



Corrosion behavior of Ti coated poly (o-phenylenediamine) conducting polymer on 316L SS as bipolar plates for fuel cell applications

A. Mugunthan¹, G. Annamalai^{2,*} and G. Elango¹

¹Department of Chemistry, Government Arts College, Tiruvannamalai -606 603, Tamil Nadu, India

²Assistant Professor, Department of Chemistry, Sun Arts and science College, Tiruvannamalai-606 755. Tamil Nadu, India

*Corresponding author: annamalaigmalai@gmail.com

Received 30 April 2021, Received in final form 12 May 2021, Accepted 12 May 2021

Abstract

Electrochemically-deposited polymer-metal coatings were explored for a variety of a lightweight metal for fuel cell bipolar plates is an attractive one towards automotive applications. The uses of metallic bipolar plates have recently concerned attention for fuel cells. Hence, the use of corrosion resistance is highly necessity for fuel cell components. The surface of 316L SS was modified by electro polymerization method. The formation of the coating and surface modification have been studied. The corrosion behavior of the uncoated and coated specimens was investigated using acid and fluoride solution. The surface morphology of the uncoated and poly (ortho-phenylene diamine) [P(o-PD)] coated Ti have been characterized by ATR-IR, SEM, Micro hardness test and contact angle analysis. The corrosion resistance of the uncoated and o-PD coated substrates were evaluated by open circuit potential (OCP) and potential dynamic polarization studies. The results of the investigation suggested that improved corrosion resistance of the 316L stainless steel may be comfortable for proton exchange membrane fuel cells.

Keywords: *o-Phenylenediamine, Titanium, Bipolar plates, Stainless steel, Proton exchange membrane fuel cells.*

1. Introduction

Global warming is one of the biggest environmental problems in 21st century. The reason behind this is the increasing concentrations of greenhouse gases. The increased amount of CO₂ (17%) emissions come from the internal combustion engines of vehicles because of petroleum burning [1-3]. Therefore, minimizing the consumption of petroleum products and oil used in transportation applications are the ways to avoid such environmental disaster. Rapid consumption of fossil fuels would eventually reach a stage of fuel deficit. Steps need to be taken on a war footing to look for other sources of energy which would become effective substitutes for fossil fuels. One such alternate source of energy is the fuel cells. Fuel cells have a remarkable potential as low emission power generating sources. Fuel cells are much sought after power sources and are expected to play a promising role in meeting the ever increasing energy demands of the world. Fuel cells are electrochemical devices that can efficiently convert the chemical energy (oxidation potential) of the fuel directly into

electrical energy. They operate like batteries and are similar in components and characteristics, but unlike batteries, they do not get exhausted and are environmentally friendly. As long as fuel is supplied to the cell along with an oxidant (typically air), the fuel cell continues to produce electrical energy and heat [4].

Proton Exchange Membrane Fuel Cell (PEMFC) is a device that converts hydrogen and oxygen (or air) to electricity directly. The chief advantage of this device is that it does not cause any pollution as it produces only water as by products besides generating electricity [5]. This property of the device is viewed favorably from the environmental point of view. Furthermore it has many advantages viz. Light weight, modestly low operating temperature, relatively high efficiency, comparatively long durability, no pollutant emission, low noise, compactness, faster response time, etc. PEMFC consists mainly of ion conducting membrane, catalyst, cathode and anode electrodes and bipolar plates. Of all these bipolar plates

perform several important functions to ensure maximum power output and a long stack life.

Bipolar plates constitute the backbone of a hydrogen fuel cell power stack, conduct current between cells, facilitate water and thermal management through the cell, and provide conduits for reactant gases namely hydrogen and oxygen. Bipolar plates are fabricated in mass production and they must be made of materials with excellent manufacturability and suitable for cost effective high volume automated production systems. Currently, graphite composites are considered the standard material for PEM bipolar plates because of its low surface contact resistance. Unfortunately, graphite and graphite composites are classified as brittle and permeable to gases with poor cost effectiveness for high volume manufacturing processes relative to metals such as aluminum, stainless steel, nickel, 316L SS, etc. Among them, stainless steel 316L SS possesses all the desired properties [6, 7]. However it undergoes corrosion due to presence of the acidic electrolytes in PEMFC. Therefore it becomes imperative to control the corrosion problem, the method itself could impose a new problem, as polymers are, in general insulators and hence would defeat the very important requirement of bipolar plates viz., electrical conductivity. However, the conductive polymers, discovered by Shirakawa provide a solution to this situation [8-11]. Many conductive polymers have been tried to face this situation. The present investigation aims at coating 316 LV SS with poly (o-phenylenediamine) (o-PD) and to evaluate its corrosion resistance performance as o-PD is a conducting polymer.

The intrinsically conducting polymers (ICPs) have been used as alternate electrodes for their potential applications in electro analytical, bio sensing and drug delivery devices. They can work as a conductometric transducer which can measure the changes of the charges produced during enzymatic conversion. Such polymer LED devices consist of several layers of polymer materials sandwiched between a metallic cathode and an inorganic or organic anode, such as indium tin oxide (ITO) or a conducting polymer. ICPs also are used as gas sensors. For this application the advantage of conducting polymers compared to inorganic materials used until now are their diversity, their easy synthesis and particularly, their sensitivity at room temperature [12]. Another possible application of ICPs is as actuators. During the reduction/oxidation processes the volume of conducting polymers changes due to incorporation or expulsion of ions and solvent. Hence the changes of a polymer volume might be used as a source of

the direct motion. The great advantage of this kind of actuators is that due to the 'muscle-like' nature they are more suitable for biomimetic. Heterocyclic conjugated polymers can be prepared by electrochemical polymerization. Due to many advantages of this method over chemical polymerization approaches it became a convenient way for the preparation of conductive polymers for research. It allows a direct polymerization of the polymer on conductive substrates eliminating problems concerned with the application of the insoluble (or difficult to solve) polymer [13, 14]. The obtained polymers are already in the oxidized state, hence further oxidation to the conductive form is not necessary. The polymers can be directly doped with various anions and the doping level can be adjusted by the proper choice of the preparation conditions [15]. Additionally, the thickness of the prepared polymer film can be well controlled during the polymerization process. The i_{corr} value of 316L SS indicates excellent corrosion resistance in PEMFC operating environment. However, higher ICR value of the substrate reduces the criteria for DOE required values. Normally, the ICR of the 316L SS substrate is higher than $100 \text{ m}\Omega \text{ cm}^2$, which is ten folds higher value compared to the DOE's required value. Therefore, 316L SS substrate has been coated with a protective material for PEMFC bipolar plate's applications.

2. Experimental

2.1 Materials and methods

Commercially available Stainless steel (SS) with the size of $25\text{mm} \times 10\text{mm} \times 2\text{mm}$ were used as substrate material in the present investigation. The chemical composition of 316 SS Metal is about Cr (16.2 wt%), Ni (10.03 wt%), Mo (2.06 wt%), P (0.033 wt%), Mn (1.48 wt%), Si (0.43 wt%), Cu (0.43 wt%) and Fe (Remaining content). The chosen 316L SS metal was subjected to several surfaces pretreatment such as grinding with SiC emery sheets upto 800 grit in order to remove the native oxide layer present on the surface and impurities. The sample was ultra sonicated using acetone and de-ionized water for about 20 minutes and then washed with double distilled water and finally air dried. After these pretreatment, the sample was subjected to surface modification. It was achieved by electropolymerization. Three electrode systems were used with 316L SS as working electrode (WE), platinum foil as counter electrode (CE) and saturated calomel electrode (SCE) as the reference electrode (RE). Chronoamperometry (CA) technique was used for electro polymerization by cycling the working electrode potential between -1 and 1 V at a scan rate

of 0.05 Vs⁻¹ for 20 cycles. Oxalic acid was used as the supporting electrolyte and its concentration was fixed at 0.15 M. The concentration of o-PD monomer was varied at 0.02, 0.04 and 0.06 M. Solutions were prepared using double distilled water. After the electro polymerization of the monomer, electrodes were removed from the cell and rinsed with double distilled water to remove any unreacted monomer molecules before being dried. After completion of the process the samples were subject to study the Surface and Electrochemical characteristics.

2.2 Characterization

FTIR spectrum of electro polymerized polymer coating over 316L SS was recorded using attenuated total reflectance infrared (ATR-IR) spectrometer model Perkin Elmer FTIR Spectrometer in the wave number range 4000-400 cm⁻¹. Scanning electron microscopic (SEM) micrographs were obtained using the Hitachi Model-S3400 instrument. The average contact angle measurement with water for all the specimens were evaluated by Euromex Optical Microscopy equipment with CCD camera. Three experiments were performed for varying time duration and the angles were calculated with help of 'UTHSHCSA image tool' software. In order to evaluate the mechanical properties of uncoated and o-PD coated 316L SS substrates, micro hardness test was carried out with a Vickers pyramid indenter (model no. MH-3). Hardness measurements were performed on top of the surfaces at a load of 0.5 kgf and dwell time of 12 s. The Vickers hardness (HV) value was determined by dividing the indentation force by the surface of the imprint observed at the microscope. For each substrate, triplicate measurements were carried out at various places to check the reproducibility of the results. All the electrochemical studies were carried out at room temperature using electrochemical workstation (760D CH Instruments, Inc. USA).

Open circuit potential is a thermodynamic parameter in which the electrode to participate in the electrochemical corrosion reaction with the surrounding environment [16]. The electrolyte used in the PEMFC environment is 0.5 M H₂SO₄ + 2 ppm. The potential of the electrodes at the cathodic and anodic reactions are equal under the absence of the applied potential. The coated and uncoated specimens were exposed in the electrolyte for about 45 minutes to attain stable open circuit potential (OCP) and the electro chemical studies were monitored in the potential based OCP.

Potentiodynamic polarization is a polarization methods involve changing the potential

of the working electrode and monitoring the current which is produced as a function of time or potential. The potentiodynamic polarization was investigated in the potential range of -0.5 to 1.2 V with the scan rate of 1mV/s. The polarization resistance (R_p) can be calculated from this equation:

$$R_p = \frac{\beta_a \beta_b}{2.3 I_{corr} (\beta_a + \beta_b)} \quad (1)$$

Where R_p is the polarization resistance, i_{corr} the corrosion current density, β_a and β_b the slopes of the cathodic and anodic reactions respectively [17, 18].

The potentiodynamic polarization studies were carried out for test specimens having an exposed area of 1 cm². A conventional three cell was used to carry out the electrochemical studies. The cell assembly consists of test specimen as the working electrode; platinum foil and saturated calomel electrode (SCE) were used as counter electrode and reference electrodes respectively. The tests were conducted in the PEMFC cathode environment solution.

3. Results and discussion

3.1 Chronoamperometry studies

The polymerization was done by chronoamperometry (CA) technique, by fixing the working electrode potential at 1.2 V. The electropolymerization was carried for 1500 seconds. Oxalic acid was used as the supporting electrolyte and its concentration was fixed at 0.2 M. The concentration of o-PD was varied at 0.02, 0.04, 0.06 M. Solutions were prepared using double distilled water.

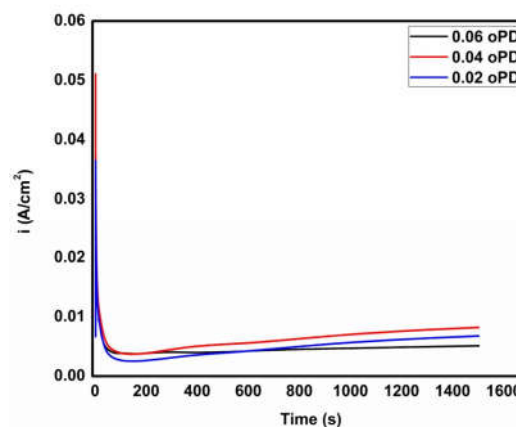


Fig. 1 Chrono amperometry of o-PD over 316L SS substrates from aqueous solutions of o-PD monomer with concentration 0.02M, 0.04, 0.06

The obtained graph is shown in the Fig. 1. From the graph, it is clear that the current falls

rapidly from 0.05 A/cm² to 0.005 A/cm² approximately for 50 seconds. This may be due to oxidation of the monomer molecules from the solution to initiate the polymerization process. After 50 seconds there is gradual increase in current. After 50 seconds there is gradual increase in current till the end of experiment. This could be attributed to the chain growth of the polymerization process.

3.2 FTIR Spectra

ATR-IR spectrum of (i) 0.02 M (ii) 0.04 M and (iii) 0.06 M of o-PD coating has shown in Fig. 2. The weak peak at about 425 cm⁻¹ might be attributed to C-H wagging deformation of benzene ring. The peak at 830 cm⁻¹ could be due to the out of plane bending motions of C H of 1,2,4,5 tetra substituted benzene nuclei of phenazine units [19]. This implies that the polymer has phenazine skeleton. The peak at about 1270 cm⁻¹ is attributed to C=N_{str} vibrations in the benzenoid and quinonoid imine units suggesting the formation of Po-PD onto Ti due to electropolymerization. The two peaks observed at about 1800-3700 cm⁻¹ are due to -C=C and -C=N_{str} vibrations of benzenoid and quinonoid structure of the phenazine ring which is characteristic of the polymer formed. The broad peaks around 3400 cm⁻¹ are characteristics of -N-H symmetric and asymmetric stretching vibrations of aromatic amine respectively [20]. These symmetric and asymmetric stretching vibrations of the polymer were present as a group of vibrations around 1270 cm⁻¹.

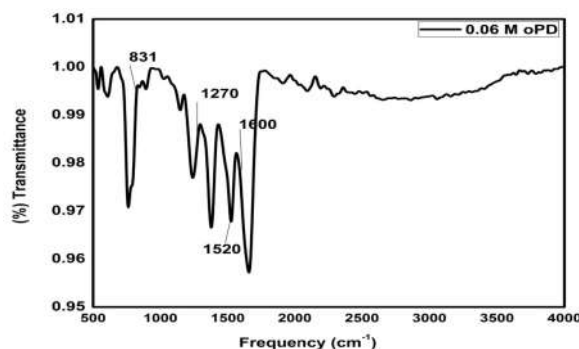


Fig. 2 ATR - IR Spectra [(i) 0.02 M (ii) 0.04 M and (iii) 0.06 M] of o-PD.

3.3 SEM Analysis

Surface morphology of the uncoated and coated 316L SS substrates was characterized by SEM analysis. From the Fig. 3, the surface morphology of uncoated 316L SS indicated the presence of few micro scratches during mechanical polishing. The SEM image of o-PD coated specimen revealed the existence of smooth and uniform morphology without any cracks. However, some of the large particles were found on the surface of the coated film.

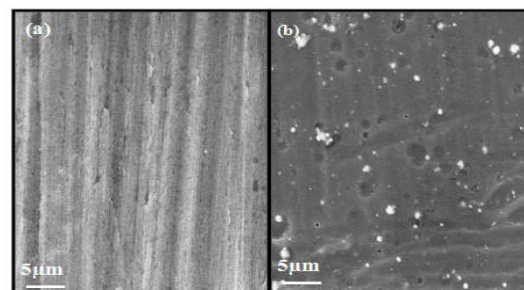
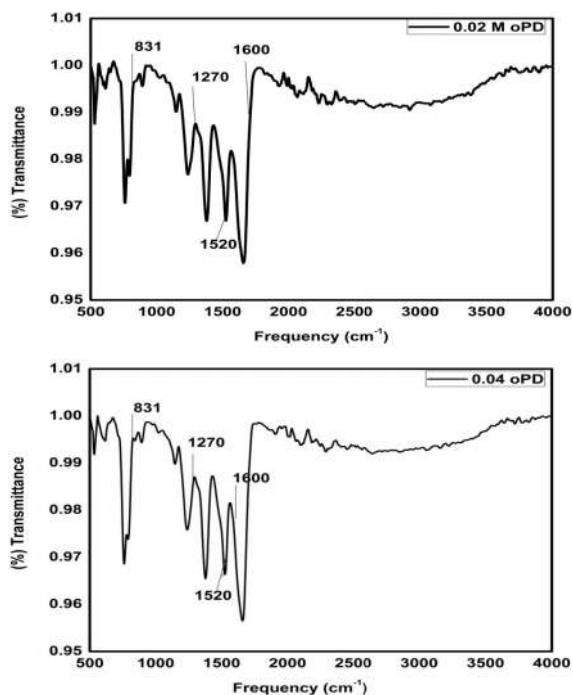


Fig. 3 SEM images of Uncoated 316L SS and o-PD coated 316L SS

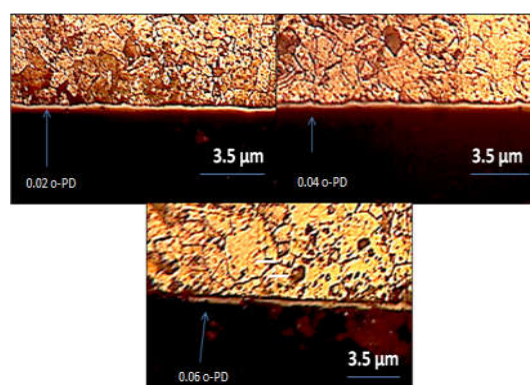


Fig. 4 SEM -optical cross sectional and optical microscopy images of (a) 0.02 o-PD (b) 0.04 o-PD (c) 0.06 o-PD coated specimens

The thickness of the o-PD coatings were confirmed by the SEM optical cross sectional images and have shown in Fig. 4. All the three coatings showed a uniform thickness of about 3-4 μm . SEM-optical images are complementing each other.

3.4 Micro Hardness studies

Micro hardness results for uncoated and o-PD coated 316L SS substrates are shown in Fig. 5. Hardness value of uncoated 316L SS was found to be 18 Gpa. O-PD coated 316LSS substrate exhibited high hardness value compared to the uncoated 316L SS which is found to be 21 Gpa. In addition to that, higher hardness value of o-PD coating is due to the incorporation of Al into the o-PD coating structure resulting in increased hardness value [21-23]. As the concentration of o-PD increases, hardness increases.

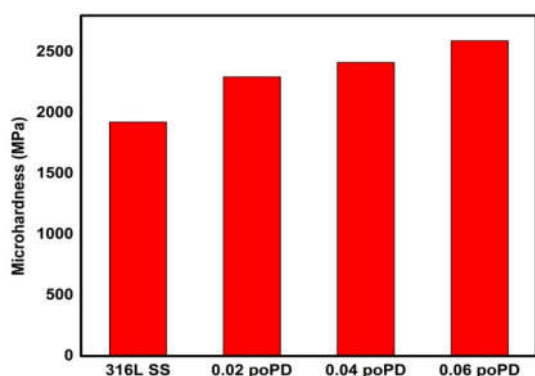


Fig. 5 Microhardness values of uncoated, 316L SS specimens

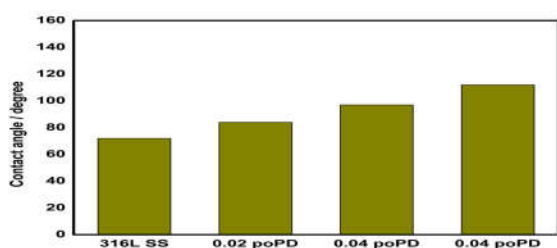


Fig. 6 Contact angle measurements with water for uncoated 316L SS and o-PD coated 316L SS

3.5 Contact Angle Measurement

In PEMFC stack, water management is one of the major functions in each cell. The material of Bps would be helpful for removal of water from the fuel cell stack to simplify the water management. The contact angle images of the uncoated 316L SS and 316L SS-o-PD coating with water shown in Fig. 6. The average contact angle value of uncoated 316L SS is $73 \pm 2^\circ$ and less than that for 316L SS-o-PD coating is 94 ± 2 [24]. The higher contact angle and

hydrophobic property of 316 L SS- o-PD coating is control the water management in PEMFC stack [25].

3.6 Electrochemical Studies

3.6.1 Open Circuit Potential Measurement

OCP measurements of the uncoated and o-PD coated 316L SS were measured for 45 min. exposure in 0.5 M H_2SO_4 + 2 ppm of HF solution are shown in Fig. 7. From the results, it is seen that the o-PD coated 316L SS showed positive potential shift of about 0.6 V compare to uncoated 316L SS. These results clearly revealed the o-PD coating act as stable passive film that resists the corrosive ion penetration and enhance the corrosion resistance [26, 27].

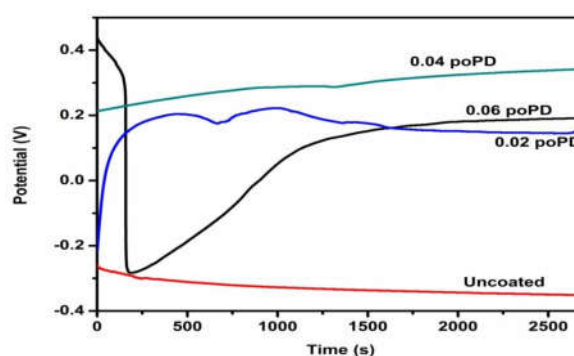


Fig. 7 OCP measurement for uncoated and o-PD coated 316L SS in PEMFC environment

3.6.2 Potentiodynamic Polarization Studies

The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_p) values were obtained from the Tafel plot and are shown in Fig. 8. These results showed towards the nobler shift in the E_{corr} value of about 600 mV and substantial reduction in the i_{corr} for 316L SS due to the deposition of o-PD coating over the surface [28]. The penetration of corrosive ions like SO_4^{2-} , F^- is very less from the electrolyte solution to coating surface.

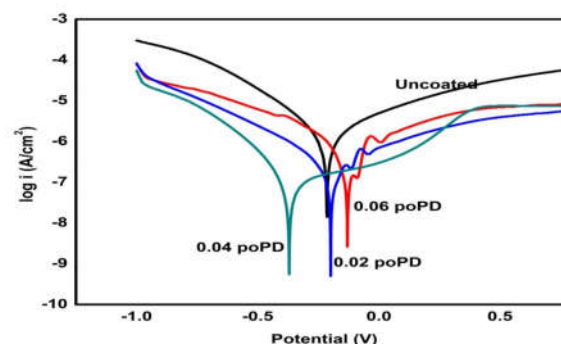


Fig. 8 Potentiodynamic polarization for uncoated and o-PD coated 316L SS in PEMFC environment

Table 2 Potentiodynamic polarization parameters for uncoated and o-PD coating in PEMFC environment

Substrate	E_{corr} (V)	β_a (1/V)	β_c (1/V)	i_{corr} (μAcm^{-2})	R_p (Kohm cm^2)	PE (%)
316L SS	-0.214	4.688	6.099	1.00	39.970	-
0.02poPD	-0.131	5.827	6.156	0.30	117.373	65.94
0.04poPD	-0.370	2.768	7.662	0.08	485.460	91.76
0.06poPD	-0.129	4.934	6.051	0.27	141.777	71.80

The higher polarization resistance (R_p) value around 4 (kohm cm^2) was attributed to a passive layer formed on surface [29, 30], which can accelerate the protection efficiency of the material. This same reason also implied for the corrosion resistance of the 316L SS- o-PD. The protective efficiency (P_i) of the coating was determined from the equation [31-35].

$$P_i(\%) = 100 \left[1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right] \quad (2)$$

Where i_{corr} and i_{corr}^0 are the corrosion current densities in the presence and absence of the deposition layer.

From the Table 2, we can see that the protective efficiency was increased about 97.05 % due to the deposition of o-PD coating over the surface [36].

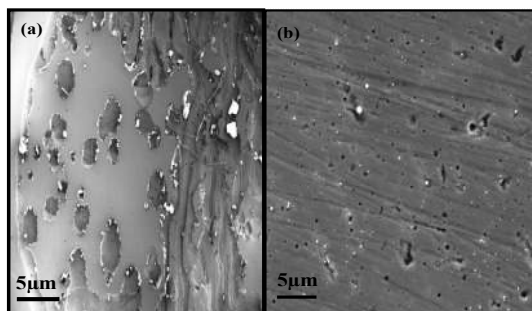


Fig. 9 SEM images of (a) Uncoated 316L SS and (b) o-PD coated T 316L SS after polarization studies

Fig. 9 shows the SEM images of uncoated and coated 316 L SS substrates after potentiodynamic polarization measurements in 0.5 M H_2SO_4 with 2 ppm HF solution. As can be seen from the SEM image of uncoated 316L SS substrate, it is clearly revealed that the surface is observed with the corrosion products due to higher rate of corrosion taking place in acidic environments [37]. On the other hand coated 316L SS substrates were observed with no corrosion product, thus revealing that there is no corrosion taking place in acidic environment.

4. Conclusions

o-PD coating deposited on 316L stainless steel was formed by electro polymerization technique as bipolar plate material for PEMFC. The IR spectrum was confirmed the formation o-PD on 316L SS metal. SEM images indicated a compact, uniform and continuous coating deposited on the surface with $4\mu\text{m}$ thickness. The results of SEM before and after corrosion tests indicate that the bipolar plate with o-PD/Ti layer coating is considerably stable and the o-PD/Ti layer coating is cost-effective, and the modification technology is simple and environmentally benign. An increased surface roughness determined by and high contact angle value with water for o-PD qualify the B_p for operating condition in PEMFC. Polarization studies revealed that the o-PD coated 316LSS shows the maximum protective efficiency and high corrosion resistance compared to those uncoated 316 L SS. Therefore, the above results indicated that the o-PD coated 316L SS exhibited good corrosion resistance, electrochemical stability and material cost. It could be used as a promising bipolar plate in PEMFC environment.

Acknowledgments

Instrumentation facility provided under FIST-DST and DRS-UGC to Department of Chemistry, Government Arts College, Tiruvannamalai are gratefully acknowledged.

References:

- [1]. H. Tawfik, Y.Hung, D. Mahajan, "Metal bipolar plates for PEM fuel cell-A review", J. Power Sources 163 (2007) 755-767.
- [2]. J. Larminie, A. Dicks (2005) "Fuel Cell Systems Explained, 2nd ed, John Wiley & Sons Ltd.
- [3]. Changhee Choe, Hyoseok Choi, Wonhyuk Hong, Jung-Joong Lee, "Tantalum nitride coated AISI 316L as bipolar plate for polymer electrolyte membrane fuel cell", Int. J. Hydrog. Energy 37 (2012) 405-411.
- [4]. Mevlut Fatih Peker, Ömer Necati Cora, Muammer Koc, "Investigations on the variation of corrosion and contact resistance characteristics of metallic bipolar plates

- manufactured under long-run conditions”, *Int. J. Hydrog. Energy* 36 (2011) 15427-15436.
- [5]. Young-Chul Park, Dong-Hwi Kim, Seongyop Lim, Sang-Kyung Kim, Dong-Hyun Peck, Doo-Hwan Jung, “Design of a MEA with multi-layer electrodes for high concentration methanol DMFCs”, *Int. J. Hydrog. Energy* 37 (2012) 4717-4727.
- [6]. Viral Mehta, Joyce Smith Cooper, “Review and analysis of PEM fuel cell design and manufacturing”, *J. Power Sources* 114 (2003) 32-53.
- [7]. R. L. Borup, N. E. Vanderborgh, “Design and testing criteria for bipolar plate materials for PEM fuel cell applications”, *Mater. Res. Soc.* 393 (1995) 151-155
- [8]. J. S. Cooper, “Design analysis of PEMFC bipolar plates considering stack manufacturing and environment impact”, *J. Power Sources* 129 (2004) 152-169.
- [9]. K. M. Kim, J. H. Park, J. H. Kim, K. Y. Kim, “Effect of chemical and heat treatment on the interfacial contact resistance and corrosion resistance of 446M ferritic stainless steel as a bipolar plate for polymer electrolyte membrane fuel cells”, *Int. J. Hydrog. Energy* 36 (2011) 9926-9935.
- [10]. H. Shirakawa, E. J. Louis, A. G. Mac Diarmid, C. K. Chiang, A. J. Heeger, “Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$ ”, *J. Chem. Soc., Chem. Commun.* 16 (1977) 578-580.
- [11]. M. Dudukcu, “The electrochemical synthesis of poly(o-phenylenediamine) on stainless steel and its corrosion protection ability in 3.5 % NaCl solution”, *Res. Chem. Intermed.* 39 (2013) 3641-3647.
- [12]. T. Dhanabal, G. Amirthaganesan, J. Ravichandran, “Pitting corrosion protection of low nickel stainless steel by electropolymerized conducting polymer coating in 0.5 M NaCl solution”, *Bull. Mater. Sci.* 34 (2011) 563-569.
- [13]. A. A. Hermas, Z. X. Wu, M. Nakayama, K. Ogura, “Passivation of stainless steel by coating with poly(o-phenylenediamine) conductive polymer”, *J. Electrochem. Soc.* 153 (2006) B199-B205.
- [14]. A. A. Hermas, “Protection of type 430 stainless steel against pitting corrosion by ladder conductive polymer”, *Prog. Org. Coat.* 61 (2008) 95-102.
- [15]. L. F. D’Elia, R. L. Ortiz, O. P. Marquez, J. Marquez, Y. Martinez, “Electrochemical Deposition of Poly (o-phenylenediamine) Films on Type 304 Stainless Steel”, *J. Electrochem. Soc.* 148 (2001) C297-C300.
- [16]. A. P. Srikanth, V. Raman, S. Tamilselvi, S. Nanjundan, N. Rajendran, “Electropolymerization and corrosion protection of polyaniline and its copolymer on carbon steel”, *Anti-corros. Methods Mater.* 55 (2008) 3-9.
- [17]. S. Sathiyarayanan, S. Syed Azim, G. Venkatachari, “Corrosion protection coating containing polyaniline glass flake composite for steel”, *Electrochim. Acta* 53 (2008) 2087-2094.
- [18]. S. Sathiyarayanan, S. Devi, G. Venkatachari, “Corrosion protection of stainless steel by electropolymerised PANI coating”, *Prog. Org. Coat.* 56 (2006) 114-119.
- [19]. E. Armelin, A. Meneguzzi, C.A. Ferreira, C. Alemán, “Polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene) as additives of organic coatings to prevent corrosion”, *Surf. Coat. Tech.* 203 (2009) 3763-3769.
- [20]. B. Lakard, G. Herlem, S. Lakard, R. Guyetant, B. Fahys, “Potentiometric pH sensors based on electrodeposited polymers”, *Polymer* 46 (2005) 12233-12239.
- [21]. M. M. Lakouraj, E. N. Zare, P. N. Moghadam, “Synthesis of Novel Conductive Poly(p-phenylenediamine)/ Fe_3O_4 Nanocomposite via Emulsion Polymerization and Investigation of Antioxidant Activity”, *Adv. Polym. Technol.* 33 (2014) 21385, 1-7.
- [22]. S. Pugal Mani, A. Srinivasan, N. Rajendran, “Effect of nitrides on the corrosion behaviour of 316L SS bipolar plates for Proton Exchange Membrane Fuel Cell (PEMFC)”, *Int. J. Hydrog. Energy* 40 (2015) 3359-3369.
- [23]. S. Joseph, J. C. McClure, R. Chianelli, P. Pich, P. J. Sebastian, “Conducting polymer-coated stainless steel bipolar plates for proton exchange membrane fuel cells (PEMFC)”, *Int. J. Hydrog. Energy* 30 (2005) 1339-1344.
- [24]. M. A. Lucio Garcia, M. A. Smit, “Study of electrodeposited polypyrrole coatings for the corrosion protection of stainless steel bipolar plates for the PEM fuel cell”, *J. Power Source* 158 (2006) 397-402.
- [25]. S. Joseph, J. C. McClure, P. J. Sebastian, J. Moreira, E. Valenzuela, “Polyaniline and polypyrrole coatings on aluminum for PEM fuel cell bipolar plates”, *J. Power Source* 177 (2008) 161-166.
- [26]. F. Cataldo, “On the polymerization of P-phenylenediamine”, *Eur. Polym. J.* 32 (1996) 43-50.

- [27]. Jaidev, S. Ramaprabhu, "Poly(p-phenylenediamine)/graphene nanocomposites for supercapacitor applications", *J. Mater. Chem.* 22 (2012) 18775-18783.
- [28]. X. G. Li, M. R. Huang, W. Duan, Y. L. Yang, "Novel Multifunctional Polymers from Aromatic Diamines by Oxidative Polymerizations", *Chem. Rev.* 102 (2002) 2925-3030.
- [29]. M. N. Vijayashree, S. V. Subramanyam, A. G. Samuelson, "A new organic conducting material derived from 1,4-diaminoanthraquinone", *Macromolecules* 25 (1992) 2988-2990.
- [30]. J. R. Locatelli, C. T. Carvalho, F. J. Cairas, M. Ionashiro, "Synthesis, characterization and thermal behaviour of heavy trivalent lanthanide malonates", *Eclat. Quim.* 35 (2010) 93-100.
- [31]. T. Ohtsuka, "Corrosion Protection of Steels by Conducting Polymer Coating", *Int. J. Corros.* 7 (2012) 1-7.
- [32]. G. Spinks, A. Dominis, G. Wallace, D.J. Tallman, "Electroactive conducting polymers for corrosion control", *J. Solid State Electrochem.* 6 (2002) 85-100.
- [33]. Madhankumar, N. Rajendran, "A promising copolymer of p-phenylenediamine and o-aminophenol: Chemical and electrochemical synthesis, characterization and its corrosion protection aspect on mild steel", *Synth. Met.* 162 (2012) 176-185.
- [34]. L. Mohan, P. Dilli Babu, C. Anandan, "Electrochemical studies and growth of apatite on molybdenum doped DLC coatings on titanium alloy β -21S", *Appl. Surf. Sci.* 296 (2014) 86-94.
- [35]. Xi-Shu Wang, Hua-Ping tang, Xu-dong li and Xin hua, "Investigations on the Mechanical Properties of Conducting Polymer Coating-Substrate Structures and Their Influencing Factors", *Int. J. Mol. Sci.* 10 (2009) 5257-5584.
- [36]. Pradeep sambyal, Gazala ruhi, Ridham Dhawan, Sandeep K dhawan, "Advanced anti corrosive properties of poly(aniline-co-otoluidine)/flyash composite coatings", *Surf. Coat. Tech.* 272 (2015) 129-140.
- [37]. Ufana riaz, Chikezie Nwaoha, S. M. Ashraf, "Recent advances in corrosion protective composite coatings based on conducting polymers and natural resource derived polymers", *Prog. Org. Coat.* 77 (2014) 743-756.