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Effect of different treatment on biometallic property of Ti-6Al-4V alloy

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Abstract

The corrosion behavior of heat-treated & coated Ti-6Al-4V alloys in Hank's Solution & Ringer's solution is studied by electrochemical method. The Icorr & Ecorr values are calculated. For heat treated & coated samples, electrochemical impedance spectroscopy (EIS) are done. Comparison of corrosion resistance properties of coated and uncoated samples revealed encouraging results.

Keywords*: *Ti-6Al-4V, polyvinyl alcohol, electrophoresis, heat treatment, biocompatibility, EIS

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1. Introduction

Metallic implants are widely used in many treatments and are fairly successful. In the field of bio-medical materials, metallic bio-materials present clear advantages such as good processability, weldability, satisfactory mechanical properties, etc. Some of the engineering materials presently used for implants include 316L stainless steel, Co-based alloys and Ti alloys. Attempts to use titanium began in late 1930s. Its low density and good mechano-chemical properties are salient features for implant applications [1]. Although pure titanium is a very useful material; alloying additives have produced even better results. Extensive research into titanium alloy systems in the early 1950s resulted in several types of alloys, the most important being Ti-6Al-4V. This alloy possesses exceptional strength to weight ratio and good mechanical properties. The main inconvenience of metallic biomaterial is their degradation upon interaction with body fluids [2], hence materials for conventional metallic implants are selected according to their corrosion resistance, i.e. their capacity to generate a protective passive film. Ti-6Al-4V alloy shows excellent corrosion resistance property due to the thermodynamically stable TiO_2, though there are various other oxides on titanium alloys that are also reported to form on the surface [3].

In this work, experiments were carried out to study the effect of heat treatment on the electrochemical behavior of Ti-6Al-4V alloy. The electrochemical experiments were carried out in Ringer's & Hank's solution by potentiostatic polarization technique.

Although there are several advantages of this alloy, its main problem is high reactivity. Different surface treatments improve this. Like coating improves surface properties of a bulk material usually referred to as substrate, such as adhesion, corrosion resistance, wear resistance, scratch resistance, appearances, etc [4].

In this work polyvinyl alcohol was coated on the surface of the Ti-6Al-4V alloy by electrophoresis and characterization was done by electrochemical potentiostatic polarization & EIS (Electrochemical Impedance Spectroscopy). The corrosion properties of the coated samples were compared with those of differently heat treated Ti6Al4V alloy.

2. Experimental

Heat Treatment of Ti-6Al-4V alloys:

As received sample Ti-6Al-4V alloy (Ti1) is an α-β alloy which respond to a variety of heat treatments. In the present work it has been stabilized at β region and furnace cooled, stabilized in β field quenched, and aged in αβ region for three different periods viz. 3, 4 & 5 hr (sample Ti4, sample Ti5 & sample Ti6). Corrosion properties of these heat-treated samples were studied in Hank's solution and Ringer's. The detailed heat treatments and treatment nomenclatures of the samples are given in Table 2.

Coating of Ti-6Al-4V alloys:

Coating was performed by electrophoretic deposition. Polyvinyl alcohol was used as electrolyte for this deposition. The sample was fine polished prior to deposition. Depositions were carried out in a glass cell where sample was used as anode and graphite plate used as cathode. Two depositions were carried out at constant current and by varying the distance between the electrodes. Corrosion properties of these samples were studied in Hank's solution.

Corrosion rate measurement:-

Standard Corrosion Cell was used to perform the electrochemical passivity & polarization tests on standard flat metal specimens. Polarization experiments were carried out using Gamry Potentiostat, in which all the electrochemical measurements were performed in a standard three-electrode system in a 1L glass cell. A three-electrode cell set up consisting of a graphite counter electrode, a saturated calomel reference electrode and specimen as working electrode was employed.

The software used was Gamry Echem Analyst. Using potentiodynamic scan rate of 1mV/sec the I_{CORR} –E_{CORR} values were obtained by Tafel's extrapolation method. All polarization experiments were done with the as received & heat-treated samples and results are given in figure 1 & 2 and table 3 & 4. The composition of Hank's solution is as follows: NaCl-.8%, Glucose- .1%, KCl-.04%, $NaHCO_3$- .035%, $CaCl_2$- .014%, $MgCl_2,6H_2O$-.01%, Na_2HPO_4,$2H_2O$- .006%,KH_2PO_4-.006%, $MgSO_4,7H_2O$- .006%. The pH 7.4 of this solution was maintained throughout the experiment. The composition of Ringer's solution was: NaCl- 8.6gm/L, KCl-0.3gm/L, CaCl-0.33gmL.

Impedance Spectroscopy measurements:-

For electrochemical impedance spectroscopy measurements an auto lab three-electrode corrosion cell was used. Potentials were measured using an AutolabPC14G300-44030 potentiostat/galvanostat, expanded with a Potsat model seriesG300. The impedance experiments were carried out using AC voltage 100mV root-mean-square & the DC voltage 1V the frequency ranged from 10 kHz to10mHz at 10 cycles per decade. The absolute impedance and phase angle were measured at each frequency. Nyquist & Bode plots were obtained. Curve fitting was done to choose the respective models and to get the rough value of all model fit parameters. From the Bode plot by rough estimation, these values were calculated. The other parameters like R_f, C_f, R_{po}, Y_o and & α were also estimated and the exact values of Rp & Ru were calculated by the Echem software. The impedance data were interpreted on the basis of equivalent electric circuit, using the Fit model (simplex model) program for fitting the experimental data. For the Ti-6Al-4V alloys EIS data obtained in Ringer's solution and Hank's solution are given in the table 6.

3. Discussion

From the Ecorr and Icorr values of heat-treated samples tested in Hank's solution and Ringer's solution it can be seen that Icorr values of all the heat treated samples are lower than the as received sample. Of these, heat-treated samples, Ti6 sample (aged for 5 hours) shows best corrosion resistance property in both Ringer's and Hank's solution. Thus heat-treatment has a positive effect on the Icorr values of the samples. In some cases even the Ecorr values of the treated samples are found to be better compared to the as received sample. The change of test solution has also an effect on the Ecorr of the Ti-6Al-4V alloy. This is because the chloride content of Hank's solution is higher than the Ringer's solution. Ti2 alloy shows poorest Ecorr value in Hank's solution among all the samples. But the same sample shows moderate nobility in Ringer's solution.

It is expected that protective coatings will improve the corrosion resistance property of the Ti-6Al-4V alloy. Two samples were electrophoretically coated with polyvinyl alcohol. Distance between electrodes has an effect on corrosion resistance property of the samples (table 5). The coated Ti-6Al-4V (80mA-1cm) shows better Icorr value (42.17nA/cm2) and also shows better nobility i.e. higher Ecorr value (-290.7mV) than the coated Ti-6Al-4V (80mA-2cm) alloy.

Polarization curve of Ti-6Al-4V alloy in Hank's solution shows clear passivity (fig 2) whereas the same alloy in Ringer's solution have no clear passive region (fig 1). In fact it shows pseudo passive region. So to know the nature of the protective passive layer electrochemical impedance spectroscopy was done in Ringer's solution.

For electrochemical impedance spectroscopy Bode plot can be used to determine the polarization resistance (Rp) & the solution resistance (Ru). The impedance spectra were analyzed using the equivalent electric circuits. For Ti-4Al-6V alloy sample in Ringer's and

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Hank's solution good fits were obtained with the constant phase element circuit (Fig 7). Constant phase element (CPE) implies a uniform passive layer and arises due to the distribution of relaxation times resulting from the electrode surface. The fitted parameters are listed in the Table 6. From the Bode phase plots shown in fig 4a it can be noted that, for all the treatment phase angle drops towards zero degree at very high frequencies, indicating that the impedance is dominated by solution resistance in this frequency range. Only for the Ti2 sample, phase angle starts near 40˚, then rises up to near 60˚ and again drops towards 40˚ at very high frequency. The phase angle of some samples (Ti2, Ti-80mA-2cm, Ti3, Ti4, Ti5, and Ti6) drops slightly towards lower values in the low frequency region indicating the contribution of surface film resistance to the impedance. However, the phase remains close to 60˚- 80˚ over a wide range of frequency indicating a near capacitive response for all the alloys. This behavior is indicative of a typical thin oxide film present on the surface.

Bode magnitude plots (fig 4b) were also similar in nature for all alloys. Bode magnitude plots were characterized by two distinct regions. In the higher frequency region (1-100 KHz), the Bode magnitude plots exhibited constant Zmod values vs frequency with a phase angle near 0˚. This was due to response of the solution resistance Ru. The Ti2 sample shows constant Zmod values vs frequency throughout the all frequency range. For other samples, the spectra displayed a linear slope of about -1 in the broad low and middle frequency range. This is the characteristic response of a capacitive behavior of surface film.

The impedance spectra (fig 5 & 6) illustrate a pure capacitive behavior for all the treatment. But samples Ti5, Ti1, Ti6 show a diffusion tail, which suggest that the sample acted as a porous electrode. The Ti2 sample shows a long diffusion tail. But the Bode phase plot & magnitude plot and Rp value (700.0e3) of this sample indicates that this sample is more corrosion resistant than the others.

4. Conclusion

1. The heat-treated Ti-6Al-4V alloy shows good corrosion resistance than the as received Ti-6Al- 4V alloy in both Ringer's and Hank's solution.
2. Variation of solution has a clear effect on Ti-6Al-4V alloy. It may be due to the different concentration of chloride ion.
3. Coating improves the corrosion resistance property of Ti-6Al-4V alloy
4. Among all the samples Ti6 shows best corrosion resistance property in both Ringer's & Hank's solution.
5. But EIS data wise Ti2 sample shows best corrosion resistance property.

References

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Table captions:

Table 1: Composition of Ti6Al4V

Table 2: Heat Treatment Details of Ti6Al4V

Table 3: Corrosion data of heat-treated Ti-6Al-4V Alloy in Ringer's solution (From fig 1)

Table 4: Corrosion data of heat-treated Ti-6Al-4VAlloy in Hank's solution (From fig 2)

Table 5: Corrosion data of coated Ti-6Al-4V Alloy in Hank's solution (from fig 3)

Table 6: Derived data from EIS curves of heat treated Ti-6Al-4V Alloy in Ringer's Solution (from fig 4(a) & (b))

Figure captions:

Fig 1 Polarization curves of heat treated Ti-6Al-4V Alloy in Ringer's solution

Fig 2 Polarization curves of heat treated Ti-6Al-4V Alloy in Hank's solution

Fig 3 Polarization curves of coated Ti-6Al-4V Alloy in Hank's solution

Fig 4: Impedance spectra of Ti-6Al-4V alloy in Ringer's and Hank's solution: (a) Bode phase plots and (b) Bode magnitude plots

Fig 5: Nyquist plots of Ti-6Al-4V alloy in Ringer's and Hank's solution

Fig 6: Nyquist plots of Ti2 in Hank's solution

Fig 7: Equivalent Circuit of CPE model

Acknowledgement

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Table 1

C	Fe	N_2	O_2	Al	V	H_2 (Sheet)	H_2 (Bar)	H_2 (Billet)	Ti
<0.08%	<0.25 %	<0.05 %	<0.2 %	5.5-6.76 %	3.5-4.5 %	<0.015 %	<0.0125 %	<0.01 %	Balance

Table 2

Serial No.	Treatment	Sample Nomenclature
1	Stabilized at 900oC followed by furnace cooling	Ti2
2	Stabilized at 900oC, water quenched, held at538oC, furnace cooled	Ti3
3	Stabilized at 900oC, water quenched, aged at 538^{0}C for 3hr,	Ti4
4	Stabilized at 900oC, water quenched, aged at 538^{0}C for 4hr	Ti5
5	Stabilized at 900oC, water quenched, aged at 538^{0}C for 5hr	Ti6

Table 3

Sample Name	**E_{CORR}(mV)**	**I_{CORR}(nA/cm^2)**
As received (Ti1)	- 577	327.9
Ti2	- 470.9	255.6
Ti3	- 430.2	240.6
Ti4	- 337.2	235.6
Ti5	- 395.3	225.6
Ti6	- 424.2	171.6

Table 4

Sample Name	E_{CORR}(mV)	I_{CORR}(nA/cm^2)
Ti1	-143.0	3890
Ti2	-364.5	1166.2
Ti3	-237.2	385.73
Ti4	-255.8	320.33
Ti5	-237.2	237.46
Ti6	-218.6	89.5

Table 5

Sample Name	Ecorr(mV)	Icorr(nA/cm^2)
Coated Ti-6Al-4V(80mA-1cm)	-290.7	42.17
Coated Ti-6Al-4V (80mA-2cm)	-407.0	100.26

Table 6

Sample Name	Rp value	Ru value	Y_0	Alpha	model type
As received (Ti1)	137.3e3	181.3	43.97e-6	789.2e-3	CPE
Ti2	700.0e3	161.8	1.695e-6	749.0e-3	CPE
Ti3	82.29e3	176.9	39.46e-6	748.1e-3	CPE
Ti4	37.65e3	25.64	56.09e-6	789.4e-3	CPE
Ti5	125.4e3	51.10	33.52e-6	732.0e-3	CPE
Ti6	43.08e3	23.13	39.57e-6	757.7e-3	CPE
Ti-6Al-4V (80mA-1cm)	85.31e^3	12.99	159.9e^{-6}	818e^{-3}	CPE
Ti-6Al-4V (80mA-2cm)	21.27e^3	22.96	156.2e^{-6}	843.2e^{-3}	CPE

Fig 1

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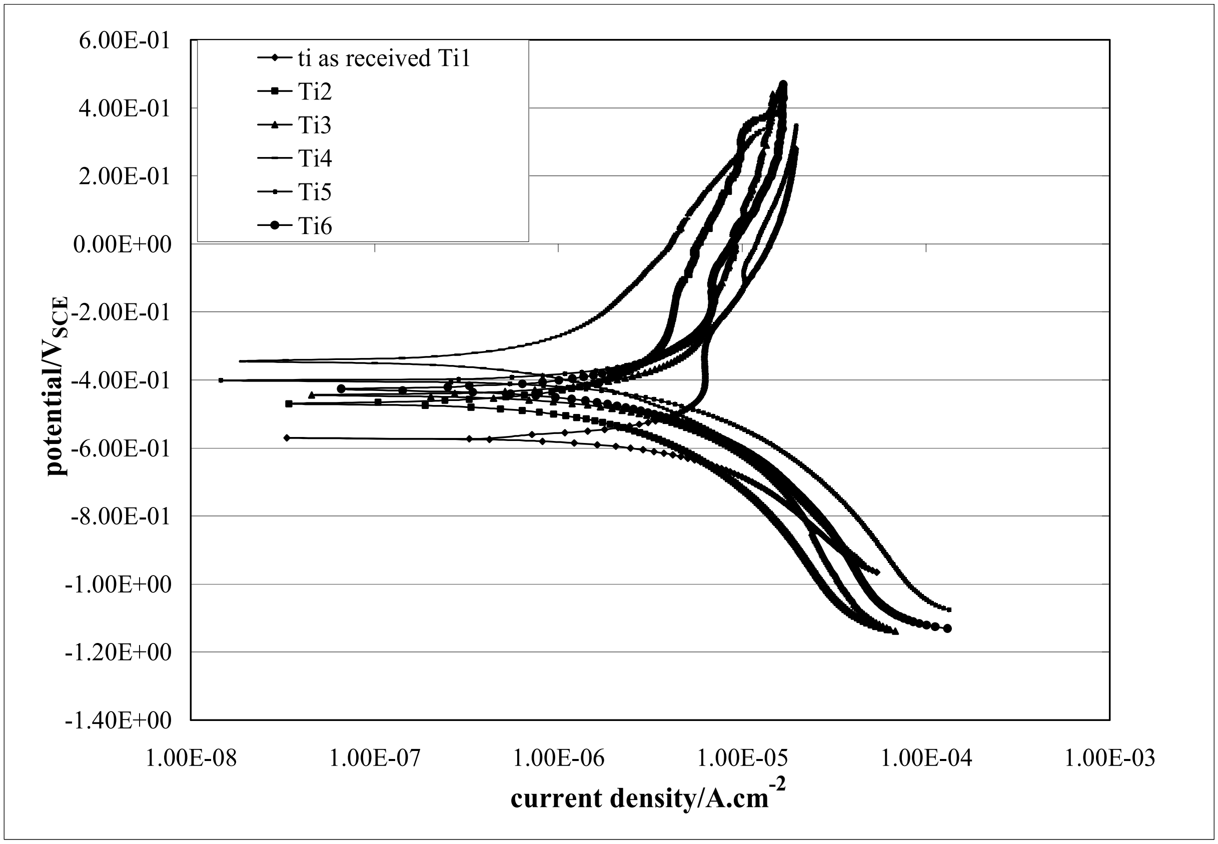
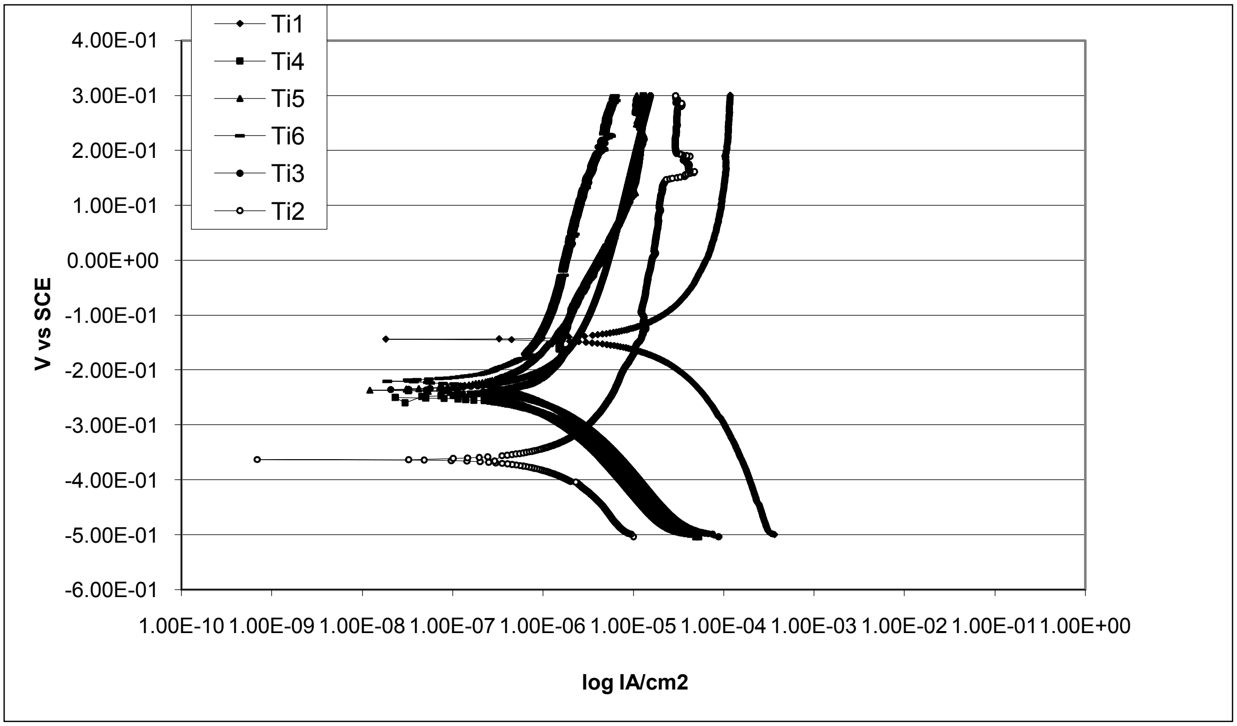


Fig 2


Ti1
Ti4
Ti5
Ti6
Ti3
Ti2
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3.00E-01
2.00E-01
1.00E-01
0.00E+00
-1.00E-01
-2.00E-01
-3.00E-01
-4.00E-01
-5.00E-01
-6.00E-01
V vs SCE
1.00E-10 1.00E-09 1.00E-08 1.00E-07 1.00E-06 1.00E-05 1.00E-04 1.00E-03 1.00E-02 1.00E-01 1.00E+00
log IA/cm2

Fig 3

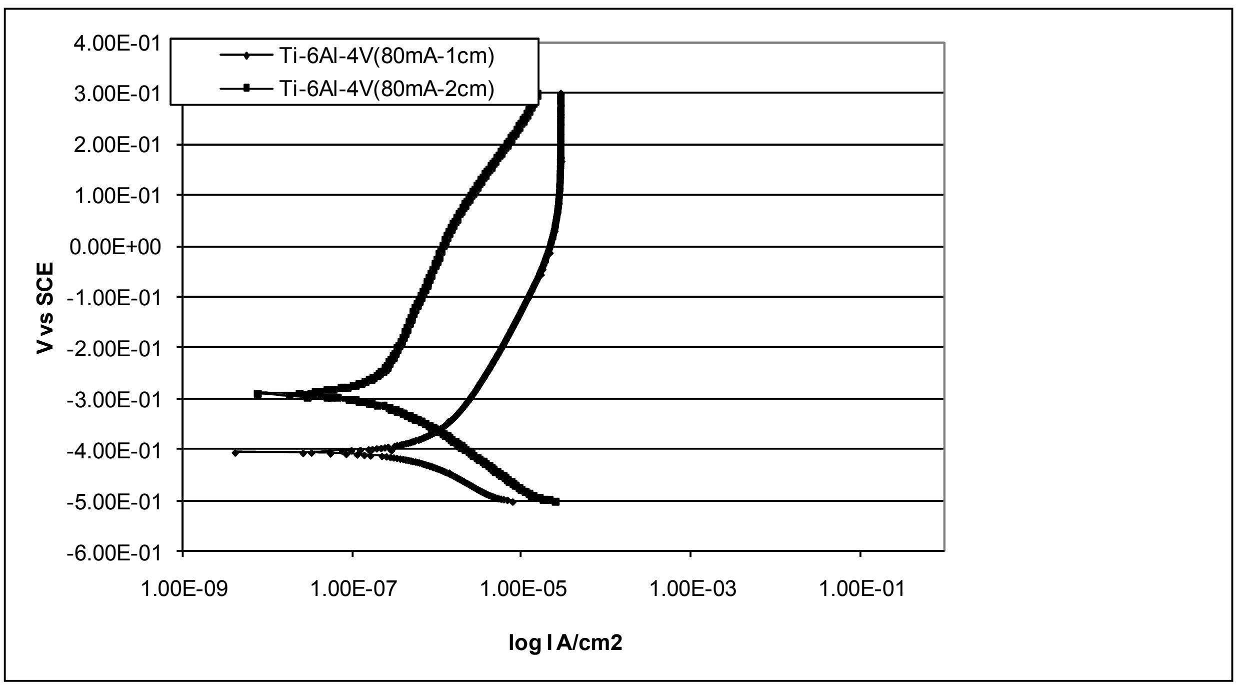

Ti-6Al-4V(80mA-1cm)
Ti-6Al-4V(80mA-2cm)
4.00E-01
3.00E-01
2.00E-01
1.00E-01
0.00E+00
-1.00E-01
-2.00E-01
-3.00E-01
-4.00E-01
-5.00E-01
-6.00E-01
V vs SCE
1.00E-09 1.00E-07 1.00E-05 1.00E-03 1.00E-01
log I A/cm2

Fig 4(a)

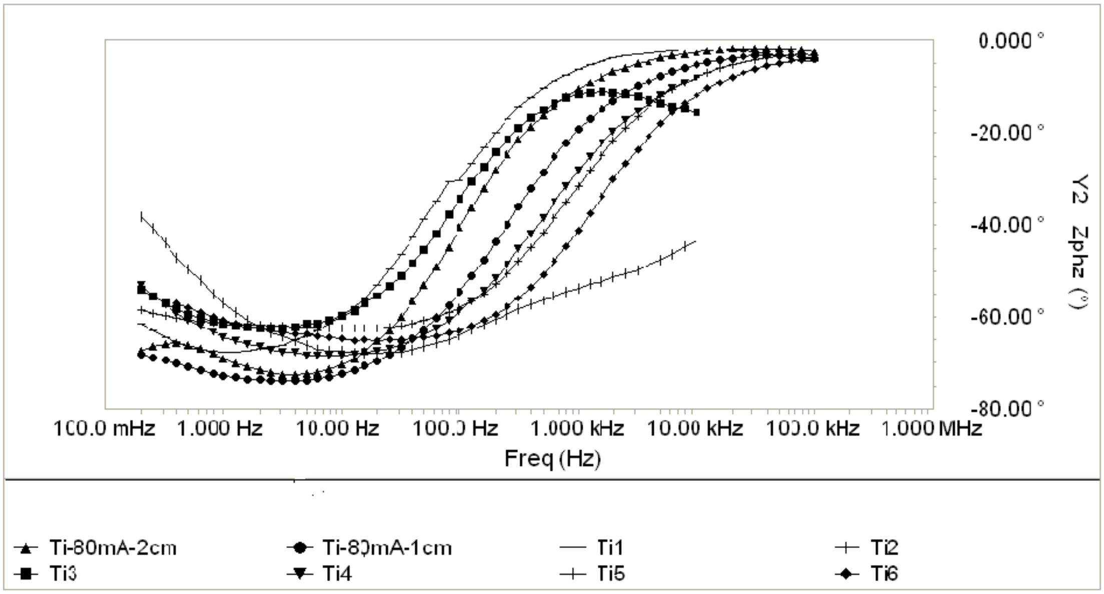
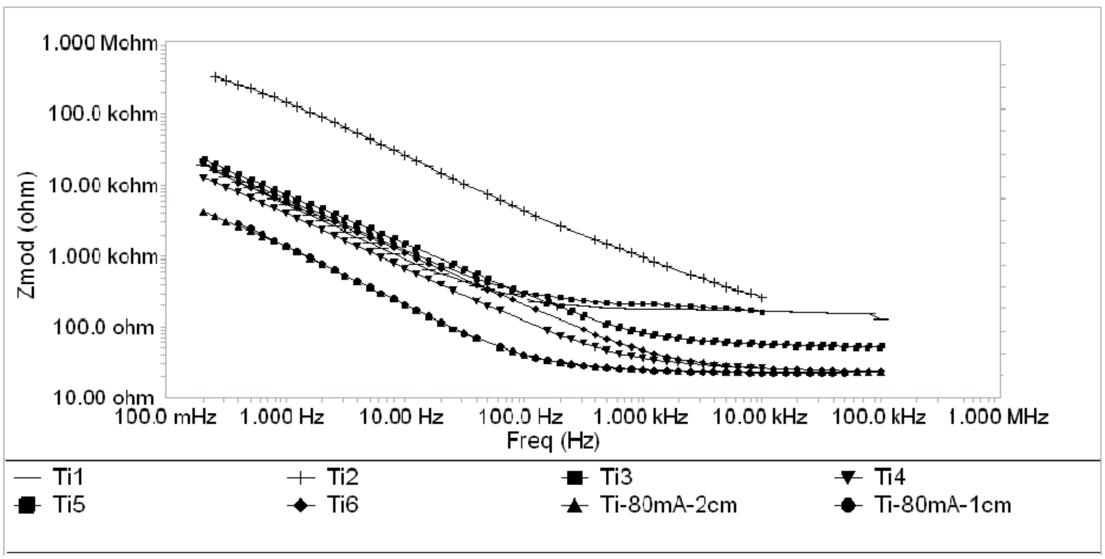

0.000 °
-20.00 °
-40.00 °
-60.00 °
-80.00 °
Y2 Zphz (°)
100.0 mHz
1.000 Hz
10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
100.0 kHz
1.000 MHz
Freq (Hz)
Ti-80mA-2cm
Ti-80mA-1cm
Ti1
Ti2
Ti3
Ti4
Ti5
Ti6

Fig 4(b)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1.000 kohm
100.0 ohm
10.00 ohm
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10.00 Hz
100.0 Hz
1.000 kHz
10.00 kHz
100.0 kHz
1.000 MHz
Freq (Hz)
Ti1
Ti2
Ti3
Ti4
Ti5
Ti6
Ti-80mA-2cm
Ti-80mA-1cm

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Fig5:

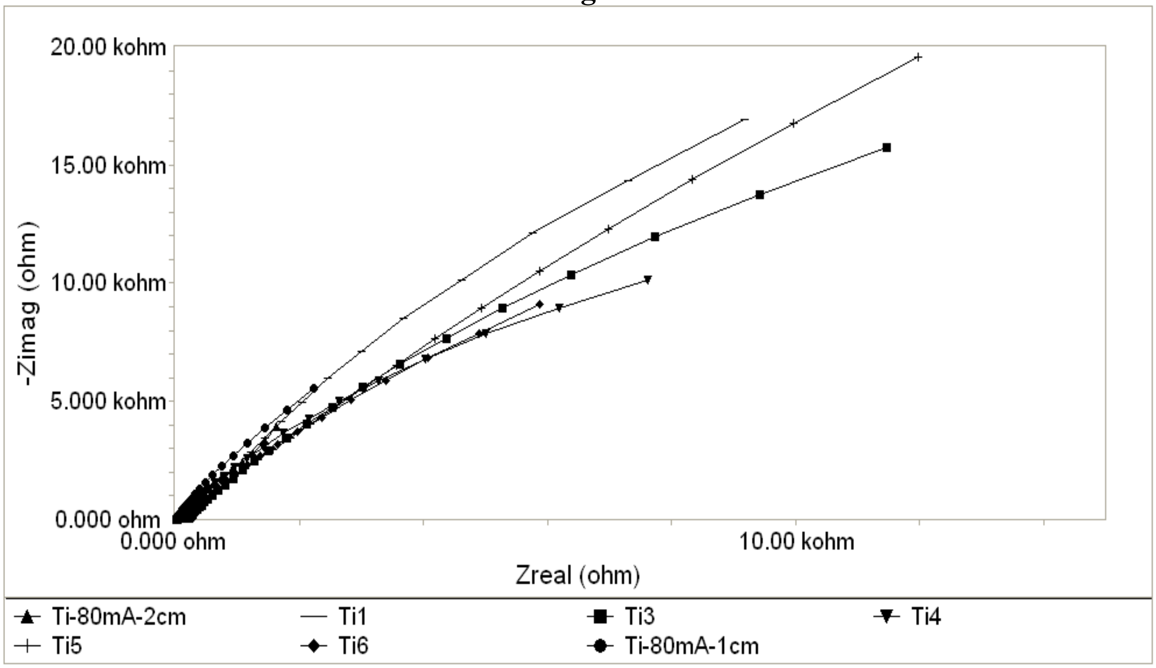

Fig6:

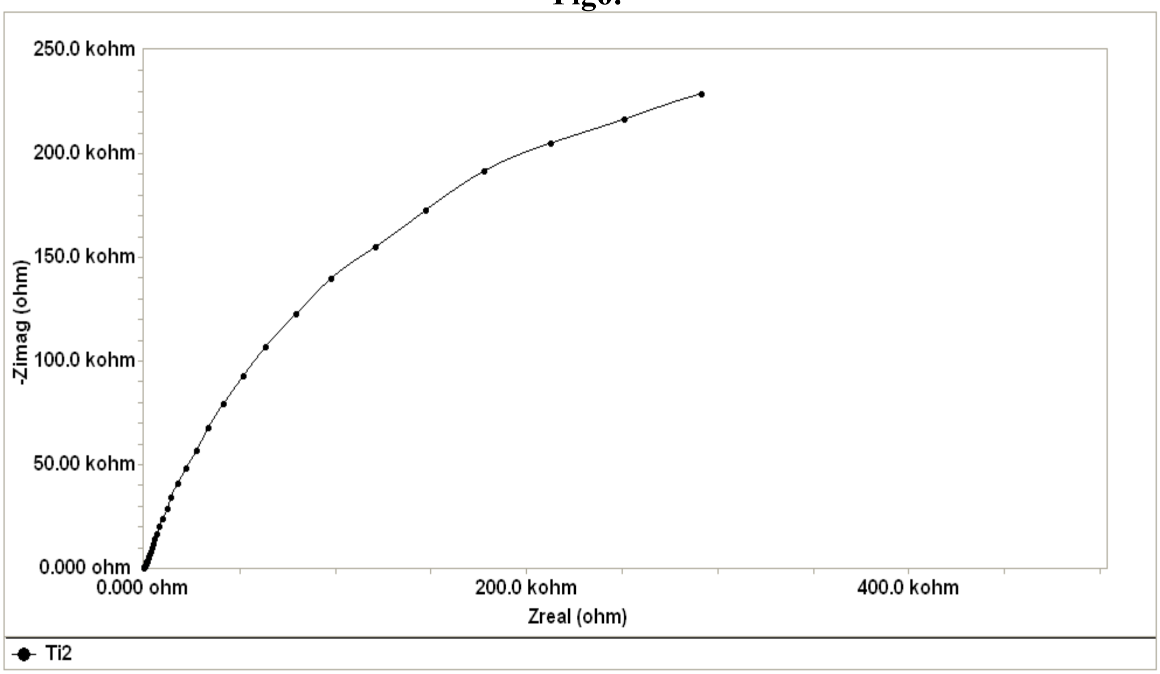

Fig 7

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