Production of carbon nano-tubes via CCVD method and their corrosion protection performance in epoxy based coatings

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Abstract. Good yield of carbon products was obtained by catalytic chemical vapor deposition (CCVD) technique using 100-500mg of ferrocene catalyst at temperature of 900 ℃ and acetylene flow rate of 150-200cc/min. The effects of amount of ferrocene, temperature and hydrocarbons precursors on the yield of carbon nanomaterial's was calculated and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) andenergy-dispersive X-ray spectroscopy (EDS). Good yield of carbon nanomaterials primarily consisted of carbon nanotubes (CNTs) and carbon nanoparticles was obtained. CNTs obtained after purification were dispersed in epoxy resin to produce composite coatings which were coated on stainless steel 316L. The coated stainless steel samples' corrosion behavior was studied using open circuit potential (OCP), cyclic polarization and electrochemical impedance spectroscopy (EIS) techniques. Results showed that epoxy coating containing 4 wt. % of CNTs offered improved corrosion resistance to stainless steel.

1. Introduction

Carbon nanomaterials such as carbon nanotubes (CNTs)are employed in numerous applications due to their remarkable electronic, mechanical and chemical properties [1]. Production of CNTs with high yield and good quality at commercial scale needs extensive study. Catalytic chemical vapor deposition (CCVD) a commercially viable process is widely used for the production of CNTs [2-3]. Many parameters are considered during CCVD process including temperature, amount of catalyst, carbon source, etc. which require optimization [4-5].

Corrosion is a process which causes destruction of metals by their electrochemical interaction with environment. This needs to be reduced to increase the life time of metals which will save capital. Several methods are employed to reduce corrosion of metals but organic coatings in the form of paints or resins are widely used due to their ease of application [6]. To protect metals in marine conditions epoxy-based organic coatings are applied due to their high adhesion and superior corrosion resistance[7]. However, due to their hydrophilic nature defects in coatings formed which eventually result in corrosion of metal underneath [8-9].Therefore, epoxy coatings are needed to be modified to enhance their performance against corrosion. One of the easiest approaches is based on incorporating nanofillers into epoxy resin such as silica nanoparticles, carbon nanotubes, carbon black and carbon nanofibers [10-12]. Carbon nanotubes (CNTs) have hydrophobic nature and their addition in epoxy coatings have beneficial effect in reducing corrosion rates of metals.

Few studies reported CNTs can increase corrosion resistance of steel, stainless steel or other metals appreciably[13]. Researchers reported that addition of carbon black nano particles or CNTs in the epoxy resin and studied corrosion resistance of such coatings[10]. The present study reports corrosion protection behavior of epoxy coatings which were prepared by mixing carbon nanomaterials (mainly CNTs) in epoxy resin. Carbon nanomaterials were produced by CCVD techniques and optimization of process parameters was carried out through manipulation of different parameters for enhancing the percentage yield of CNTs. The epoxy coatings containing CNTs were coated on 316L stainless steel and their effect on corrosion resistance of316L stainless steel was studied in simulated sea water.

2. Experimental

Ferrocene (a product of Merck), commercial grade xylene and acetylene were used for CCVD process. First of all, catalyst, ferrocene $(C_6H_5)_2Fe$, was weighed precisely and poured into a stainless steel chamber encapsulated with a heater which was sealed with high temperature RTV silicone gasket maker sealant. The stainless steel chamber had inlet for purgingacetylene gas and nitrogen gas into the stainless steel chamber to allow hydrocarbon source and carrier gas to be thoroughly mixed with the catalyst already placed in the chamber. The outlet of the chamber was connected to a quartz tube. The gases mixed with a catalyst came out from the outlet and entered into the quartz tube that was placed in a tube furnace and it was maintained at temperature of 800-1000 °C depending on the experimental conditions. One end of quartz tube was connected with the stainless steel chamber and other end was connected with a bubbler. The flow rate of gases was controlled so that a controlled amount of carrier gases and catalyst vapors enter into the reaction chamber (quartz tube). Before running experiments, only nitrogen gas was passed through the quartz tube to remove any air and then furnace was turned on to set temperature. When the desired temperature was attained in the quartz tube, heater was turned on to convert catalysts into vapors. As soon as catalyst vaporized, acetylene gas was introduced which was mixed with catalyst vapors and entered into the reaction zone. After 3-4 minutes of reaction, carbon product was seen in the quartz tube. The reaction continued for 30-60 min depending on experiment. After certain time, furnace was switched off and the product was allowed to cool to room temperature. Product of CCVD reaction was carefully retrieved from quartz tube and weighed to calculate % yield of the reaction. Stainless steel heating chamber was also disassembled to observe the amount of catalyst that was left behind. The schematic of setup is shown in Figure 1.

For purification of CCVD products, 3 g of the product was added in 100 ml concentratedHNO$_3$. The resulting mixture was stirred for 4 husing magnetic stirrer. After four hours, distilled water was added to make 500 ml solution which was stirred for 5 h. Filtration of solution was carried out and purified product was obtained after drying.
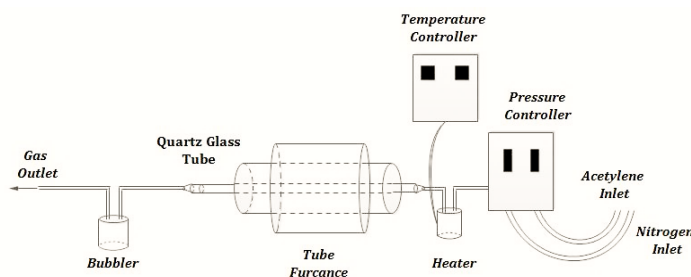

Figure 1. Schematic of CCVD process apparatus used in present study

The carbon products of CCVD reaction were characterized using field emission gun scanning electron microscope (FEG-SEM), energy dispersive x-ray spectroscopy (EDX) and X-ray diffraction (XRD).

CNTs were well dispersed in epoxy resin to produce CNT/epoxy coatings. These coatings were prepared by first dispersing a known amount of purified CNTs in the acetone by ultra-sonication (Sonicator, 35 Hz frequency) for 5 h. After 5 h, an appropriate amount of epoxy resin was poured in CNT/acetone dispersion. The resulting dispersion was again sonicated for 30 min so that CNTs get adequately disperse into epoxy resin. Later, acetone was evaporated from the dispersion. To the resulting dispersion of CNT and epoxy resin (a product of ICI, Pakistan), amide hardener was poured and was thoroughly mixed with a high speed mechanical stirrer. The ratio of epoxy and amide hardener was 80:20. The resulting dispersion of CNT/epoxy/hardener was coated on polished (2 μm diamond paste used for polishing) 316 L stainless steel samples with an applicator capable of applying coating thickness of 25 μm. Coatings were abbreviated as 316L+E-1% and 316L+E-4% coatings, having 1 wt. % CNTs and 4 wt. % CNTs in epoxy resin, respectively. Figure 2 shows a complete flow diagram of processes adopted in preparation of coatings.

Electrochemical measurement techniques, open circuit potential (OCP), cyclic polarization and electrochemical impedance spectroscopy (EIS) were performed to evaluate corrosion behavior of coatings using PC14/750 (Gamry Instruments, Inc., USA) and resultant spectra were analyzed by Echem analyst software version 5.68. Prepared samples were used as working electrode, graphite was used as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode in freshly prepared 3.5% NaCl electrolyte.
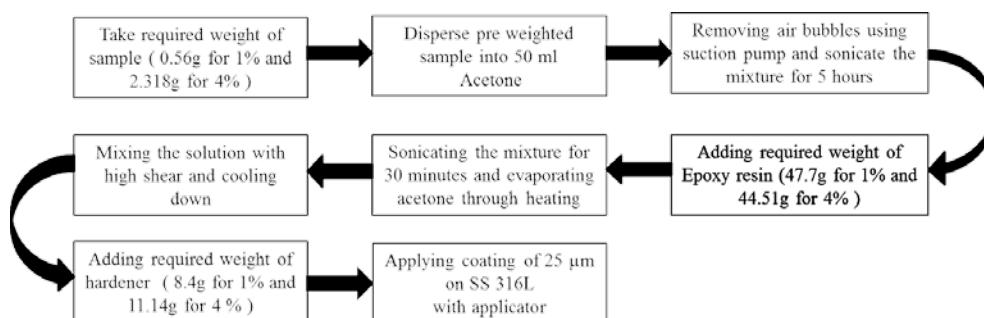

Figure 2. Flow chart of procedure adopted for preparation of coatings

3. Results and discussions

3.1. Effects of amount of catalyst, reaction temperature and carbon precursor type on carbon product
The yield of carbon product obtained after CCVD process was calculated by formula given in (1)[14],

$$\% \; yield = \frac{M_{total} - M_{cat}}{M_{cat}} \times 100 \tag{1}$$

Where, M_{total} is the weight of carbon product and catalyst and M_{cat} is the weight of catalyst, respectively.

The effect of amount of catalyst on carbon product yield is presented in Figure 3(a). High yield of CCVD carbon nanomaterials was obtained when amount of catalyst was in the range of 100–500 mg and temperature, reaction time and acetylene flow rate were 900°C, 10 ± 5 min and 150–200 cc/min, respectively. Agglomerated metal catalysts may have formed due to large amount (1g) of catalyst. This agglomeration reduced the efficiency of carbon diffusion into the metal. In contrast, small amount of catalyst (100 and 500 mg) delivered higher amount of product.

Figure 3(b) shows the effect of reaction temperature on percentage yield of carbon product. When the amounts of catalyst, time and flow rate of acetylene were kept constant then temperature of the reaction zone also influenced the productivity of carbon product. High yield of carbon product was obtained in the temperature range of 800-900°C. As the temperature of the reaction zone increased

further, the yield of carbon product decreased as high temperature decreased reactivity of metal catalyst with carbon and somehow combustion of carbon takes place [4].

Figure 3(c) shows the effect of type of hydrocarbon precursor on percentage yield of carbon product. Acetylene source provided higher yield than the combination of xylene and acetylene. The xylene promoted formation of nano sized carbon black particles in the reaction chamber as shown in Figure 4 (b). Since ferrocene was dissolved in xylene before CCVD process, it might have hindered evaporation of ferrocene or have reacted with ferrocene to inactivate the catalyst. It might be possible that xylene have diluted the amount of catalyst in the reaction chamber resulting in lower yield of carbon product.

Figure 3(d) shows XRD patterns obtained on the carbon products obtained from CCVD process using different parameters. XRD pattern (center) of a product obtained using 100–500mg of ferrocene catalyst at a temperature of 900 ℃ using acetylene flow rate of 150-200cc/min showed high intensity of (002) peak at 26º 2θ, indicating presence of graphitic plane having interplanar spacing of 0.33 nm. This confirms the formation of CNTs in our carbon product [15]. The peak at 47º is due to presence of iron particles. The XRD patterns obtained when excess of catalyst (Figure 3(d), top) and higher temperature (Figure 3(d), bottom) showed high intensity of iron peaks at 47º and low intensity of (002) graphite peak. It can be concluded from XRD analysis that good yield of CNTs can be obtained if ferrocene amount and temperature of reaction zone are controlled as mentioned above.
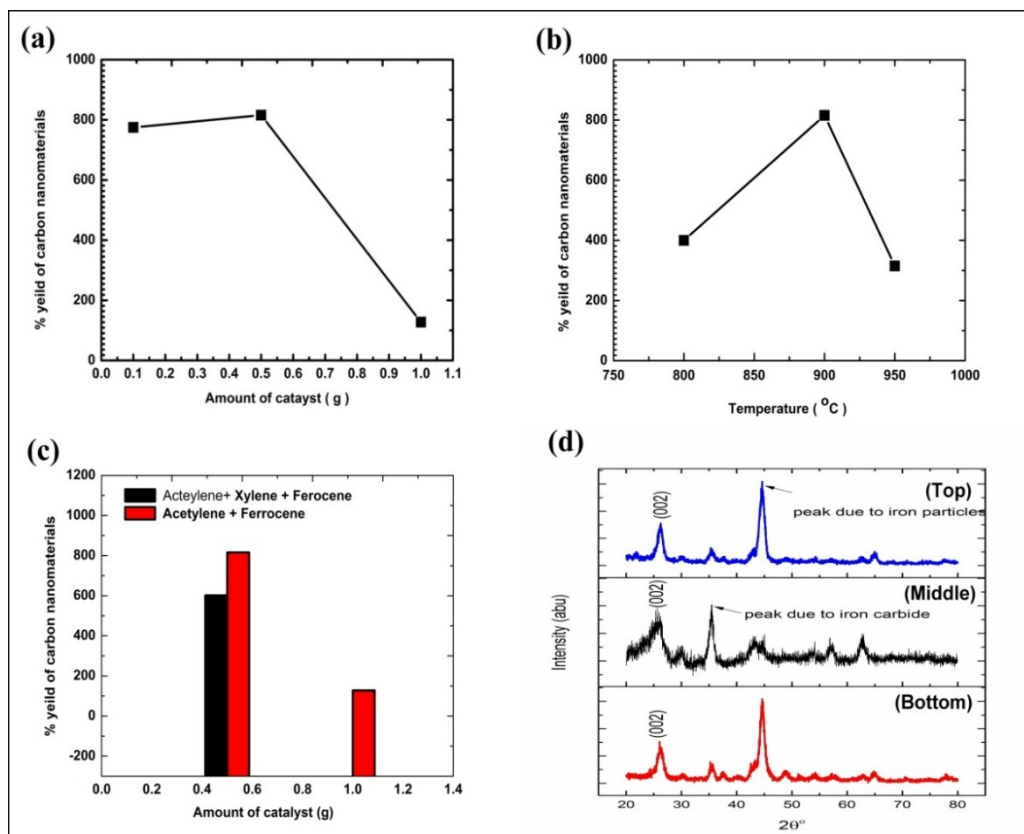

Figure 3. (a) Percent yield of carbon product with respect to catalyst (b) percent yield of carbon product with respect to temperature (c) percent yield of carbon product with respect to source of carbon precursor and (d) XRD patterns obtained at different temperatures respectively

Figure 4 shows scanning electron micrographs (SEM) microgrphsof CNTs produced using different carbon precusors. Figure 4(a) represents carbon products obtained using acetylene gas and ferocene as

catalyst. The product contains high yield of carbon nanotubes with average diameter of ~27 nm. In addition, carbon nanofibres (diameter=140 nm) (Figure 4(b)) and carbon black nanoparticles (diameter = 40 nm) (Figure 4(a)) were also observed in SEM analysis. On the other hand, SEM of the product obtained using ferrocene and combination of xylene and acetylene shows the product has mainly carbon particles having sizes in range of 0.6-1.0 μm (Figure 4(c)). This result clearly shows that accetylene in the presence of ferrocene can produce CNTs with high yield. The EDX analysis clearly confirms carbon and iron peak in CCVD products as shown in Figure 5.
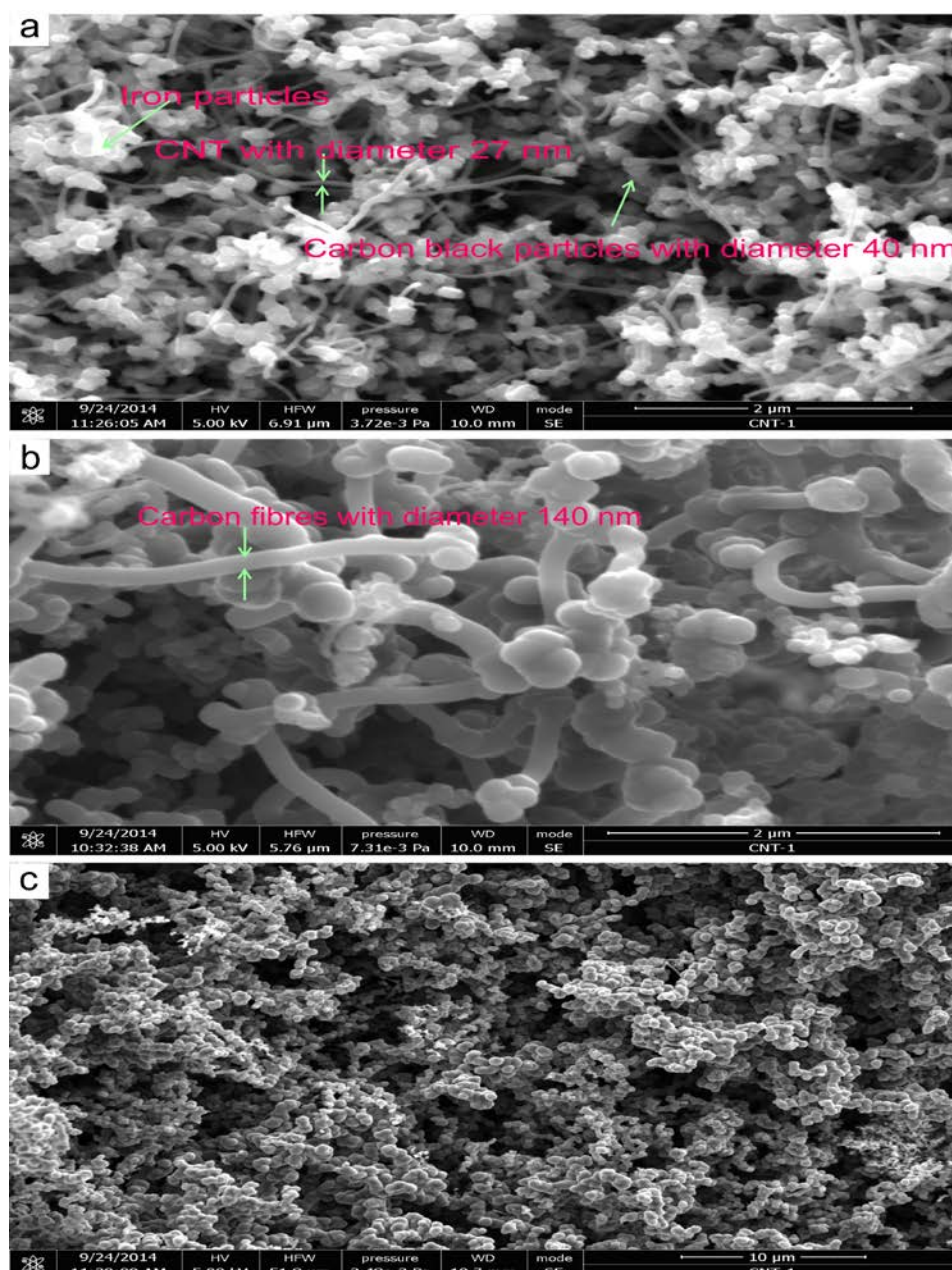

Figure 4. SEM of CCVD carbon product (a & b) ferrocene and acetylene only
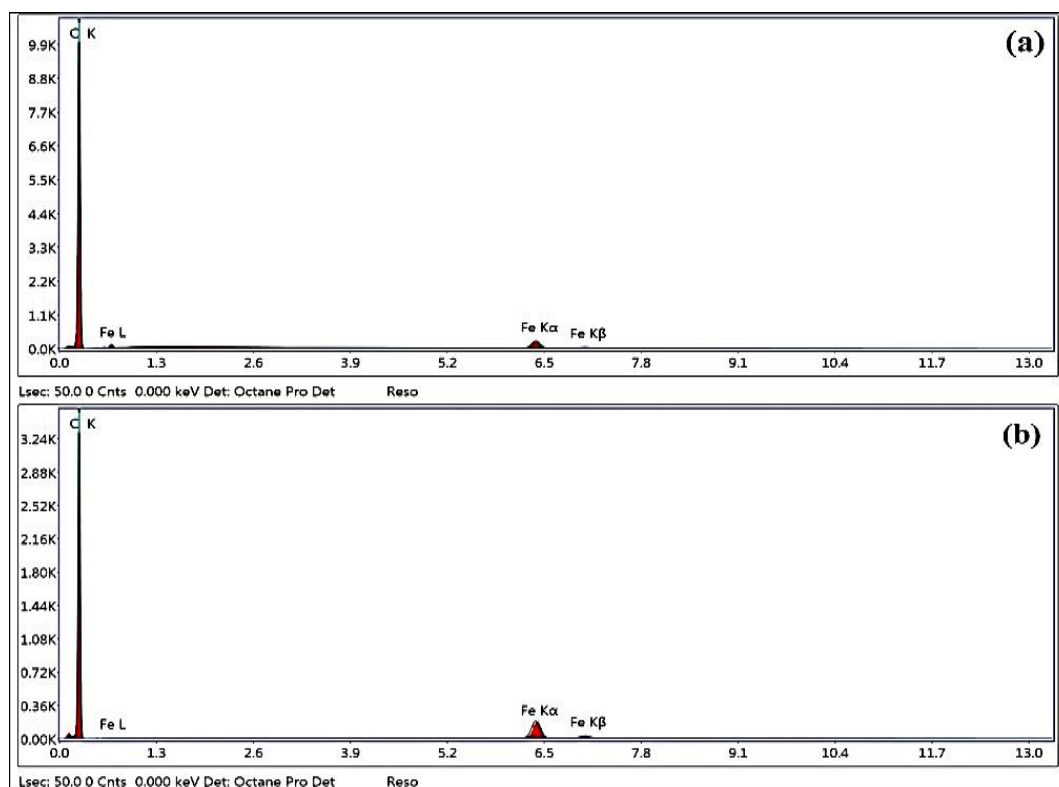(c) ferrocene and combination of xylene and acetylene

Figure 5. EDX analysis of CCVD product a) ferrocene and acetylene only (b) ferrocene and combination of xylene and acetylene

3.2 Electrochemical studies

Open circuit potential (OCP) of specimens were measured for 500s having stability of 0 mV/s. Cyclic polarization tests was carried out at forward scan rate of 5 mV/s and reverse scan rate of 2.5 mV/s with initial potential of -0.5 V to final potential of +0.3 V with respect to OCP to measure kinetic parameters. Figure 6 shows cyclic polarization curves of bare metal and epoxy containing CNTs in 3.5 % NaCl solution (simulated sea water).Epoxy coatings 316-E+1% and 316-E+4% showed higher breakdown potential (E_b = 475.5 mV) than bare stainless steel (E_b=111.9 mV) as shown in Figure 6 and Table 1. Higher breakdown potential indicates higher resistance to localized corrosion. Thus epoxy coatings containing CNTs showed higher resistance to localized corrosion. The positive hysteresis loops was observed for all coated samples. The area of hysteresis loop indicate amount of pitting on the samples. Although, epoxy coatings resisted initial localized corrosion on stainless steel surface but once the potential exceeded E_b limit the pitting phenomenon becomes more prominent which can be observed from the large area of hysteresis loop of epoxy coated samples as shown in Figure. 6. The increased pitting tendency of the coated samples was due to presence of pores or defects in the coatings.

Table 1 show kinetic parameters calculated from the curves in Figure 6 using Tafel relationship [32].Epoxy containing CNTs showed less corrosion rate as compared to bare metal. Corrosion current density of CNTs coatings 316-E+4% and 316-E+1% is 6.030 ($\mu A/cm^2$)and 67.50 ($\mu A/cm^2$), respectively, showing less corrosion current density as compared to bare metal 144 ($\mu A/cm^2$).
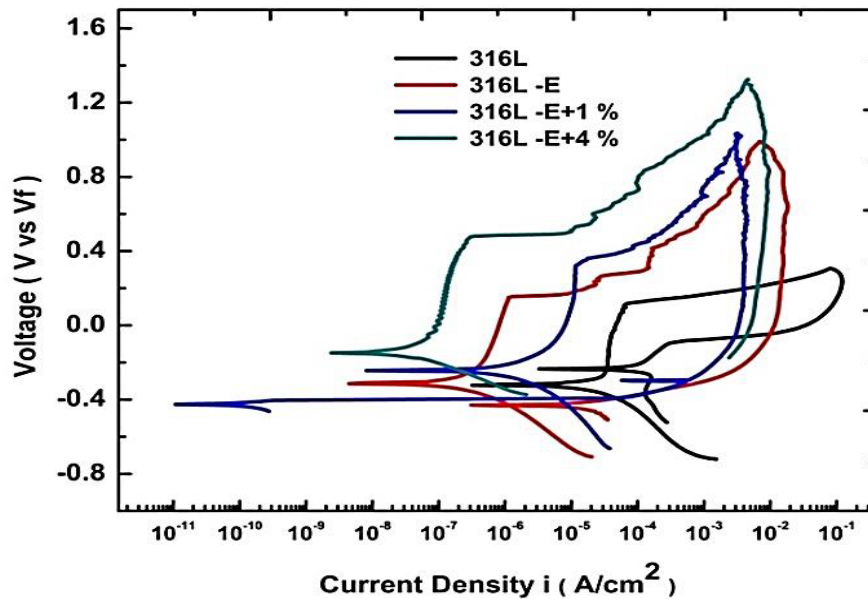
Figure 6. Cyclic polarization curves obtained in 3.5 % NaCl solution

Table 1. Kinetic parameters calculated from Polarization curves

Material	E_{corr} (mV)	Eb (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)	OCP (mV)
316L	-323	111.9	144.0	62.62	-221
316L-E	-314	150	110.0	48.03	-208
316-E+1%	-243	320	67.50	29.42	-163
316-E+4%	-148	475.5	6.030	2.627	127

In order to further evaluate corrosion behavior, EIS was conducted on coated samples in 3.5 % NaCl solution at AC voltage of ±10 mV$_{(rms)}$ amplitude with change in frequency from 10 mHz to 100 kHz. Figure 7(a) shows the Nyquist curves of coated samples obtained in 3.5 % NaCl solution. Nyquist curves tell about charge transfer mechanism. Higher the resistance to charge transfer, greater will be the area of Nyquist curve. Figure 7(b) showed bode plot indicated that 316L+ E-4% and 316L+E-1% coatings showed higher impedance |Z| than bare stainless steel. It was indicated that at low frequency CNTs-based coatings showed inductive behavior due to initiation of localized attacks caused by Cl⁻ ions. On the other hand, double layer capacitance behavior showed by bare stainless steel due to accumulation of charges eventually increases corrosion as indicated by Tafel values (Table 1).At higher frequencies 316L+E-1% and 316L+E-4%coatings showed higher |Z| values than bare metal which suggest that coatings were compact. The316L+E-1% coatings showed no significant reduction in corrosion due to more aqueous transport probably due to pores present in the coating and low percentage of CNTs. On the other hand, the coating316L+E-4% containing higher amount of CNT showed much better results due to higher wt. % of CNTs and hydrophobic nature of CNTs[16]which acted as barrier for aqueous transport through the coating.
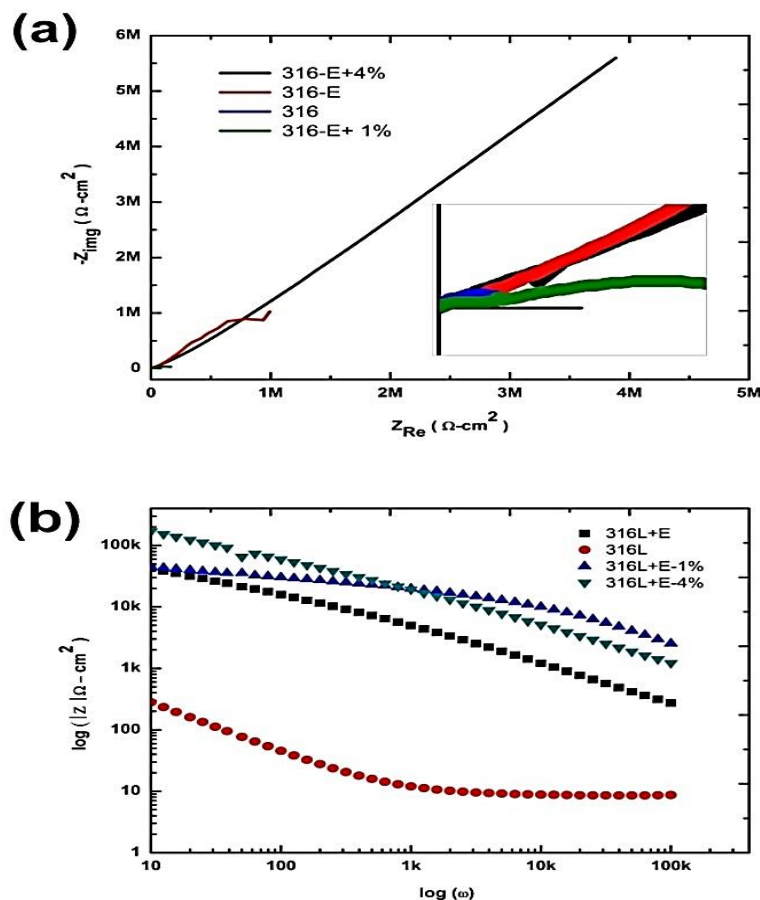
Figure 7. EIS curves obtained in 3.5 % NaCl solution (a) Nyquist curves
(b) Bode plot

4. Conclusions

I. Good yield from CCVD process can be obtained using 100-500mg of ferrocene at temperature of 900 ºC using acetylene flow rate of 150-200cc/min.
II. SEM/EDX results showed higher yield of CNTs were obtained by using acetylene as hydrocarbons precursors than xylene plus acetylene.
III. Electrochemical results indicated that CNTs-based epoxy coatings increased corrosion resistance of bare metal to significant level and this increases with increase of wt. % of CNTs in epoxy resin which hindered the diffusion of aqueous solution in the coatings.

5. References
[1] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes: Their Properties and Applications, Elsevier Science1996
[2] P.R. Birkett, A.J. Cheetham, B.R. Eggen, J.P. Hare, H.W. Kroto, D.R.M. Walton, Chemical Physics Letters, 281 (1997) 111-114
[3] J. Liu, H. Dai, J.H. Hafner, D.T. Colbert, R.E. Smalley, S.J. Tans, C. Dekker, Nature, 385 (1997) 780-781
[4] N.M. Rodriguez, Journal of Materials Research, 8 (1993) 3233-3250
[5] K.-E. Kim, K.-J. Kim, W.S. Jung, S.Y. Bae, J. Park, J. Choi, J. Choo, Chemical Physics Letters, 401 (2005) 459-464

[6]   Z.W. Wicks, F.N. Jones, S.P. Pappas, D.A. Wicks, Organic Coatings: Science and Technology, Wiley2007

[7]   G. Tesoro, Journal of Polymer Science Part C: Polymer Letters, 26 (1988) 539-539.

[8]   M.T. Aronhime, X. Peng, J.K. Gillham, R.D. Small, Journal of Applied Polymer Science, 32 (1986) 3589-3626

[9]   J. Zhou, J.P. Lucas, Polymer, 40 (1999) 5505-5512.

[10]   X.H. Chen, C.S. Chen, H.N. Xiao, F.Q. Cheng, G. Zhang, G.J. Yi, Surface and Coatings Technology, 191 (2005) 351-356

[11]   L.H. Yang, F.C. Liu, E.H. Han, Progress in Organic Coatings, 53 (2005) 91-98.

[12]   B.M. Praveen, T.V. Venkatesha, Y. Arthoba Naik, K. Prashantha, Surface and Coatings Technology, 201 (2007) 5836-5842

[13]   Journal of Composites for Construction, 5 (2001) 200-210

[14]   C.-M. Chen, Y.-M. Dai, J.G. Huang, J.-M. Jehng, Carbon, 44 (2006) 1808-1820

[15]   A. Cao, C. Xu, J. Liang, D. Wu, B. Wei, Chemical Physics Letters, 344 (2001) 13-17

[16]   H. Jeon, J. Park, M. Shon, Journal of Industrial and Engineering Chemistry, 19 (2013) 849-853