CHAPTER -IV-

EXPERIMENTAL PROCEDURE

4.1 Metallic Materials Used

In the present investigation four types of metallic materials have been used to evaluate corrosion and passivity behavior. Austenitic stainless steel 304 and titanium metal, with and without addition of alloying elements, viz. ~2.0% Mo in SS 304 and ~ 5.0% Ta in titanium, have been investigated. The chemical compositions of the materials used are given in table-4.1, which were determined using Nuclear Analyzer TN model 9266.

4.2 Environmets

Environments used in this work are 5 and 10% HCl, 10 and 20% H_2SO_4, H_3PO_4 commercial grade and H_3PO_4 laboratory grade All the solutions are prepared using laboratory grade concentrated acids and double distilled water. The solutions of these acid concentrations were used considering that these are the most commonly encountered media in the chemical processing streams. Details of physical and chemical properties of these acids are given in table 4.2

4.3 Specimen preparation

Specimens were cut from the plates of 3mm thickness in the size 12X12mm. and their corners were round off by grinding. This size is most suitable to fit in specimen teflon holder providing circular exposed surface area of 0.5cm diameter. The round tablet shaped samples prepared were then belt ground for surface flatness. Then the specimens were subjected to mechanical polishing, using emery paper from course [0/1] to fine [0/4] size and lastly to get mirror like surface finish, polishing was carried out, on wheel polishing unit. These surface preparations were carried out as per ASTM practice G1-72 (1979). These samples were finally cleaned with acetone and dried in atmosphere.

All the specimens of ASS were normalized at 850° C and Ti & Ti-5% Ta at 450° C to obtain uniform structures of as received material. Photomicrographs and grain size of 304, 316, Ti and Ti-5Ta were evaluated after normalizing using image analyzer. These are shown in figures 4.1, 4.2, 4.3 and 4.4 respectively.

TABLE-4.1: CHEMICAL COMPOSITION OF MATERIAL

MATERIAL	C%	Si%	Mn%	Cr%	Ni%	Mo%	Fe%	
ASS-304	0.024	0.35	1.84	16.83	9.94	-	Bal.	
ASS-316	0.025	0.35	1.82	17.62	11.76	2.12	Bal.	
	C%	**Si%**	**Ti%**	**Fe%**	**N_2%**	**O_2%**	**H_2%**	**Ta%**
TITANIUM	0.04	0.03	Bal.	0.15	0.03	0.09	0.008	-
Ti-5%Ta ALLOY	0.005	0.01	Bal.	0.027	.0034	0.081	0.01	4.72

Table - 4.2: Composition of Laboratory Grade Acids

ACIDS	HYDROCHLORIC ACID	SULPHUIRIC ACID	PHOSPHORIC ACID Lab. Gr.	PHOSPHORIC ACID omm.Gr.
ASSAY%	35.38	97.99	85.00	86.97
Wt./mL at $20^{O}C$	1.18	?	1.719	386ppm (HF)
Non Volatile Matters %	0.01	0.01	-	5ppm (SiO_2)
Free Chlorid%	0.0005	-	0.005	nil practically.
H_2SO_4 %	0.02	-	0.01 (SO_4)	8.46
HNO_3 %	-	0.001	0.01 (NO_3)	-
HCl	-	0.01	-	-
Arsenic	0.0001	0.0002	0.00004	-
Iron	0.0005	0.0005	0.01	5ppm
Lead	0.0005	0.002	0.0002	-

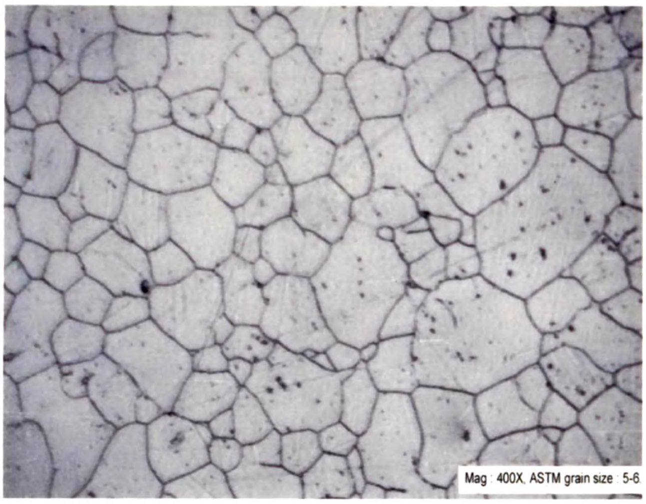


Figure - 4.1 : Photomicrograph of Normalized SS - 304 showing grains.

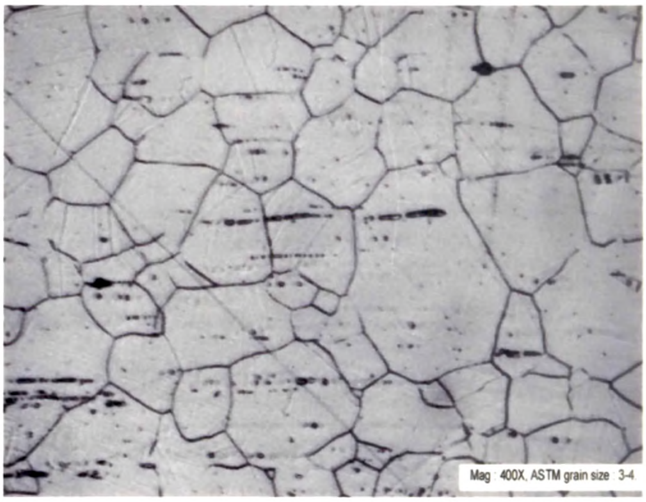


Figure - 4.2 : Photomicrograph of Normalized SS - 316 showing grains.

Figure - 4.3 : Photomicrograph of Normalized Titanium showing grains & hydrides of Titanium.

Figure - 4.4 : Photomicrograph of Normalized Ti - 5Ta Alloy showing grains of Alpha & Beta Phase & hydrides of Titanium.

Any surface treatment, which will thicken and improve stability of passive film, will enhance the corrosion resistance. Simple and economic treatments like; thermal oxidation and anodizing have been thought to thicken and strengthen the film on the surfaces of titanium and titanium-5tantalum alloy (1). However these treatments are not applicable to the stainless steels. Treatments employed to modify the passive films on titanium metal and titanium-5tantalum alloy specimens are given below:

- Thermal Oxidation: - Heating at 680°C in Air, for 30 minutes, Air cool to room temperature (2).
- Chemical Anodizing: - Electrolytic anodizing at 80 V, 1Amp, for 90 Seconds, in 10% $(NH_4)_2 SO_4$ bath (3).

Environment used for corrosion evaluation after enhancement in passivity and corrosion resistance was the solution of 10% concentrated HCl in distilled water. This environment was selected to explore the utility of Titanium and Titanium + 5% Tantalum alloy in reducing acid, after modifying the passive film by the surface treatment. The results obtained have been suitably reported and discussed plausibly.

4.4 Tests performed

To study passivity and corrosion behaviors of SS304, SS316, Ti and Ti + 5%Ta two corrosion evaluation methods have been employed using EG & G, M273 Electrochemical measurement system incorporated with Model 352 and Model 398 software with lock in amplifier:

(a) Potentiodynamic method to study the passivity and corrosion behaviors

(b) Electrochemical Impedance Spectroscopy (EIS) method to study the film characteristics.

The ex-situ methods for surface analysis and topological structure were employed to support the basic results of potentiodynamic polarization & electrochemical impedance spectroscopy techniques. The techniques adopted are SEM, EDAX and wherever needed XRD techniques for the said purpose. All these studies were carried out apart from this department, at different laboratories viz. SICART, B.A.R.C. and others, where such facilities were available. All the studies on S.S. 304,316 and with and without surface treated titanium and titanium-5tantalum alloy were carried out at room temperature. The procedural details are given below.

4.4.1 Potentiodynamic Method :

Since passivity of SS304, SS316, Ti and Ti - 5%Ta has the major importance in their applications, potentiodynamic studies were carried out to obtain potential v/s log current density plot, commonly known as polarization curve. The potential range was selected in a manner so that sample could be polarized in both ways i.e. calhodically as well as anodically. Varieties of formats that can be used for potentiodynamic testing and the various parameters required to be set are given in are given in Appendices.

The samples cut, ground, normalized and polished were tightly held in specimen holder with the help of teflon bolt such that area exposed to environment is circular with 5 mm diameter. Electrical contact is made by using S.S. rod of suitable size from the transverse side, avoiding the contact between electrolyte medium and S.S. rod, as shown in figure 4.5. This single set up was used for both the potentiodynamic and Electrochemical Impedance Spectroscopy studies.

The standard reference test used for Polarization measurement is issued under designation ASTM G5-87 and G-3 the practice of conventions applicable for testing. The testing apparatus used in the present study is given below;

(i) Standard corrosion cell

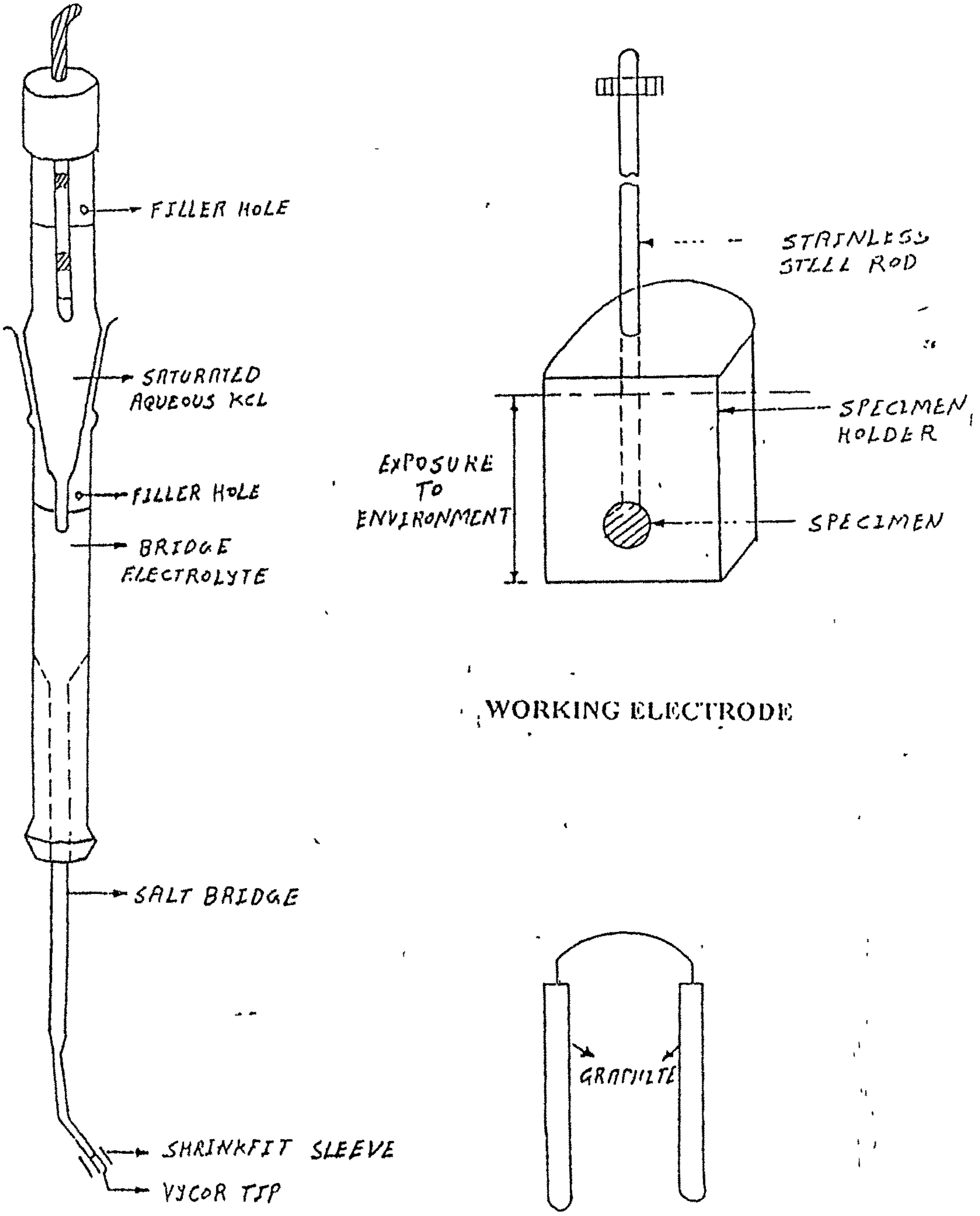
A cell with round bottom flask as shown in figure (4.6), which holds environmental fluid and have various necks to permit insertion of

(i) The working / test electrode
(ii) The auxiliary / counter electrodes.
(iii) Standard calomel reference electrode
(iv) Inlet and outlet for inert gas
(v) Positioning thermometer

Cell is constructed of material that does not corrode or contaminate the test results and is generally made or borosilicate glass or TFE –Fluorocarbon.

(ii) Electrodes: [Fig, 4.5]

(i) **Working electrode**: Specimen under study of tablet form is placed inside the specimen holder. The area exposed will be a small spot only. The continuity heck was made by digital multimeter.



WORKING ELECTRODE

REFERENCE ELECTRODE

COUNTER ELECTRODE

FIG 4.6 SCHEMATIC DIAGRAM OF ELECTRODES AND TEFLON SPECIMEN HOLDER

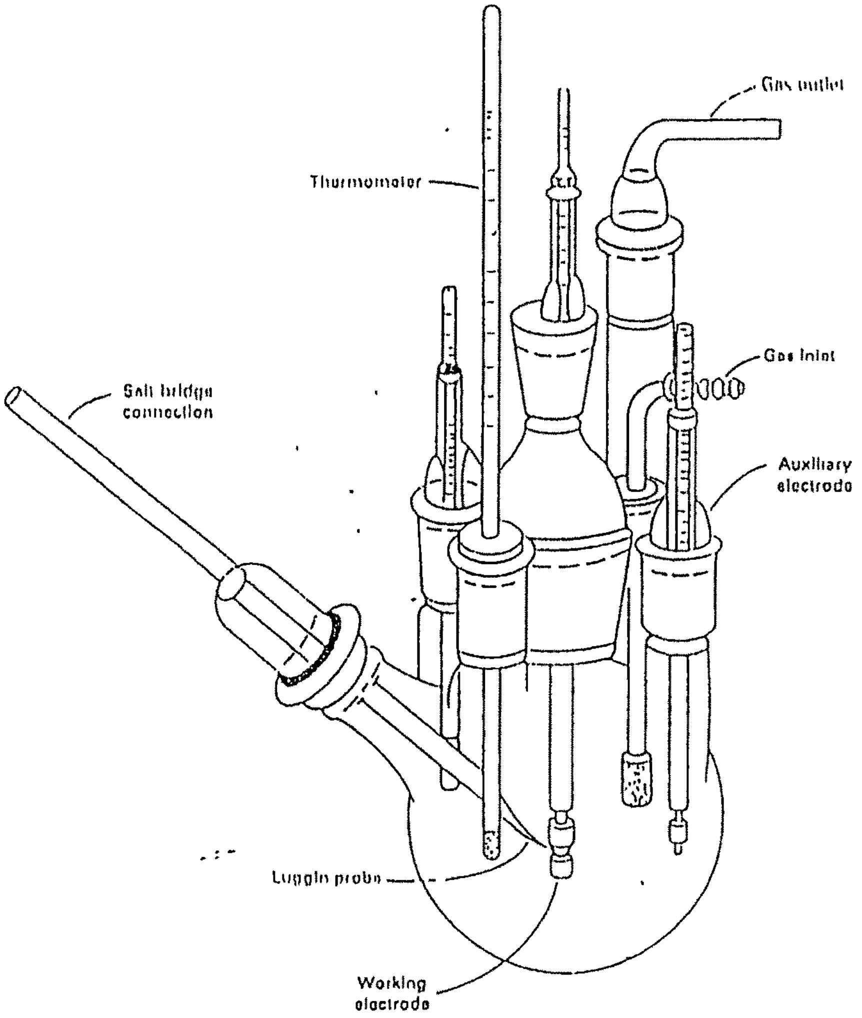
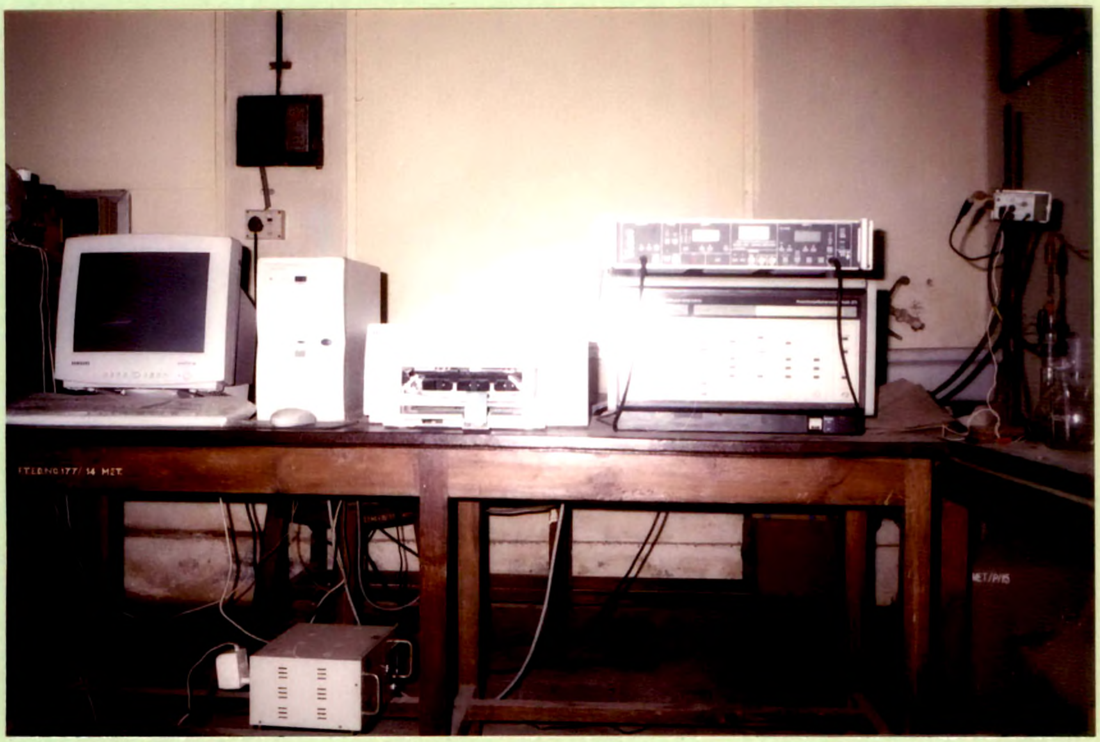


FIG 4.5 TYPICAL ELECTROCHEMICAL POLARIZATION CELL ILLUSTRATING LOCATION FOR WORKING AND AUXILLARY ELECTRODE AND ASSOCIATED CELL COMPONENTS.



IT.ENG177/14 MET.

(ii) **Reference electrode**: Saturated calomel electrode, with standard potential of + 0.2415V was used. It was kept near working electrode to reduce IR drop due to electrolyte.

(iii) **Counter electrode:** It works here as a current carrier in the circuit. Graphite electrodes were used, as having properties of being chemically inert, conductive and less expensive. Pt or platinized Pt can also be used but they are expensive. Two rods are used for proper polarization with respect to counter electrode and to take care of area effects.

(iii) Potentiostat (EG & G, PARC MODE 273)

It is used to polarize the sample anodically or cathodically. It maintains electrode potential within 1mV of preset value over a wide range of applied current used. It should have a range of applied current used. It has a range of −10.0 V to +10.0V, but used in practice is very less, and anodic current output range from 1A to10 nA. It works on the principle of Wheatstone's bridge. It applies predetermined potential to working electrode against the reference electrode by changing current through counter electrode.

The predetermined area of material is exposed to given medium in the cell, which gets polarized as per the data fed and Tafel's-Potentiodynamic plots were obtain. Also using plots and software M352 the other electrochemical parameters and corrosion rates are obtain for a given material exposed in the different environments under study.

4.4.2 Procedure

Insert a sample, prepared as described, into specimen holder and check the continuity of exposed area of sample with other ends of supply, i.e., S.S. rod. The specimen holder is then immersed into media up to a level, such that the given area of specimen is fully exposed to the media without coming in contact with S.S. rod. Lastly all the connections of other electrodes were checked by digital multimeter.

Before commencing any kind of measurement, Rest potential measurement is carried out to have on hand information about behavior of metal/alloy as soon as it enters the given environment. This potential is recorded just after circuit is connected and before applying current.

The parameters required to commence the experiment are equivalent weight, density and area of exposure. These were fed before switching on the current and starting the experiment. The other essential parameters are:

(i) Initial Voltage (mV): It is the potential at which scan begins. In the present work i.e. – 250 mV vs. OC

(ii) Final voltage (mV): It is the potential at which scan ends, i.e., between 1.6V to1.8V. (Vs. SCE)

(iii) Scan rate (mV/Sec): The rate at which the applied potential changes the scan, i.e., 0.5 mV/s

(iv) Conditioning voltage: It is the potential at which the specimen is polarized cathodically for conditioning the surface of the specimen, before the scan begins. It is to make the samples surface more active/electronegative, further the bubbling of respective species of environment on the surface of sample helps in removing any deposits or foreign material. In the present work it is kept at – 1.0V

(v) Conditioning time: Time for which specimen is conditioned, i.e., 60s.

(vi) Initial delay: It is the time during which the spesimen reaches its original potential from where scan begun, i.e., 120s. (Commonly active metal needs 40-50s and passive metal needs1 to 2min.)

Finally the cell is connected to the potentiostate and scan is initiated. Polarization curve is obtained on the computer screen as E_{SCE} vs. log i print out of which is taken and kept as record. Finally calculations for corrosion rate and other electrochemical parameters were being carried out and recorded.

As weight loss data is not available in the electrochemical test, it is obtained from Faraday's law as below:

SAMPLE CALCULATION;

CORROSION RATE (MPY) = 534 W/ DAT,

Where: D = Density (mg/cm^3), A = Area of exposure (sq.in.) ;

T = Time of exposure (hrs), and W is the weight loss in mg.

96500 Coulomb (Q) liberates → 1g-Equivalent weight of metal

Therefore, Q_{corr} coulomb liberates → Q_{corr} x Equ. Wt./ 96500 g of metal

But $Q_{cor} = i_{coor} \times T$;

Hence, Q_{corr} coulomb liberates → i_{coor} x T x Equ. Wt./ 96500 g of metal

→ i_{coor} x T x Equ. Wt./ 96500 x 1000 mg of metal

Thus, **mpy = (534 x i_{coor} x T x Equv.Wt.) / (D A T 96500 x 1000)**

Corrosion rate can also be determined, if value of i_{corr} is known, from following relationship:

$$R\ mm/y = 0.0033 * i_{corr} * e / \rho$$

Where, e = Equivalent weight

And ρ = Density.

4.5 Ac impedance Measurements

As mentioned earlier this techniques is used to analyze the surface characteristics of the passive oxide film developed. It does not affect the surface and hence the surface properties do not diminish. The variety of formats can be used in Ac impudence studies and are listed in appendix E. In present study emphasis is given on Nyquist plot.

The same set-up, as used in polarization studies, is used for obtaining Nyquist plots for ASS 304, ASS 316, titanium-5tantalum alloys and titanium metal in different acid media as mentioned above. The polished surface of specimen was exposed to the environment having circular area of 5.0 mm diameter, using teflon sample holder. All the connections of electrochemical cell were checked and experiment commenced giving 'run' command from computer using the software M398.

The measurement of impedance involves applying a small DC potential to the specimen and superimposing a small AC potential (~ 10mV) on fixed DC potential (0.00 vs. OC in the present work). The sinusoidal current, potential and phase shift between the two were measured, employing frequency response analyzer. Impedance values were obtained from these results and plots were display on the computer screen, either as Nyquist plots or Bode plot, as per requirement.

The whole experiment was carried out in two consecutive steps, since complete range of frequencies to be scanned is difficult to perform in one step. As low and high frequency waves have different characteristics, the scanning was done using single sine and multi-sine techniques, which are discussed in the next section.

In the present work, combined techniques of single and multiple sine were used consecutively to avoid the limitations of both. It provides voltage at different frequencies across the electrodes and signals in terms of impedance were registered on the screen as points. When complete range of frequency was scanned, number of points were obtained on the screen, which then connected to get Nquist plot of the system under study.

The parameters' setting employed for commencement of experiment and obtaining Nyquist plot are given below:

PARAMETERS TO BE SET FOR NYQUIST PLOT

S.No.	Paramiters Set for this study	
1.	Conditioning time	60 Sec.
2.	Conditioning Potential	(-) 1.0V.
3.	Initial Delay	120 Sec.
4.	Equivalent Time	0.0 Sec.
5.	Data Quality	4.0

6.	Working electrode	Solid
7.	Electrode Area	0.25 cm^2
8.	Initial Frequency	100 mHz
9	Final Frequency	100 kHz
10.	Reference Electrode	SCE

The software M349 available in the instrument facilitate to chane one type of format to another type with the same data. Thus, once a plot Bode or Nyquist is acquire on the computer screen, it can be interchanged from $|Z|$ Vs log (ω) to phase shift (Φ Vs log (ω) to $|Z|_{rc}$ Vs $|Z|_{igm}$ and vice-versa. A photograph of complete setup with computer is given to provide an over view.

4.6 Electrochemical Impedance Spectroscopy

The technique is relatively new in the field of electrochemical measurements. It is used in this work for evaluating nature and quality of the passive film, although technique is being used for variety of other measurements and applications.

When current of different frequencies are flowing through a passive film having -ve charge ion accumulation on one surface (film/media interface) and +ve on the other (metal/film interface). Passive film is thought to act as a parallel plate capacitor in the field of alternative potential field. Total impedance offered therefore, can be resolved into two components;

(A) In phase with voltage called real impedance

(B) Out of phase voltage called imaginative impedance.

Former deals with passage of current through film. Its value corresponds to resistance offered by the passive film. Such as resistance to charge transfer and polarization resistance. Later one gives measure of charge accumulation at the surfaces and corresponds to capacitance of the film also called double layer capacitance.

In general, therefore, when an electrochemical system is studied by applying AC voltage, it provides information of kinetics and mechanics of the system. Applied voltage of sinusoidal nature gives sinusoidal current signals, which is more penetrating than D.C. Thus, it enjoys advantages of evaluating film formation, double layer capacitance, under-film studies and measurements in low conductive media. The technique is becoming very popular for the study of corrosion, semiconductors, batteries, coatings, electroplating phenomena, and Electro-organic synthesis.

The AC impedance approach offers some distinct advantages over DC techniques.

(i) It uses very small excitation amplitudes, i.e. in the range of 5 to 10 MV peak-to-peck. Excitation amplitudes of this magnitude cause only minimal Perturbation of the electrochemical test system, thus reducing errors caused by the measurement technique itself.

(ii) AC impedance experiments can provide data on both electrode capacitance and charge transfer kinetics, it offers valuable mechanistic information.

(iii) Since the method does not involve a potential scan, measurement can be made in low conductivity solutions where DC techniques are subject to serious potential-control errors.

(iv) It is used to determine the uncompensated resistance of an electrochemical cell

(v) Because of the more Penetrating applied sinusoidal wave form, it can measure double layer capacitance, film formation, under firm studies and corrosion measurement in less conductive media.

4.5.1 AC Circuit Theory and Representation of Complex Impedance Values

Impedance definition: concept of complex impedance·

Almost everyone knows about the concept of electrical resistance. It is the ability of a circuit element to resist the flow of electrical current. Ohm's law (Equation 2-1) defines resistance in terms of the ratio between voltage E and current

$$\mathbf{R = E/I}$$

While this is a well known relationship, it's use is limited to only one circuit element: the ideal resistor. has several simplifying properties:

· It follows Ohm's Law at all current An ideal resistor and voltage levels.

· It's resistance value is independent of frequency.

· AC current and voltage signals through a resistor are in phase with each other.

Applying an AC potential to an electrochemical cell and measuring the current through the cell measures Electrochemical impedance. Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and it's harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).

Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. Linearity is to be maintained for simplification of analysis. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoidal at the same frequency but shifted in phase.

For AC, where frequency is non-zero the analogous equation is

$$\mathbf{Z = E/I}$$

Where,

E - Sinusoidal wave form amplitude for potential,

I - Sinusoidal wave form amplitude for current

Z - Impedance, the AC equivalent of resistance

4.5.2 Impedance

The terms resistance and impedance both imply an obstacle to the current or electron/ion flow. In DC only the resistor provide this resistance whereas in AC, circuit elements such as capacitors and inductors also influence electron flow. These elements can affect not only the magnitude of an AC waveform, but also its time dependent characteristics like phase shift.

Vector expression of AC impedance is:

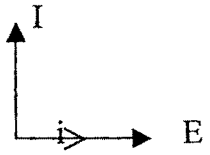
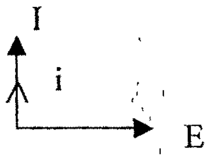
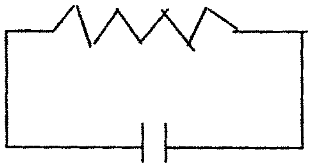
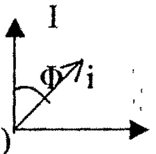
$\mathbf{Z = Z' + Z'' j}$ {j is a complex number = $\sqrt{-1}$}

Where, Z', Z" are real & imaginary components of impedance giving its magnitude and direction and forming axes of Nyquist plot. The impedance vector at particular angular frequency ω (= 2π f) is given as:

$|\mathbf{Z}| = \sqrt{(\mathbf{Z'})^2 + (\mathbf{Z''})^2}$ And, $\mathbf{\tan\Phi} = \mathbf{Z' / Z''}$ (θ is phase shift)

The impedance of a resistor has no imaginary component at all. The phase shift is zero degrees, i.e. the current is in-phase with the voltage. The AC impedance of a capacitor on the other hand has no real component and but only imaginary component, which is a function of both capacitance and frequency. These are the common elements of AC circuits applied to electrochemical system; their impedance equations are given below. Electrochemical system can be examined with respect to their equivalent electrical circuit. A simple system with activation polarization is represented as Shown in fig 4.5

Table 4.3 AC circuit elements and their impedance

Circuit element	AC impedance equation	
	$Z = R + 0j; \quad j = \sqrt{-1}$	
	$Z = 0 - j/\omega C; \quad \omega = 2$	
	$Z = R/(1+\omega^2C^2R^2) - \dfrac{j\omega CR}{1+(\omega^2C^2R^2)}$	

E

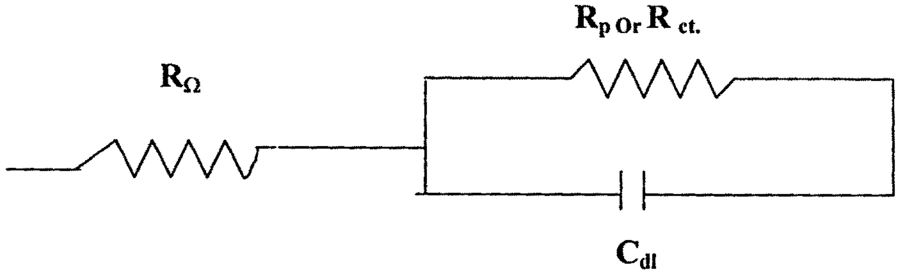


Fig. 4.5 System with activation polarization

Where,

R_Ω - Uncompensated resistance between working electrode and the reference electrode / solution resistance.

R_p - Polarization resistance at the electrode / solution interface.

R_{ct} - Resistance to charge (ions/ electrons) transfer.

C_{dl} - Double layer capacitance.

4.5.3 AC Impedance Formates :

Once the experiment is complete, the raw data at each measured frequency consist of:

1) The real component of voltage (E')
2) The imaginary component of voltage (E")
3) The real component of current (I')
4) The imaginary component of current (I")

From these data it is possible to compute

- The phase shift of response, Φ
- The real impedance, Z'
- The imaginary impedance, Z", and
- The total impedance, |Z|. For each applied frequency.

Variety of formats used for AC impedance study as listed in Appendix-III. Appendix IV gives the parameters required to be set.

(A) Nyquist plot :

Figure 4.6 shows a technique very popular for evaluation AC impedance data. This format is also known as a **cole-cole plot** or a **complex impedance plan diagram.** The imaginary component of impedance (Z") is plotted versus the real impedance (Z') for each excitation frequency. The plot given illustrates the expected response of the simple circuit with ohmic resistance, polarization resistance and capacitance (fig. 4.5). At high Frequencies only the uncompensated resistance contributes to the real portion of impedance. On the other hand at low frequencies the polarization resistance also contributes to this measurements.

Once the excitation waveform becomes much faster than the change transfer rate, the electrochemical impedance Rp becomes transparent to the technique. An ohmic resistance on the other hand, will represent constant impedance at all frequencies this is consistent with the fact that Rp can also be measured by DC technique but not solution resistance. Rp can be used to calculate corrosion rate of an electrode material in an electrolyte.

(B) Bode Plot :

The figure 4.7 shows Bodes plot. This format permits examination of absolute impedance and phase angle, θ, of the resultant wave form, each as a function of frequency .The log $|Z|$ vs. logω as curve yield values of $R\rho$ and $R\Omega$. At intermediate frequencies, the break point of curve should lie on straight ling with slope of -1. Extrapolating this line to log $|Z|$ axis at $\omega = 1$ ($\log \omega = 0$) yields the value of C dl from the relationship.

$$|Z| = 1 / C_{dl}$$

The θ Vs. log ω plot yields a peak at a frequency corresponding to $\omega^{\theta \max}$ is the frequency in radians per second. at which phase shift of the response is maximum. From this frequency C_{dl} cal be calculated according to:

$$\omega^{\theta max} = 1/ CR\rho\sqrt{(1 + R\rho/R\Omega)}$$

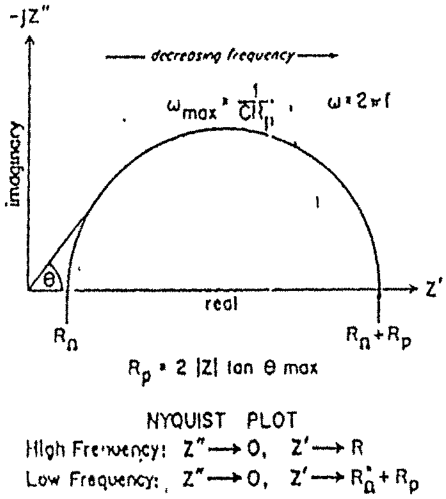
where , $\omega^{0max} = 2\pi f^{\theta max}$

c) Advantages of Bode's plot over Nyquist plot :

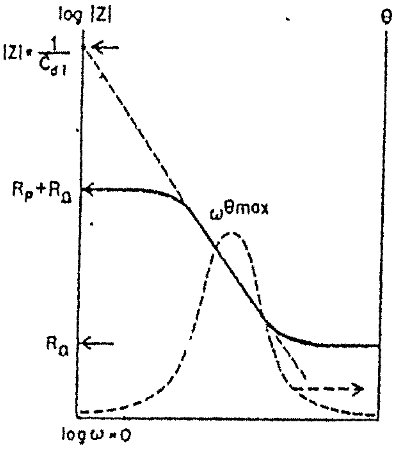
The Bode plot is a useful alternative to the Nyquist plot to avoid the longer measurement times associated with low frequency R'' determinations. This is because the log | Z | Vs logo w) plot sometimes allows more effective extrapolation of data from higher frequencies. The Bode format is also desirable when data scatter precludes adequate limiting of the Nyquist semicircle. In general, the Bode plot provides clearer description of the electrochemical system's frequency-dependant behavior than does the Nyquist plot. Where frequency values are implicit.

a) Single sine technique:

The term single sine derives from the type of waveform used in the technique a fixed frequency sine wave. In the single-sine technique, small amplitude of fixed frequency sinusoidal signal is applied to the test cell and measures the response signal. then the response signal is used to determine the in-phase (real) and out of phase (imaginary') components of the total impedance. From this information, one can determine the degree of phase shift between the input and the output waveforms and thus calculate the magnitude of the impedance.



Nyquist plot
AC impedance profile for a simple electrochemical system.



Bode plot

FIG 4.7 DIFFERENT FORMATE OF ELECTRO CHEMICAL IMPEDANCE

The single-sine techniques involve a series of measurements. To develop an impedance spectrum, one must step through a number of frequencies and make a discrete measurement at each frequency. In a typical experiment, one begins at the highest frequency (100kHz) and repeats the measurements at each successive lower frequency until (10Hz) enough information is gathered to determine the impedance as a function of frequency. Starting from the higher frequency minimize sample perturbation.

b) Multi sine technique:

In an actively corroding system, the electrode undergoes a reaction, making the measurement time a more critical parameter in an impedance experiment. In such a system, the single sine technique has serious limitations that can cause misleading results at lower frequencies.

The multi-sine technique uses a Fast Fourier Transform (FFT) algorithm to process signals in the 100 micro hertz to 11Hertz range. The computer analyses the response and extract impedance information at each of the discrete frequencies used to generate the excitation signal.

The advantages and disadvantages of single and multi-sine techniques :

Single-sine	Multi-sine
Advantages:	
1. High quality data	1. Fast measurements
2. Fast high frequency Measuremenis	2. Mild perturbation
3. Simple instrumentation	3. Improved signal/noise ratio
4. Wide bandwidth	4. More reliable plot
Disadvantages:	
1. Slower low frequencies Measurements	1. Sensitive to harmonic distortion
2. Severe perturbation	2. Vulnerable to alaising

In the present work, combined techniques of single and multi sine are use consecutively to avoid the limitations of both. It provides voltage at different frequencies across the electrodes and signals in terms of impedance were register on the screen as points. When the complete range of frequency is scanned, numbers of points were obtained on the screen, which when connected gives Nyquist plot of the system under study.

The multi-sine technique uses a Fast Fourier Transform (FFT) algorithm to process signals in the 50 micro hertz to 11Hertz range. The computer analyses the response and extract impedance information at each of the discrete frequencies used to generate the excitation signal.

Equivalent electrical circuit Models

In the following section we show some common equivalent circuits models. These models can be used to interpret simple EIS data. Many of these models have been included in the standard modern analysis package.

Model #1 – A Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is shown below:

Purely Capacitive Coating

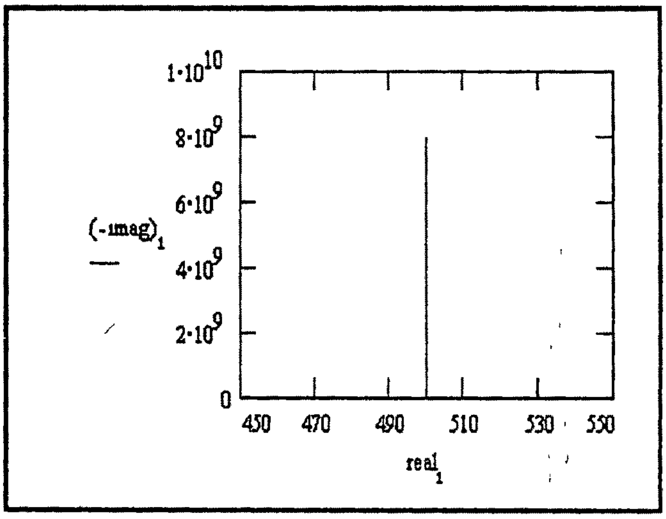
The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.A Nyquist plot for this model is shown in the figure given here. In making this plot, the following values were assigned:

R = 500 W (a bit high but realistic for a poorly conductive solution)

C = 200 pF (realistic for a 1 cm^2 sample, a 25 mM coating, and $e_r = 6$)

$F_i = 0.1$ Hz (lowest scan frequency -- a bit higher than typical)

$F_f = 100$ kHz (highest scan frequency)



Nyquist Plot for an Excellent Coating

The value of the capacitance cannot be determined from the Nyquist plot. It can be determined by **a curve fit** or from an examination of the data points. Notice that the intercept of the curve with the real axis gives an estimate of the solution resistance.

The highest impedance on this graph is close to 10^{10} μohm. This is close to the limit of measurement of most EIS systems. Water uptake into the film is usually a fairly slow process. It can be measured by taking EIS spectra at set time intervals. An increase in the film capacitance can be attributed to water uptake.

Model #2 – Degradation of Coating on Metal

The impedance behavior of a purely capacitive coating was discussed above. Most coatings degrade with time, resulting in more complex behavior. After a certain amount of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can occur at this new interface. The impedance of coated metals has been very heavily studied. The interpretation of impedance data from failed coatings can be very complicated. Only the simple equivalent circuit will be discussed here.

Even this simple model has been the cause of some controversy in the literature. Most researchers agree that this model can be used to evaluate the quality of a coating. However, they do not agree on the physical processes that create the equivalent circuit elements. The discussion below is therefore only one of several interpretations of this model.

The capacitance of the intact coating is represented by C_c. Its value is much smaller than a typical double layer capacitance. Its units are pF or nF, not mF. R_{po} (pore resistance) is the resistance of ion conducting paths that develop in the coating. These paths may not be physical pores filled with electrolyte.

On the metal side of the pore, we assume that an area of the coating has delaminated and a pocket filled with an electrolyte solution has formed. This electrolyte solution can be very different from the bulk solution outside of the coating. The interface between this pocket of solution and the bare metal is modeled as a double layer capacity in parallel with a kinetically controlled charge transfer reaction.

When you use EIS to test a coating, you fit a data curve to this type of model. The fit estimates values for the model's parameters, such as the pore resistance or the double layer capacitance. You then use these parameters to evaluate the degree to which the coating has failed. In order to show a realistic data curve, we need to do this operation in reverse. Assume that we have a 10 cm^2 sample of metal coated with a 12 mM film and that we have 5 delaminated areas. 1% of the total metal area is delaminated. The pores in the film that access these delaminated areas are represented as solution filled cylinders with a 30 mM diameter.

The parameters used to develop the curves are shown below:

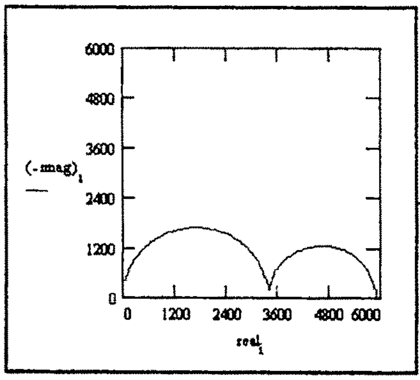
$C_c = 4$ nF Calculated for 10 cm^2 area , $e_r = 6$ and 12 mM thickness

$R_{po} = 3400$ W Calculated assuming $k = 0.01$ S/cm $R_s = 20$ W Assumed

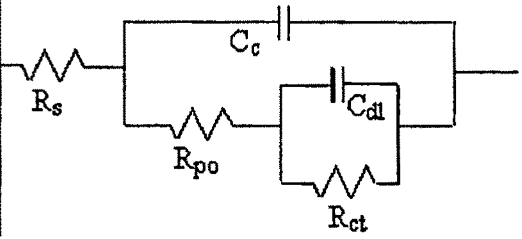
$C_{dl} = 4$ mF Calculated for 1% of 10 cm^2 area and assuming 40 mF/cm^2

$R_{ct} = 2500$ W Calculated for 1% of 10 cm^2 area and using Polarization Resistance assumptions from an earlier discussion

With these parameters, the Nyquist plot for this model is shown in Figure 2-23. Notice that there are two well defined time constants in this plot.



Nyquist Plot for a Failed Coating



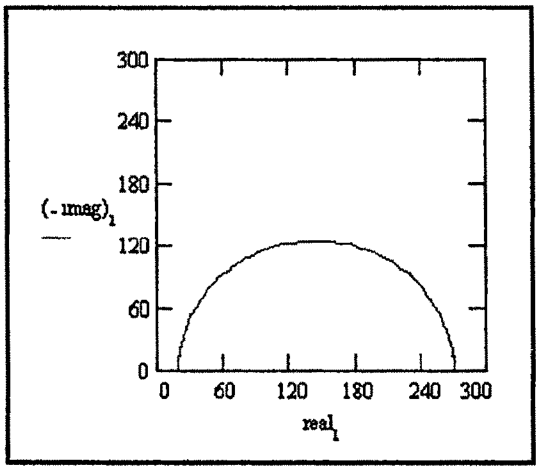
Equivalent Circuit for a Failed Coating

Model #3 -- Randles Cell

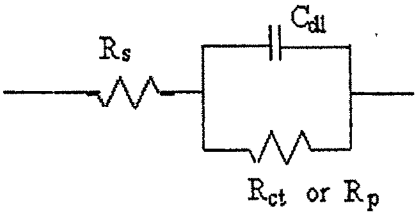
The Randles cell is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer or polarization resistance. In addition to being a useful model in its own right, the Randles cell model is often the starting point for other more complex models.

The equivalent circuit for the Randles cell is shown under. The double layer capacity is in parallel with the impedance due to the charge transfer reaction.

Following is the Nyquist plot for a typical Randles cell. The parameters in this plot were calculated assuming a 1cm^2 electrode undergoing uniform corrosion at a rate of 1 mm per year. Reasonable assumptions were made for the b coefficients, metal density and equivalent weight. The polarization resistance under these conditions calculated out to 250 W. A capacitance of 40 mF/cm^2 and a solution resistance of 20 W were also assumed.



Nyquist Plot for 1 mm/year Corrosion Rate



Randles Cell Schematic Diagram

The Nyquist plot for a Randles cell is always a semicircle. The solution resistance can found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that R_s = 20 W and Rp= 250 W.

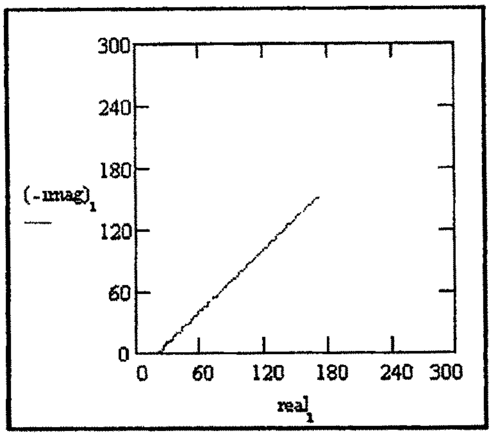
The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance (in this case 250 W).

Model #4 -- Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.

A Nyquist plot for this cell is shown in Figure 2-17. R_s was assumed to be 20 W. The Warburg coefficient calculated to be about 120 Wsec$^{-1/2}$ at room temperature for a two-electron transfer, diffusion of a single species with a bulk concentration of

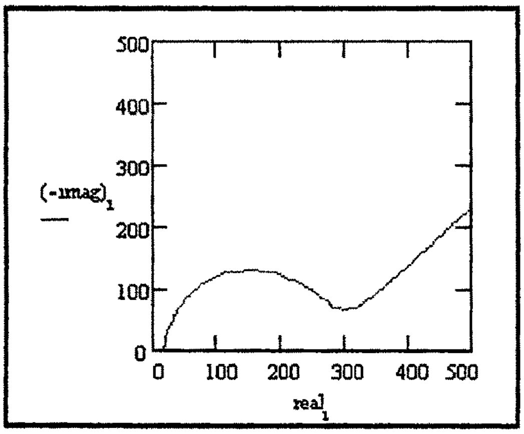
100 mM and a typical diffusion coefficient of 1.6 x10-5 cm^2/sec. Notice that the Warburg Impedance appears as a straight line with a slope of 45°.



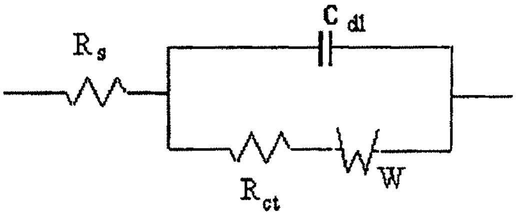
Nyquist Plot for a Warburg Impedance

If the same data are plotted in the Bode format. The phase angle of a Warburg impedance will also turns out to be 45°. Adding a double layer capacitance and acharge transfer impedance, we get the equivalent circuit as shown below:

This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist plot for this circuit is shown under.



Nyquist Diagram for Mixed Control Circuit



Equivalent Circuit with Mixed Kinetic and Charge Transfer Control

Literature on Electrochemical A.C. Impedance

1. J.S.Pettibone and R.L.Kane, " Titanium", in 'Corrosion Resistance of Metals and Alloys', 2nd Ed., Ed. F.L.Laque and H,R.Copson, Reinhold Publishing Crporation, p. 646,(1965).
2. D.Tomashov and P.M.Altovskii; Corrosion and Protection of Titanium, Scientific-technical Publication of Machine-Building literature (Russian Translation), 1963.
3. K..R Trethewav and J.Chamberlain Corrosion for students of science and engineering, Longman scientific and technical. UK edition, p.356, (1988).

4. ASTM G-5: 87, Standard reference test method for making Patentiostatic and Potentiodynamic anodic Polarization measurements
5. Basic of A.C. Impedance Measurements, EG & G Princeton Applied Research, Princeton, NJ, (1983).
6. ASTM B-457. Impedance test.
7. Impedance Spectroscopy; Emphasizing Solid Materials and Systems , J.R. Macdonald, Wiley Interscience publications, 1987
8. Electrochemical Methods; Fundamentals and Applications, A.J. Bard, L.R. Faulkner, Wiley Interscience publications, 1980.
9. Walter, G.W., "A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals", Corrosion Science 26(9), pp 681-703, 1986.
10. Kendig, M., J. Scully, "Basic Aspects of Electrochemical Impedance Application for the Life Prediction of Organic Coatings on Metals", Corrosion 1990 (1), pp 22
11 Electrochemical Methods; Fundamentals and Applications, A.J. Bard, L.R. Faulkner, Wiley Interscience publications, 1980.
12. Electrochemical Impedance: Analysis and Interpretation, J.R. Scully, D.C. Silverman, and M.W. Kendig, editors, ASTM, 1993.
13. Physical Chemistry, P.W. Atkins, Oxford University Press ,1990.
14. Signals and Systems, A.V. Oppenheim and A.S. Willsky, Prentice-Hall, 1983.
15. The Use of Impedance Measurements in Corrosion Research; The Corrosion Behavior of Chromium and Iron Chromium Alloys, J.A.L. Dobbelaar, PhD thesis TU-Delft, 1990.
16. Characterization of Organic Coatings with Impedance Measurements; A Study of Coating Structure, Adhesion and Underfilm Corrosion, F. Geenen, PhD thesis, TU-Delft, 1990.
17. Identification of Electrochemical Processes by Frequency Response Analysis, C. Gabrielle, Solartron Instrumentation Group, 1980.
18. Comprehensive Treatise of Electrochemistry; Volume 9 Electrodics: Experimental Techniques; E. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapani, Chapter 4 "AC Techniques", M. Sluyters-Rehbach, J.H. Sluyters, Plenum Press, 1984.
19. Mansfeld, F., "Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigation Methods of Corrosion Protection", Electrochimica Acta 35(10), pp 1533-1544, 1990.