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Evaluation of Corrosion and Contact Angle of Medical Implants Coated with DLC

Eraj Humayun Mirza and WMA Ibrahim
Department of Biomedical Engineeing, University of Malaya, Kuala Lumpur, Malaysia, 50603.
erajhumayun@hotmail.com and wmohdazhar@yahoo.com

Abstract—Biomaterials are widely being used as coatings on various medical implants and devices to prevent implants and medical devices from the environment they interact with; to be precise the coatings prohibit any unwanted biocompatibility issue. A research was carried out on stainless steel disks that commonly become the very foundation of medical implants such as artificial hip bones or other plates that are used invasively for fixation of fracture. For the purpose of coating Diamond-Like Carbon (DLC) coating was used because they can be coated on wide range of materials that include: metals, ceramics, glasses and plastics. DLC coatings exhibit low friction, wear resistance, corrosion resistance and biocompatible properties. The DLC coatings when combined with different elements can be tempered as per required. Diamond-Like Carbon (DLC) coatings with various Silicon and Fluorine content were deposited on 10mm 316L Stainless Steel disks. The samples were investigated for their surface energies and their corrosion resistance. The corrosion resistance behavior was tested in 4 different testing solutions, which were the Phosphate Buffer Saline, 3.5% NaCl and two different concentrations of HCl. To test the surface energies, contact angle measurement was adopted and the result showed significant decrease in the total surface energy for the Fluorinated coatings. While potentio-dynamic polarization test method were performed for testing the corrosion resistance properties of the samples. The corrosion rates revealed that 20.7% F-DLC coating had promising results which was showing the best corrosion resistance; also the 19.7% Si-doped DLC had the best corrosion resistance in its class.

Keywords-component; Bacterial adherence, Biocompatibility, Coatings, Corrosion, Stainless Steel.

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I. Introduction

The field of medicine has grown very much and it is not just stuck to the normal routine check-ups. The medical device industry is a vast field which combines many different areas of specialization.

For biomedical implants and devices it is very important that they resist the wear and tear of daily routine and the way they are used. The Diamond-Like Coatings (DLC), provide a suitable basis for the medical implants. The DLC are of diamond family and their properties can be altered as required, also further their properties can be adjusted by the infusion of Silicon, Titanium, Sulphur, Tungsten, Nitrogen or Silver [1]. The project deals with the testing of corrosion properties of different DLC Coatings.

A. *Medical Devices*

A device or any equipment used for the diagnostic, therapeutic or surgical purpose can be named as medical device. From pacemaker to artificial heart valves and from medical thermometers to X-ray machines, all are rated as medical devices. By definition the medical devices are defined in a various ways, one according to the "Council of the European Communities" and another by the "US Food and Drug Administration" more commonly called FDA [2].

According to the Council of the European Communities, in a council directive 93/42/EEC of 14 June 1993 concerning medical devices the medical devices are defined as:"instrument, apparatus, appliance, material or other article, whether used alone or in combination, including the software necessary for its proper application intended by the manufacturer to be used for human beings for the purpose of:

- Alleviation of disease, its treatment, diagnosis, disease prevention and monitoring.
- Alleviation of injury, its treatment, diagnosis, disease prevention and monitoring.
- Investigating the replacement or modification of anatomy or of a physiological process,

- Control of conception, and which does not achieve its principal intended action in or on the human body by pharmacological, Immunological or metabolic means, but which may be assisted in its function by such means." [2].

Medical devices are usually coated with different materials as per requirement to prevent any bacterial adhesion that may further harm the patient's well-being. A medical implant such as hip joint, knee joint, patellar implant, pace maker, heart valves all are medical devices.

B. *Coatings*

To protect patient and the pupil against different biocompatibility issues related to the medical device that is in direct or indirect contact, different types of coatings are used that may be altered according to the requirements. Coatings for the medical device involves plastic coatings on the device, high performance ceramic coatings, diamond like carbon (DLC) coatings, fluorine coatings and many others. Shown in figure 1 is the structure of a-C: H system.

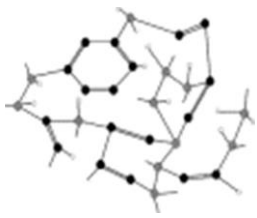

Figure 1. Structure of amorphous Diamond-like Carbon [6]

C. *Corrosion*

Corrosion can generally be defined as it is the destruction or deterioration of any material by a chemical interaction with the environment, or any sort of electrochemical reaction. It is derived from a Latin word "corrodere" which means to eat away [3]. There exist different types of corrosion ranging from uniform corrosion, galvanic corrosion to pitting corrosion. The corrosion of any metal in aqueous solution is considered as it is in an equilibrium situation and the rate of dissolution of metal is equal to that of the deposition rate of the metal. The metal for consideration is (Ma) so the electrode potential will be given by the Nernst equation.

$$E_O = E_O^O + \frac{RT}{nF}\ln[Ma^{n+}] \quad (1)$$

Where R is the universal gas constant, T is the absolute temperature, n is the number of electrons involved, F is the Faraday Constant, E_O^O is the standard potential for the metal and Ma^{n+} is the concentration of the metal ions.

The Nernst equation plays an important role in relating the cell potential E to the standard potential E0 and concentration of the electro-active ion.The oxidizing and reducing conditions plays an important role in corrosion. As far as this project is concerned it relatively emphasizes more on to the electrochemical corrosion.

D. Electrochemical Corrosion

The process of electrochemical corrosion involves cell reaction in two steps. One is oxidation reaction that occurs at anode and the other at cathode which is reduction. An example is given below which shows corrosion of metal in water.

- Considering iron in water

Anode reaction: $2Fe \Rightarrow 2Fe^{2+} + 4e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

The reactions shown above will be different in the case of other metal and aqueous solution respectively. In figure 2, complete process of corrosion is shown, that depicts how a metal corrodes. The charge is transferred through the corroding surface followed by flow of current by movement of ions. Then within the metals there is electron transfer and the anode corrodes while there is a deposition at cathode.

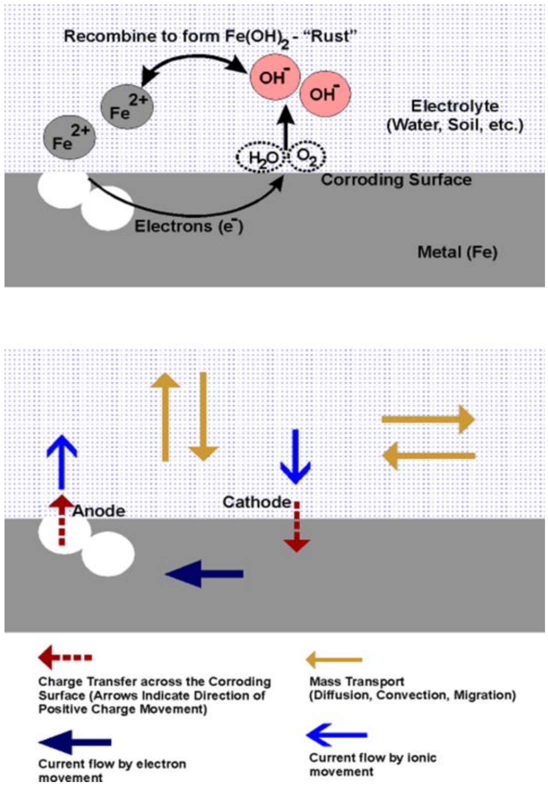

Figure 2. Electrochemical corrosion process of iron in water [7]

E. *Contact Angle*

The measurement of contact angle is useful as all the solids when immersed in aqueous solutions exhibit a property called physico-chemical property of a solid surface. The interaction between the molecules of aqueous solution and the solid depend upon the chemistry of both, the solid and the liquid. So the surface energy measurement gives a measure of the intermolecular forces. So the surface energies are calculated to minimize the bacterial adhesion to any surface by modifying the surface. To find the surface energies a measure of contact angle is required. The contact angle measurement system comprises of a CCD camera, a system of micro syringes and a temperature control chamber. The camera measures the angles from both the left and the right side of the drop. The liquid generally used for calculating the surface energies are water, Di-iodomethane and ethylene glycol.

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II. MATERIALS AND METHODS

A. Preparation of Coatings

1) Fluorinated DLC Coating Preparations

The diamond-like carbon coatings (DLC) were prepared by radio frequency plasma-enhanced chemical vapor deposition (rf-PECVD) [4]. 316L Stainless steel was selected for the deposition of the coatings. The samples were 10mm or 1cm disks in diameter. The coating deposition equipment comprised of, a plasma reactor with pumping system with rotary and turbo molecular pumps which had a controlled gas supply. In the chamber, base pressure of 1x10-3Pa was maintained before the deposition started. The process gases that were used are Acetylene (C2H2), carbon tetra fluoride (CF4) and argon (Ar) as shown in figure 3.

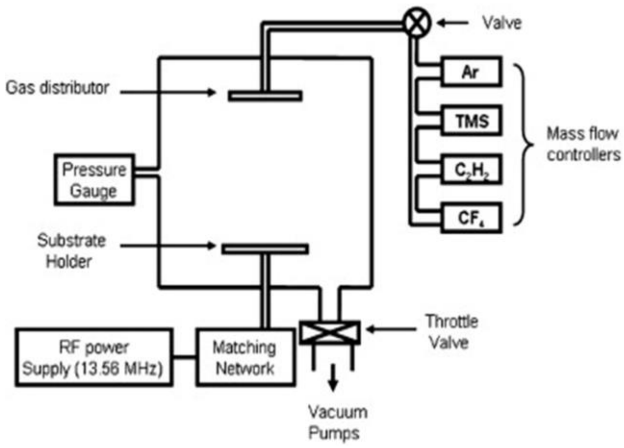

Figure 3. Schematic representation of radio frequency Plasma-enhanced Chemical Vapour Deposition. [4]

The infusion of gasses into the chamber was controlled by the mass flow controllers. A valve was present at the combined inlet of the gasses just before the chamber, which allowed a total pressure to be set. Before the deposition started the substrates were cleaned for 5 minutes with argon plasma at a pressure of 3.3 Pa. for better adhesion an interlayer of hydrogenated amorphous silicon carbide (a-SiC:H) was deposited on the substrate using tetra methyl saline (TMS) which act as a precursor for an improved adhesion. The deposition rate of the interlayers was 3.3 Pa and the thickness of interlayer was about 50 nm. The Fluorinated

Diamond-like carbon coatings were then deposited on the substrates using a mixture of acetylene and carbon tetra fluoride. The flow rate of carbon tetra fluoride was varied for depositing different concentrations of the fluorinated diamond-like carbon coatings. The Fluorine contents were 6.5, 20.7 and 39.2 atomic per cent.

2) *Silicon Doped DLC Coating Preparation*

As in the Fluorinated DLC preparation here also the 316L stainless steel was used. The disks were 1cm or 10 mm in diameter. In the case of silicon doping, magnetron sputtering technique was used. The stainless steel disks were first cleaned in an ultrasonic bath for 10 minutes containing acetone. It was then rinsed with distilled water and left to dry. Before deposition the substrates were further cleaned by Ar+ bombardment. Tetra methyl saline was used for doping silicon into the DLC films. The flow rate was changed as silicon content required was 3.7, 9.0 and 19.7 atomic per cent.

B. *Contact Angle and Surface Energy Measurements*

The contact angles of all the coatings were measured by sessile drop method with Data physics OCA-20. The instrument is having a CCD video camera attached to it which is having a resolution of 768 x 576 pixels; it can capture up to 50 images per second. Attached with the equipment are a micro syringe system and a temperature control chamber. Software is provided with the equipment which is compatible on a windows based computer system. The drop is analysed by the analysis software which calculates the right and left contact angles with an accuracy of ± 0.1 o. The flow of the process is shown in figure 5 that shows a proper flow of steps in measuring the contact angle.

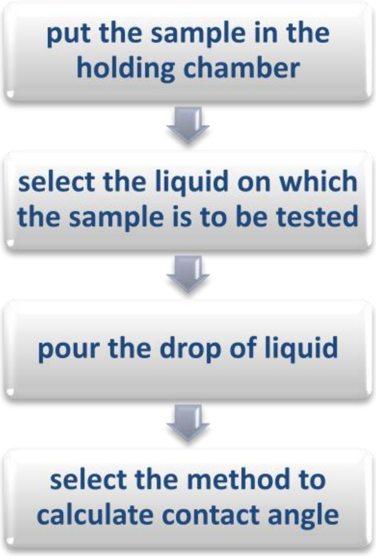

Figure 5. Steps involved in contact angle measurement

The three liquids used are water, Diiodomethane and ethylene glycol. The surface tension components which are the dispersive components γ_L^{LW}, electron acceptor component γ_L^{+} and the electron donor component γ_L^{-} of all the three test liquids were calculated at room temperature.

The process started by dispensing a drop of water and then calculating its surface tension components by the software provided. Similar steps were followed by the remaining two test liquids. The method used for calculating the components was Van Oss acid-base approach. The readings for all the test liquids were tabulated and are shown in table I.

TABLE I. TEST LIQUIDS AND THEIR SURFACE TENSION COMPONENTS

Surface tension data (mN/m)	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^{+}	γ_L^{-}
Water H_2O	71.45	21.40	50.05	25.03	25.03
Diiodomethane, CH_2I_2	49.55	49.55	0	0	0
Ethylene glycol, $C_2H_6O_2$	47.25	28.55	18.70	1.89	46.25

C. Solution Preparation

1) Phosphate Buffer Saline (PBS) Solution

The DLC coatings are usually used in the medical devices in the form of various implants so for testing the samples in simulated body fluid environment a solution of 0.9% NaCl by weight is used. To replicate body fluid environment PBS is used. To make the solution, one tablet of PBS was dissolved in 100 ml of distilled water and magnetic stirrer was used to dissolve the tablet completely. The stirrer was set at a speed of 600 RPM and the solution was left over the stirrer for about 2 minutes until the tablet dissolves. The procedure was performed at room temperature.

2) *Sea Water*

The corrosion is best tested in aggressive conditions, so firstly the corrosion was tested in artificial seawater conditions. The constituent used was pure Sodium Chloride (NaCl). For making NaCl solution 3.5% by weight, 3.5gms of NaCl was measured by digital electronic balance the measured salt was then placed into a beaker and the beaker was then filled up by distilled water up to a 100 ml mark. For mixing the solution magnetic stirrer was used, the stirrer was set at 500 RPM and after a minute the beaker was removed from the stirrer. The procedure was performed at room temperature.

3) *Hydrochloric Acid 0.05M*

Apart from the corrosion testing in seawater environment or the simulated body like environment the corrosion of the DLC is more visible in the acidic solution. The 0.05M HCl solution was prepared by pure HCl solution which was 37%. Out of pure HCl acid 4.2 ml was taken out from an electronic pipette and was poured into a beaker. The beaker was then filled by distilled water till the 1000 ml mark. The procedure was performed within the safety cabinet and at room temperature.

4) *Hydrochloric Acid 2.0M*

The DLC samples were tested against all odds and to analyze the corrosion in 2.0M HCl the solution was carefully prepared in safety cabinet and 166 ml of pure HCl was taken out from an electronic pipette and then was dispensed into a beaker. The beaker was filled up to the

1000 ml mark. Preparation of HCl solution was carried by simple calculation involving the concentration and volume equation which is stated below.

$$C_1V_1 = C_2V_2 \tag{2}$$

Here

C_1 is original concentration of the solution.

C_2 is final concentration of the solution, after dilution.

V_1 is volume about to be diluted

V_2 is final volume after dilution

D. *Electrochemical Corrosion Tests*

The corrosion tests that were performed were based on simple electrochemical theory which comprises of an anode, a cathode and a conducting medium for the movement of ions which is more generally called an electrolyte and an electrical connection between cathode and anode for the flow of electron current as sketched in figure 4. A simple three electrode system was set up which had a Potassium Chloride (KCl) reference electrode, it is also said to be a saturated calomel electrode. A simple counter electrode and a working electrode which had the sample attached to it were used. Figure 4, is a schematic representation of the experiment, it gives an overview of the experimental setup.

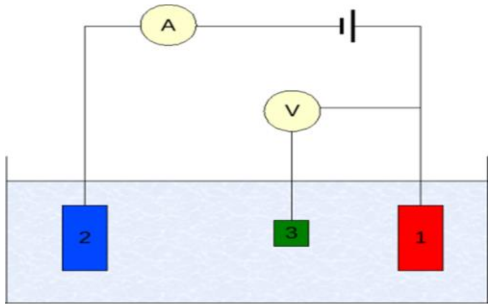

Figure 4. Schematic of three electrode Electrochemical cell system

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III. RESULTS AND DISCUSSION

A. Surface Characterisation

Figure 5, shows the steps in the process of measuring contact angle. Contact angles of all the eight samples which were measured by Data physics OCA-20, the test liquids were Water (H2O), Diiodomethane (CH2I2) and Ethylene glycol (C2H6O2). The tests were carried at room temperature. Figure 6 shows the contact angle of all the samples. Starting from sample 1 which is stainless steel followed by standard DLC which is 2 and then the Si-Doped DLC with silicon content of 3.7%, 9.0% and 19.7% respectively and from 6 to 8 are the Fluorine coated DLC with contents of Fluorine 6.5%, 20.5% and 39.2% respectively. There was a similar trend in all the three liquids, the water had the highest contact angle measurements followed by ethylene glycol and Diiodomethane respectively. All the angles were measured in degrees.

The results of the contact angle show that the Si-doped DLC coatings which were 3, 4 and 5 had the lowest contact angles while the one with fluorine which were 6, 7 and 8 had grater contact angles. The stainless steel which was 1 had a high contact angle and it was somewhere in the middle between the 20.7 % and 39.2 % F.DLC coatings. This shows that higher the Fluorine contents the greater the contact angle and lesser would be the adhesion.

The results obtained are having similar trend as it was reported by (X.J. Su et al., 2010) [5]. So it can be said that, higher Fluorine content is favourable for lesser bacterial adhesion. These results may be helpful in modification of new coatings for the medical devices especially the medical device implants. The corrosion rates of all the 32 samples in 4 different testing conditions were calculated by performing Tafel analysis using their potentio-dynamic polarization scans and are listed in 4 different categories according to the testing liquids. First is the PBS followed by 3.5% NaCl that simulates the seawater environment, then 0.05M HCl and in the last for an extreme condition test 2M HCl.

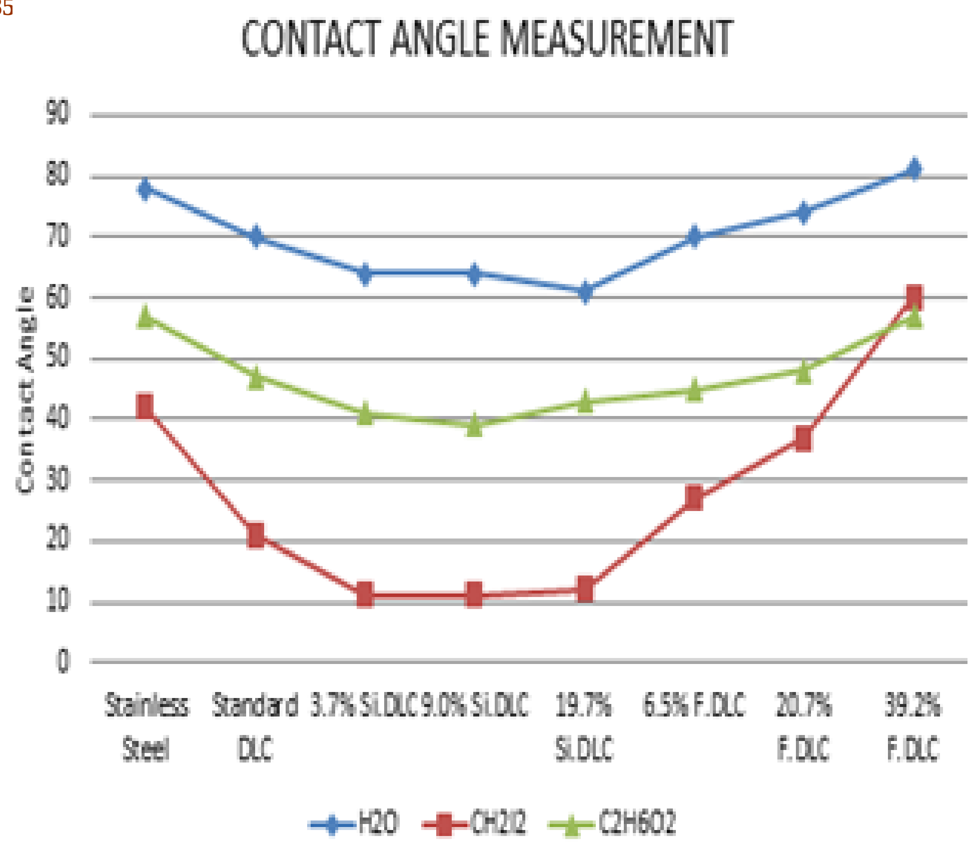

Figure 6. Graphical representation of contact angles of all the tested DLC coatings.

All the corrosion rates represented as millimetre per annum i.e. mm/a, figures 7, 8, 9 and 10 are the bar graph representations of all the samples in PBS, 3.5% NaCl, 0.05M HCl and 2M HCl respectively.

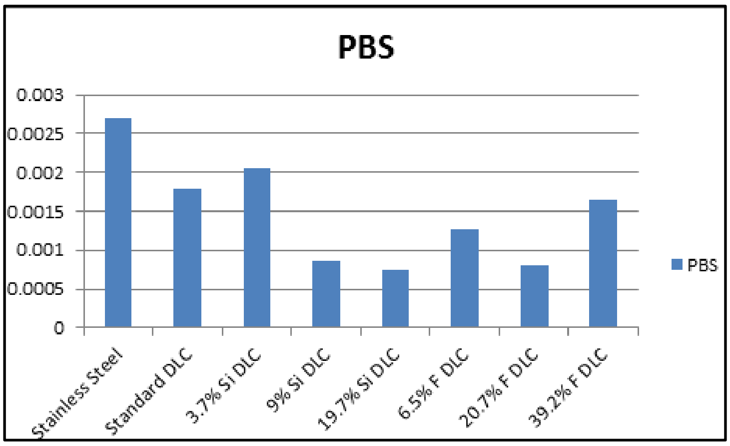

Figure 7. Corrosion rates of all samples in PBS solution.

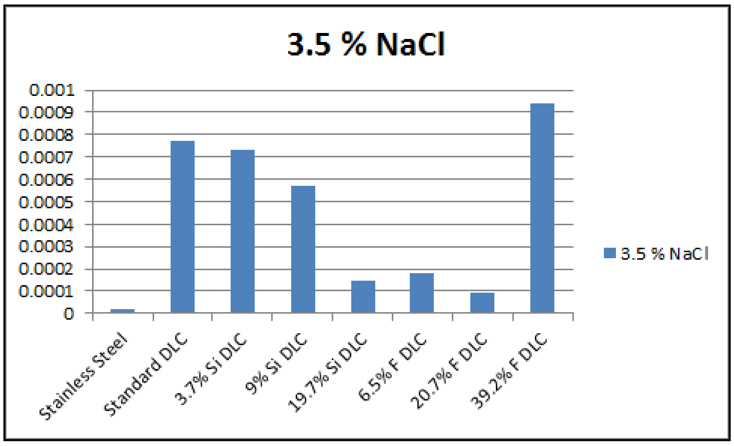

Figure 8. Corrosion rates of all samples in 3.5% NaCl solution.

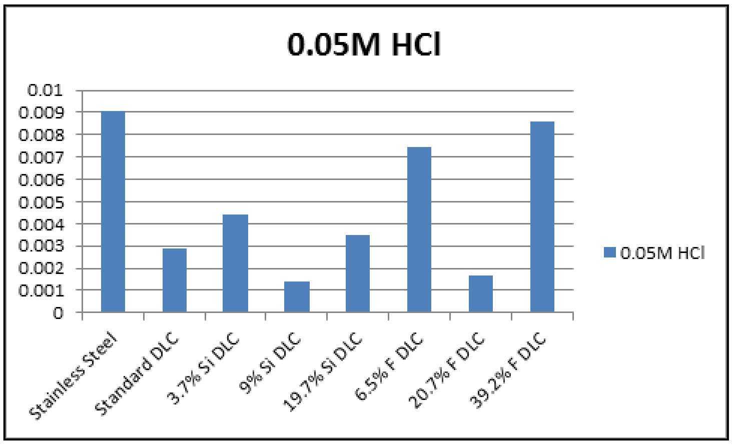

Figure 9. Corrosion rates of all samples in 0.05M HCl solution.

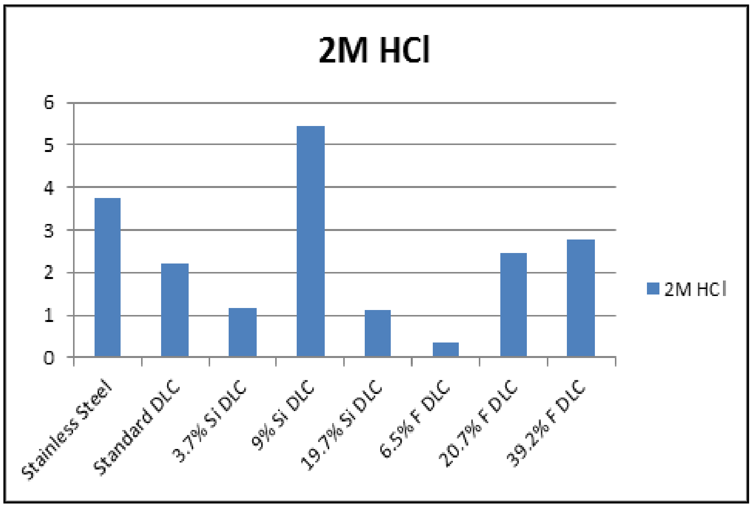

Figure 10. Corrosion rates of all samples in 2M HCl solution.

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B. Corrosion Rates

It can be said that there was noise in the potentio-dynamic polarization scans at times, especially in the seawater and PBS test solutions. As far as the acidic solutions are concerned, they did not had much noise but the scans deviated very much thus resulting in false corrosion rates like in 6.5% F-DLC in 2M HCl solution. Also in the same graph, the tangential lines were not accurate. This might be the result of problems in the deposition of coatings. The corrosion trend for all the coatings explain one thing and that is, that all the tested coatings can be reliably used in medical devices as and as far as other applications are concerned for example in chemical industry or in a textile factory, the coatings won't work well as they were tested in 2M HCl solution. With the increase in the fluorine content there was a decrease in the corrosion rate, an interesting thing was noted in the F-DLC that up till 20.7% of F-DLC the corrosion rate was fine but as the fluorine content was increased an increase in corrosion rate was also seen. The results revealed that more the fluorine content better the corrosion resistance. Similar results were reported by (X.J. Su et al., 2010) [5]. Amazingly the seawater corrosion rates were lower than the body fluid environment. This was the cause of poor experimental setup. As the contacts were loose, the test solution needed to be changed after some time. Considering the corrosion trend it was also seen that DLC coating with 19.7 % Silicon had best corrosion rate among the Si-doped DLC coatings. Polarization graph of stainless steel is shown in figure 11.

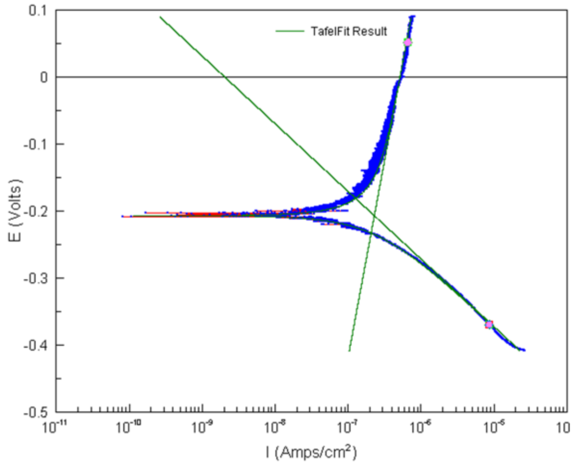

Figure 11. Polarisation graph for pure stainless steel

IV. CONCLUSION

The DLC coatings with Fluorine content were prepared by rf-PECVD technique while Si-doped DLC coatings were prepared by magnetron sputtering method, on the stainless steel substrates. Firstly the surface energies of all the coatings were calculated and the results revealed that as the Fluorine content increased there was a decrease in surface energy. Which means that bacterial adhesion will be less as the Fluorine content is increased. Whereas the stainless steel, the standard DLC and all other Si-doped DLC had high surface energy, which promotes more bacterial adhesion which is unfavourable for the medical implant. The corrosion tests were performed in PBS, 3.5% NaCl, 0.05M HCl and 2M HCl. From the results it can be said that the corrosion trend was similar and the 20.7% F-DLC coating showed the best corrosion resistance properties. High corrosion rates were seen in 2M HCl solution which suggests that the coatings were damaged greatly, hence the DLC coatings can be used only for the medical device implant and not in any more extreme condition. The incorporation of Fluorine content significantly increased the corrosion resistance and another interesting thing that was seen by comparing all the potentio-dynamic scan was, the resting potential was decreasing as the increase in the acidic content of the electrolyte. In PBS it occurred around -0.1V – -0.2V while in acidic conditions it occurred at -0.3V – -0.4V. The studies finally

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revealed that incorporation of Silicon or Fluorine content into medical devices may hinder the corrosion rates and these coatings are having a promising future in biomedical applications.

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