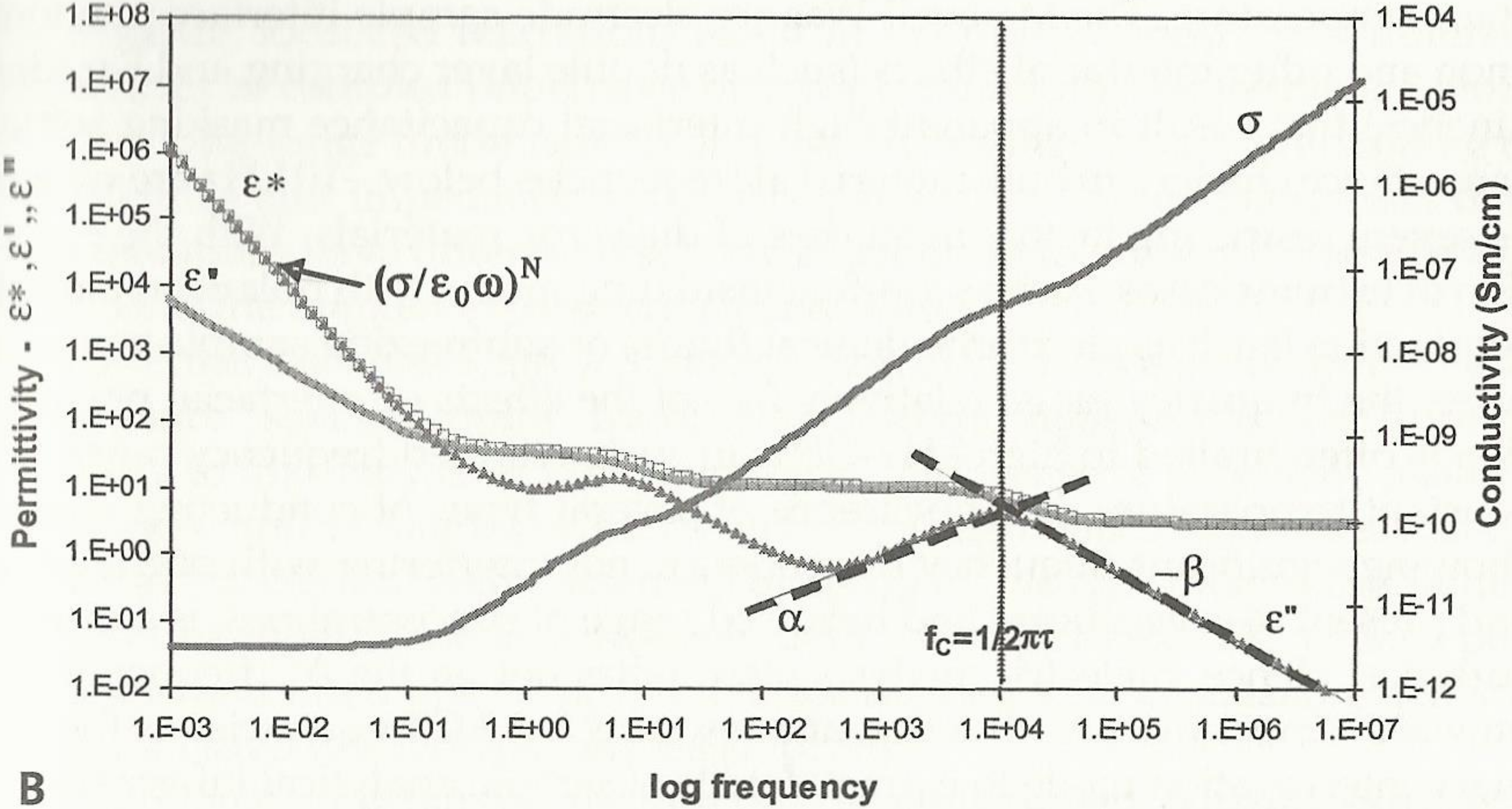


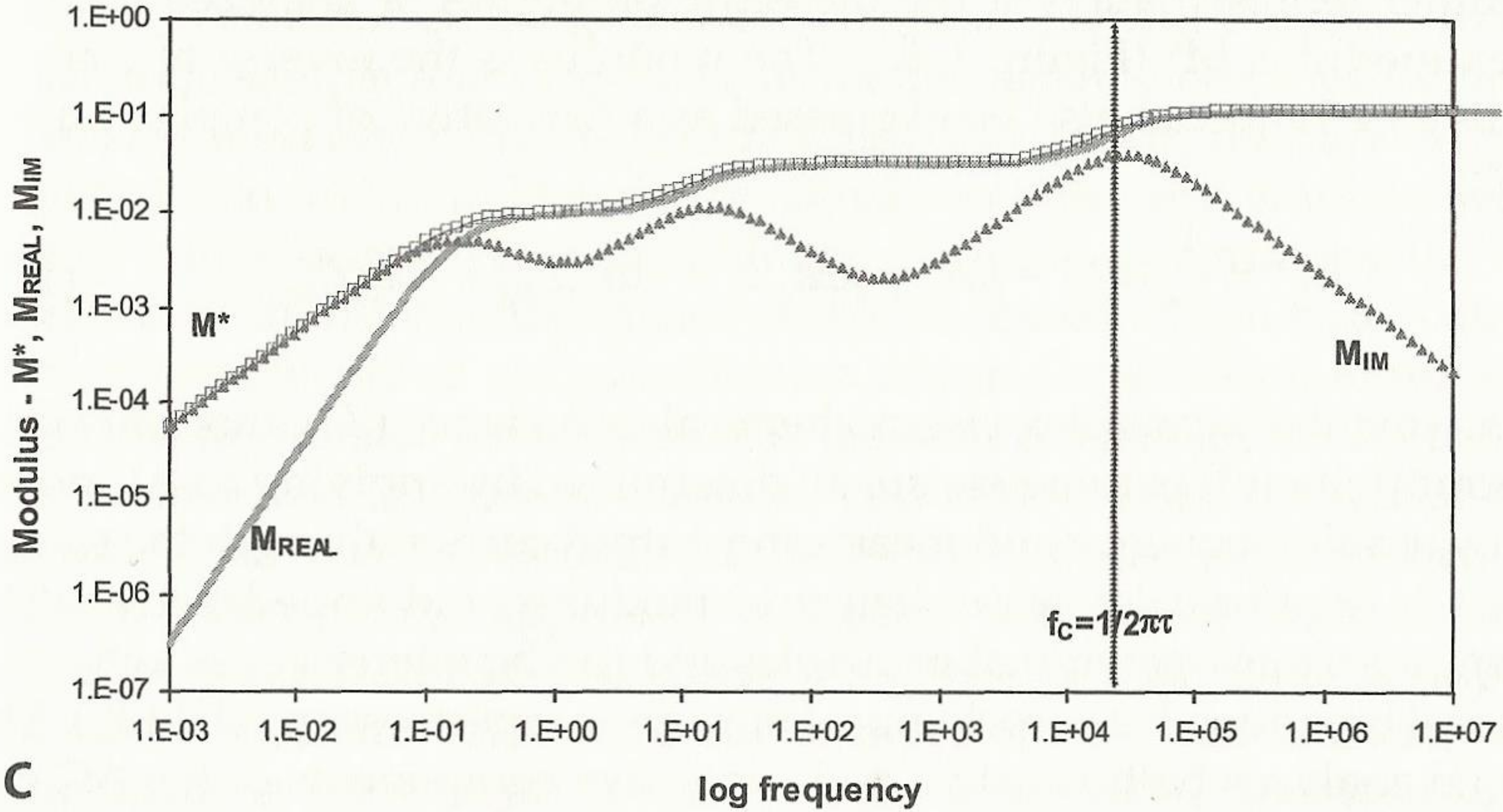
FIGURE 1-6 A. Interfacial electrochemical reaction with diffusion and double layer components; B. Representative electrical circuit


1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
Impedance Z_A, Z_{REAL}, Z_{IM} (Ohm)
Z_A
Z_{IM}
phase angle
Z_{REAL}
$f_C=1/2\pi\tau$
90
80
70
60
50
40
30
20
10
0
Phase angle, degrees
1.E-03
1.E-02
1.E-01
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
log frequency
A



1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
Permittivity - ε*, ε', ε"
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
1.E-12
Conductivity (Sm/cm)
ε*
ε"
(σ/ε0ω)N
σ
α
–β
ε"
fC=1/2πτ
1.E-03
1.E-02
1.E-01
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
log frequency

B



1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
Modulus - M*, MREAL, MIM
M*
MREAL
MIM
fC=1/2πτ
1.E-03
1.E-02
1.E-01
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
C
log frequency

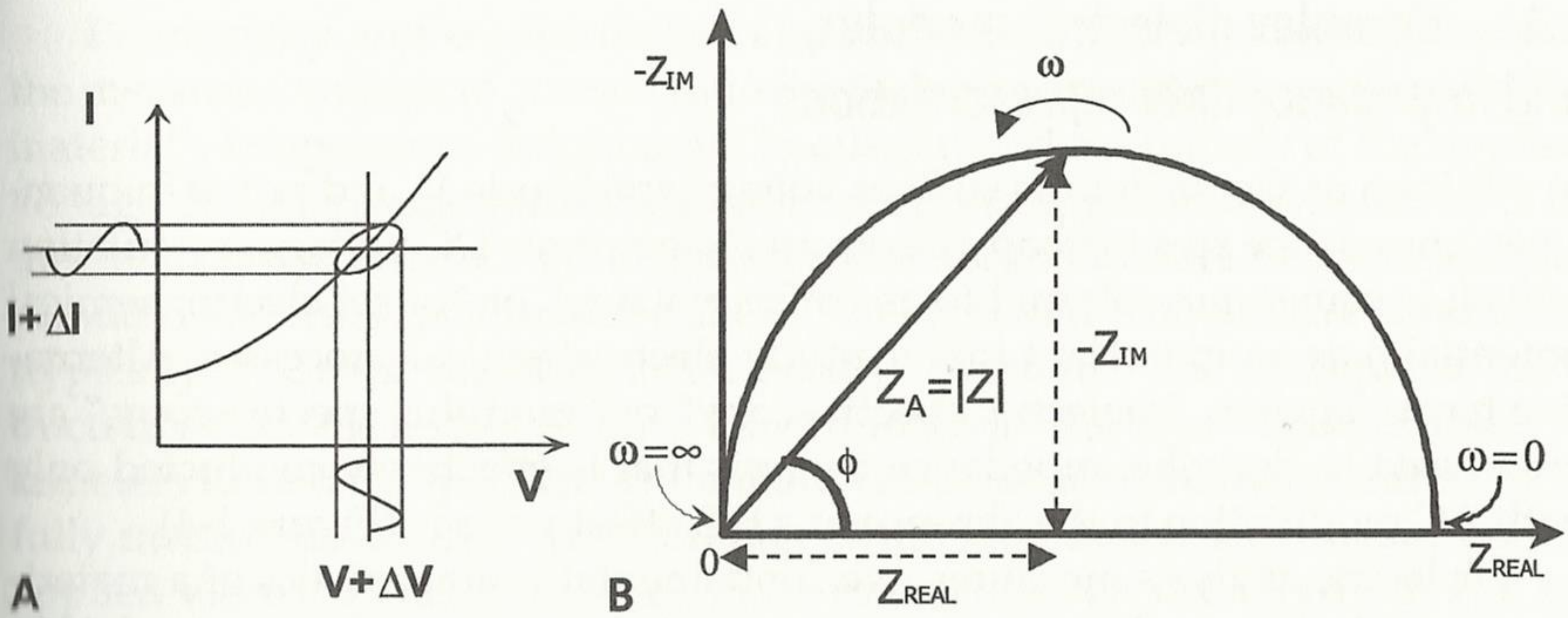


FIGURE 1-3 Impedance data representations: A. Lissajous figure; B. Complex impedance plot

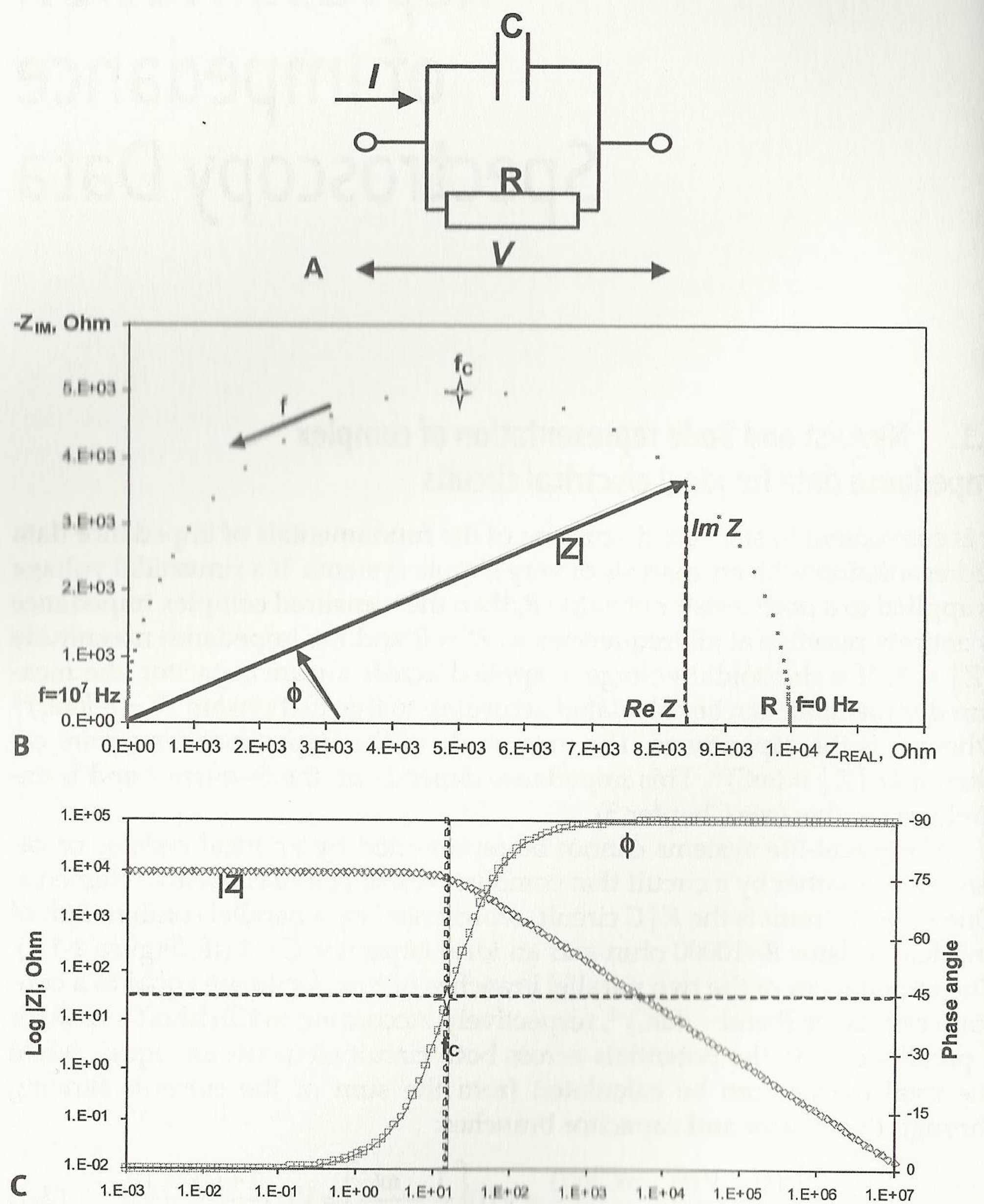


FIGURE 2-1 A. Equivalent circuit; B. Nyquist; C. Bode plots with impedance vector for the R|C circuit

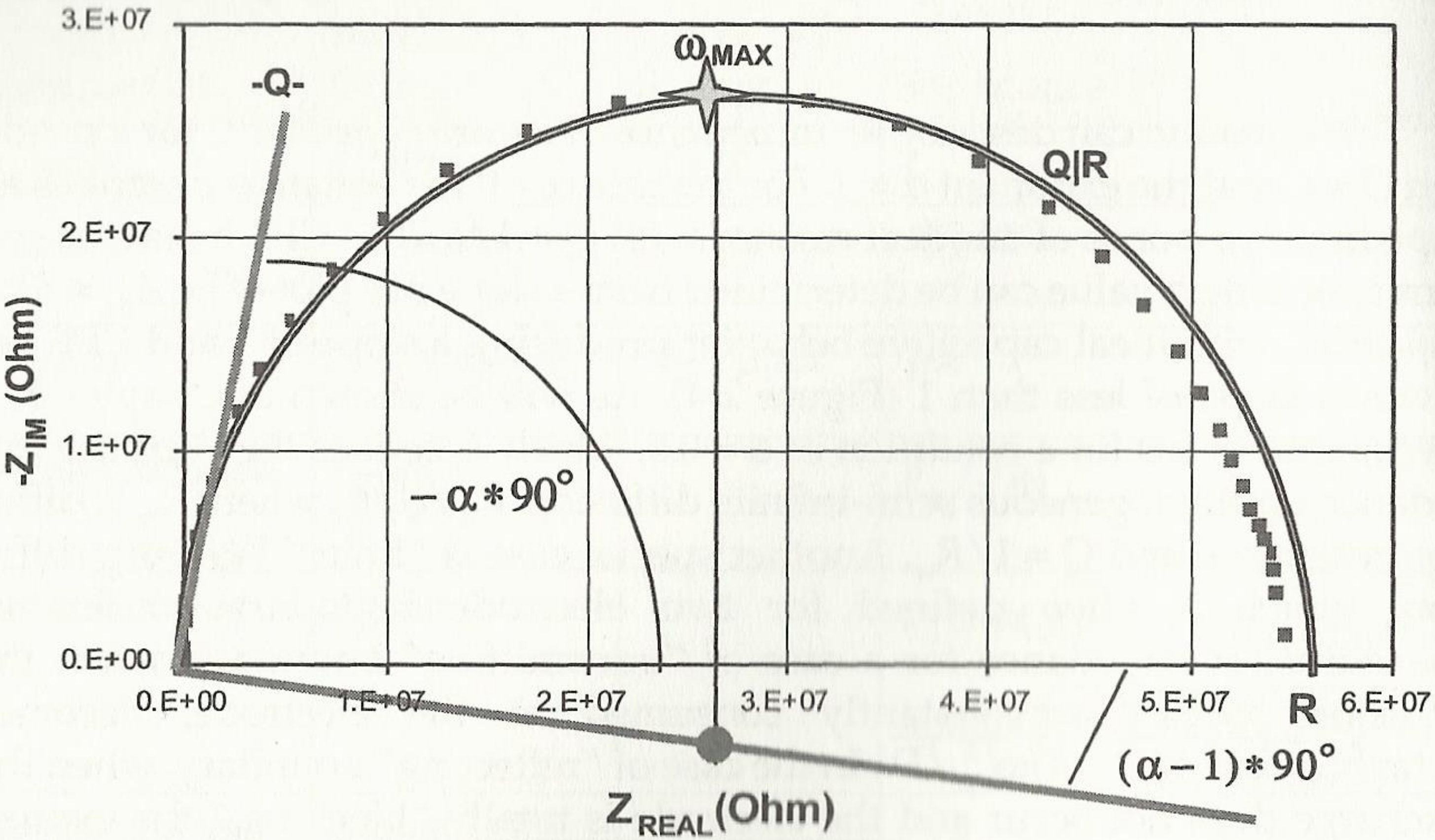


FIGURE 3-1 The Nyquist plot of a single CPE (Q) and a parallel resistor and CPE circuits.

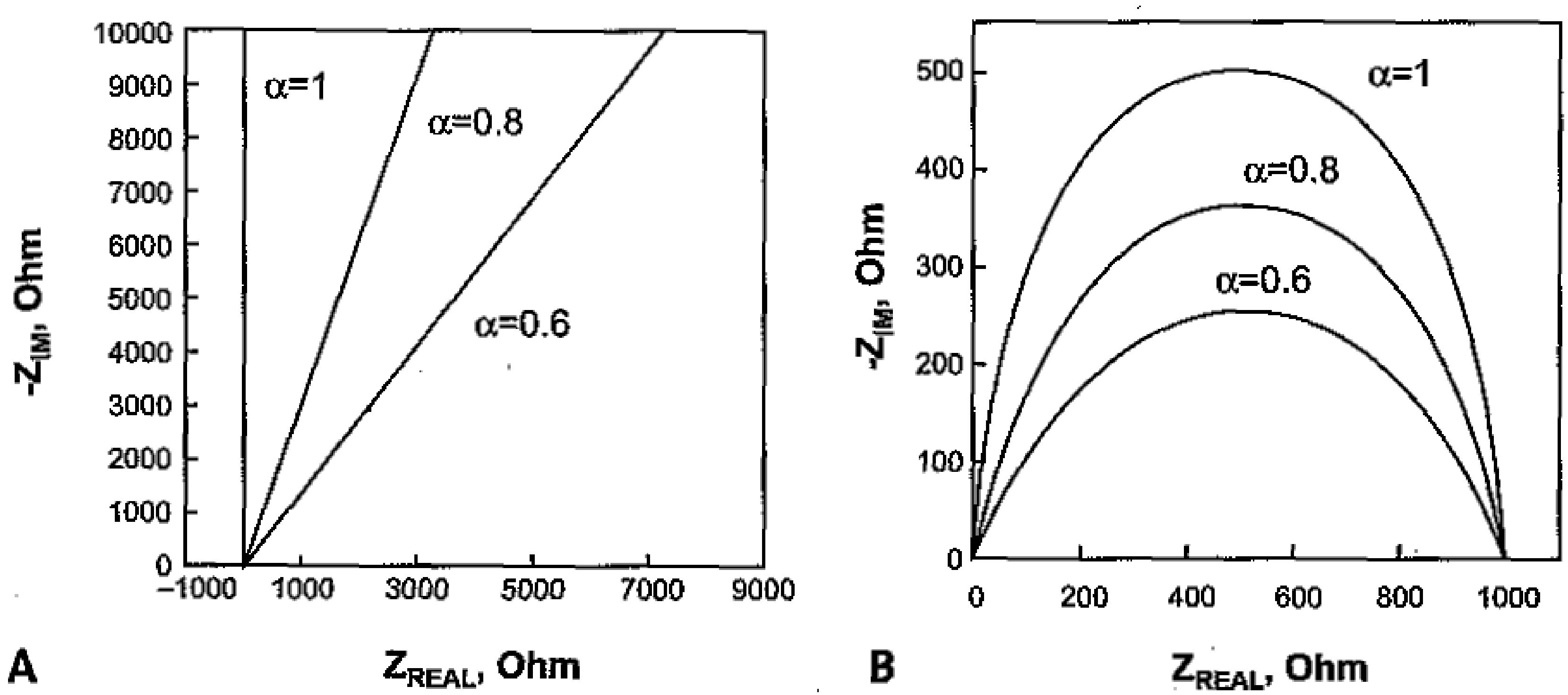
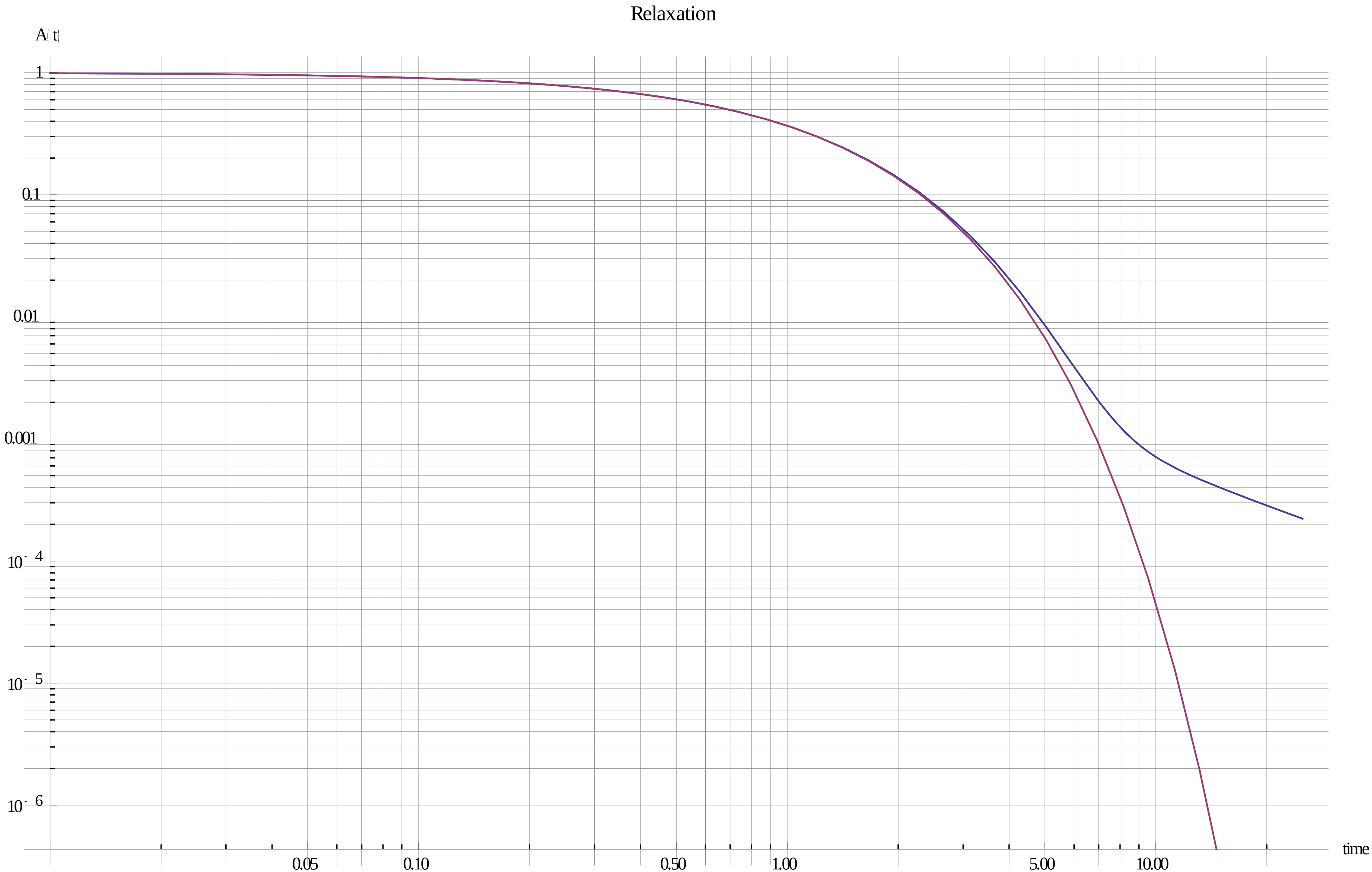


FIGURE 3-2 The Nyquist plots of: A. single CPE (ideally polarizable electrode); B. parallel resistor and CPE circuits

Common Capacitor Dielectrics

Dielectric		ε_r	**tan δ** 10^{-4}	**exponent**
poly(vinylidenefluoride)	PVDF	11.0	350	0.9776
metalized paper	MP	5.3	280	0.9821
polycarbonate	PC	2.9	35.0	0.9978
polyethelenerephthalate	PET	3.3	24.7	0.9984
polysulfone	PES	3.0	14.0	0.99911
polyphenylenesulfide	PPS	3.0	5.6	0.99964
polystyrene	PS	2.4	1.33	0.999916
polypropylene	PP	2.2	0.75	0.999952

From: S. Westerlund & L. Ekstam, "Capacitor Theory," *IEEE Trans. Dielectrics and Electrical Insulators*, **1**, pp 826-839, 1995



Relaxation
A[t]
1
0.1
0.01
0.001
10^{-4}
10^{-5}
10^{-6}
0.05
0.10
0.50
1.00
5.00
10.00
time

Dynamic trapping model