A Photo-Cathodic Protection System Utilizing UV Radiations

Intesar Ahmed*, Zaki Ahmad**, Faheemuddin Patel**, M. Shuja Khan*
**Mechanical Engineering Department,
**King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
*Department of Electrical Engineering,
*COMSATS Institute of Information Technology, Lahore, Pakistan
Email: *drintesarahmad@ciitlahore.edu.pk, **ahmadz@kfupm.edu.sa

***Abstract*-- Metallic corrosion of steel can be successfully prevented by using a TiO_2 based photo-electrochemical system under UV radiations. A TiO_2 semiconductor in a scavenging medium (water or formate) generates photocurrent and shifts the potential of steel to more negative values. This paper describes a cathodic protection system using a TiO_2 photoanode. The system has a potential to be developed for field applications because it is capable of fulfilling the dual functions of both cathodic protection as well as environmental cleaning.**

***Index Term*-- UV radiation, Photo-electrochemical process, TiO_2, C.B (Conduction Band).**

1. INTRODUCTION

Corrosion is a major threat to the integrity of costly hydrocarbon assets such as onshore and offshore plants, transport pipelines, infrastructure and process systems and its devastating regimes extending to critical assets, utilities and buildings as well. Cathodic protection and coatings are the two largest contributors to the direct cost of corrosion, which shows the importance of these techniques to mitigate corrosion. In cathodic protection, a substantial progress has been made which is shown by the development of computerized surveillance and mitigating techniques for AC and DC couplings [1]. New anodes comprising of conductive ceramic tubes or cylinders of metal matrix oxide composites (MMC) coated with titanium solid in mesh form are being produced. With the emergence of nanotechnology and increasing demand on green environment, investigations have been undertaken to study the photocatalytic effect of titanium dioxide [2-5]. Photo-electrochemical techniques of corrosion prevention of steel and have been suggested [6-12]. Studies undertaken in recent papers have shown that the cathodic protection of steel by TiO_2 under UV illumination is highly promising. This system offers a method of galvanic system without anode consumption. Photocathodic protection using n-TiO_2 (Nanostructured TiO_2) film on a steel substrate has shown to clean the environment while protecting the structural integrity because of photocatalytic properties of TiO_2 [7].

This paper describes the design of a novel multi functional cathodic protection system using n-TiO_2 photoanode.

2. THEORY OF PHOTOCATHODIC PROTECTION

The basic idea of photocathodic protection is to replace the sacrificial anodes such as Mg, Zn or Al with a semiconductor such TiO_2 and ZnO photoanodes that generate CB electrons upon band gap irradiation (Fig. 1). The principle is to use the reductive energy of photo-exited electrons in the UV irradiated TiO_2 an n-type semiconductor. On contact with steel, the electrons are injected to the metal being protected via conduction band. Hence, the potential of the steel can be polarized in a direction more negative than the flat band potential of TiO_2. If the potential is kept more negative than the corrosion protection of steel, it can be protected [3, 13]. When TiO_2 was galvanically connected to a steel electrode in the absence of light the mixed corrosion potential was close to the Ecorr of steel. However, on illuminating by UV radiations, the TiO_2 electrode became more negative than steel because of photo-generated electrons. The counter reaction is the oxidation of water or any organic contaminants by photo-generated holes but not the oxidation of TiO_2. Hence, TiO_2 photoanode would continuously discharge current without being consumed unlike the conventional Zinc or Magnesium anodes. This makes it an attractive candidate as non-sacrificial anode [5].

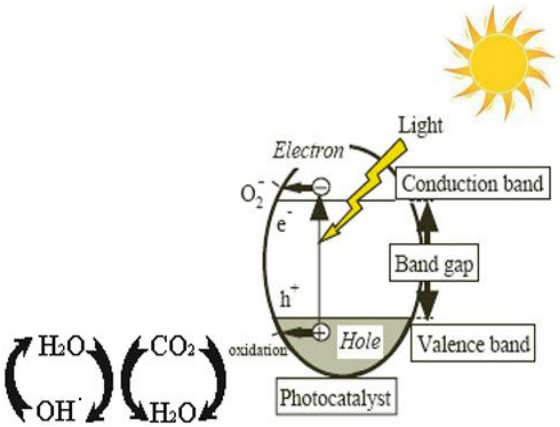

Fig. 1. Photocatalytic effect- Release of electrons and holes and production of OH^- radicals.

$$H_2 + OH^+ \rightarrow \frac{1}{2} O_2 + 2H^+$$

One more problem in using TiO_2 n-type semiconductor is the presence of combination of electrons (e-) and holes (h+). Scavengers may be used to reduce the charge pair combination and enhance electron flow [5]. Pure water and formate solution are useful scavengers. The scavenging medium could be filled to make it regenerative.

$$H_2O_2 + 2h_{vb} \rightarrow O_2 + 2H^+$$

$$H_2O_2 + 2H^+ + 2e^-_{cb} \rightarrow 2H_2O$$

Hence, the plain water serves as a non-depleting hole scavenger. However, the technology needs to be further developed. Whereas conventional CP system requires buried sacrificial anodes system, photoanodes can be installed at ground without being consumed, which is a novel feature of this system. The electrons are transferred from the photoanode via the scavenging medium and steel electrode to the structures buried in water or soil. The principle is illustrated in Fig. 2. The absence of UV radiation at night, which is a limitation of this system, can be compensated by utilizing a solar powered rechargeable battery charging by day and releasing the current at night. Coupling of materials such as Ti-WO_3 and Ti-SnO_2 is expected store energy to be released at night in the absence of UV radiations [9]. If one can suppress the electron-hole recombination process of by channelizing the excess electrons to some other source during illumination, which can be released to outer circuit (substrate) during dark, the metal could be protected day and night. It can be done by connecting the system with semiconductor pair of TiO_2 and WO_3.

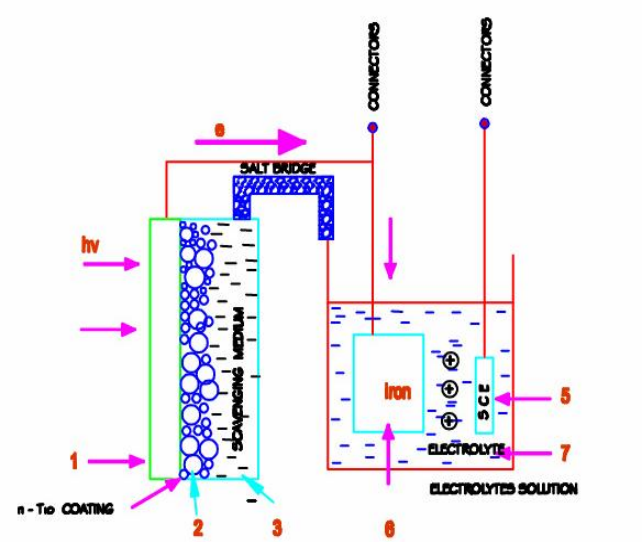

Fig. 2. Photo electrochemical cell for steel corrosion prevention.

Photocathodic protection system has the following properties

- Galvanic cathodic protection capability of structures at ground level
- Sustainable maintenance
- No external power
- No replacement of galvanic anode

3. METHODOLOGY

3.1. Preparation of substrate

It is necessary to produce a two level nano/micro hierarchical surface roughness to repel water and dust for clean environment and efficiency. It is only possible if a nano-micro hybrid surface is created. A two level surface roughness may be achieved by cavitation shot penning (CSP) followed by annealing at 200ºC or 400ºC and followed by furnace cooling [15]. The surface is viewed with a field emission gun scanned electron microscope (FEGSEM) to ensure that the grain size ranges from micrometer to nanometers. The grain size obtained was 20nm.

3.2. Preparation of TiO_2 film for fabrication of photoanode

After the surface preparation, the substrate is coated with n-TiO_2. The well-known sol-gel technique [3, 10, 16 and 17] is used to deposit TiO_2 on indium tin oxide (ITO) glass. This technique is easier and could be used at large scale. In this method, 20 ml of ethanol and 1 ml of ethylacetoacetate (EACAC8) are mixed with 2 ml of tetra-n-butyl titrate and the solution is continuously stirred for one hour. For hydrolysis 0.2 ml distilled water is added after 30 minutes and the solution is kept stirring for 10 hours. The transparent solution is aged for 24 hours before applying on the substrate. It is cleaned and dried in an oven for 30 minutes. The coated substrate is exposed to 450ºC for solvent removal and again aged in furnace for 10 minutes at 450ºC. A solution of fluoralkyl silane solution (1%) is prepared, hydrolyzed and heated to 140ºC before application. This provides water repellency effect. Titanium nanotubes could be introduced to improve water repellency and self cleaning effect. However, the process becomes economically unviable. Other techniques such as plasma spraying, chemical vapor deposition and physical vapor deposition techniques are available. Most of these techniques are cost-intensive; however, the sol-gel technique is economical and more commonly used.

4. GALVANIC PHOTOCATHODIC PROTECTION STUDIES

Experimental cathodic protection studies were conducted in a custom made electrochemical polarization cell. The cell had optical quartz windows for the passage of Ultra-Violet radiation (5mm) with inlets for gas. It also had

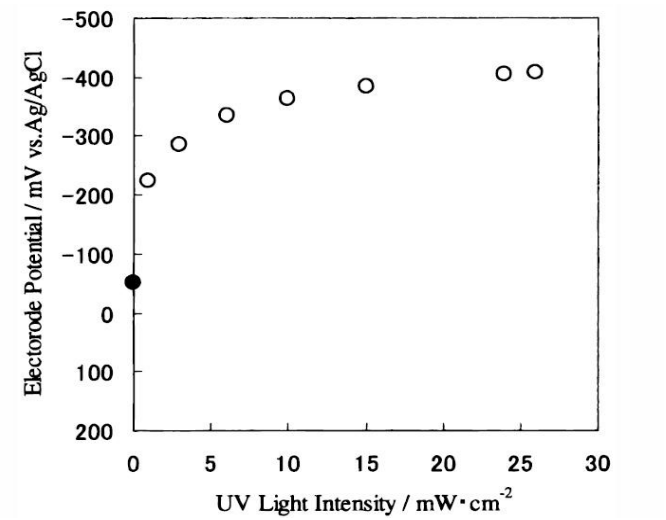

Fig. 3. Variation of electrode potential with UV light intensity.

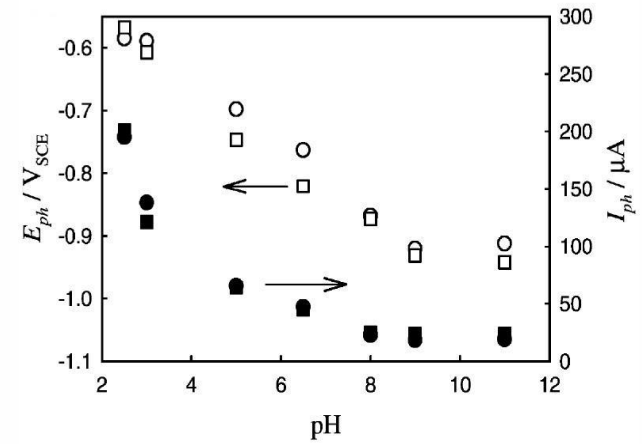

Fig. 4. Variation of E_{ph} with pH [5].

temperature controller, magnetic stirrer and electrodes (Calomel, Platinum and working electrode). The electrolyte was an aerated 3.5 wt% sodium chloride solution. The specimen was made of 2.5cm3 diameter n-TiO2 coated steel. UV light source was Mercury-Xenon lamp with a working life of at least 1000 hours. The lamp current was 15-20A DC and provides continuous spectrum in UV range. The UV source was used with a 400nm band pass filter. A switching type of power supply was used for this lamp. A portable UV meter with USB port and sensor probes was used. For measurement, UV-VIS sensors with radiometer and controller were used. A photometer was used for the measurement of gas, liquid and solid transmission [7]. Starting from the open circuit potential stabilizing for 45 minutes, polarization curves were obtained in anodic and cathodic directions. Polarization current was recorded both in dark and under UV radiation. The shift of Ecorr under open circuit to negative value of polarization was recorded. In this study, an Ecorr of –0 mV vs. Ag/AgCl, was obtained for TiO2 coated 304 steel in dark. On illumination of n-TiO2 under UV radiations, the Ecorr of TiO2 coated steel shifted to a value of -350mV vs. Ag/AgCl, (Fig. 3) which shows the beneficial effect of UV radiation on its capability to cathodically protect steel [7]. The photo potential of TiO2 coated 304 Steel remained constant. The photo potential, however, varied with PH, NaCl concentration, area coverage and UV light intensity. These factors needed to be optimized to keep the photo-potential in the desired range. Under, more acidic conditions electron transfer at steel/solution interface increased due to proton (H+) induction ($2H^+ + 2e \rightarrow H_2$) and cathodic protection decreased. Under high PH, the photocurrent is increased as shown in Fig. 4 [5]. A good evidence of photo protection of steel [8] and copper alloys [18] by n-TiO2 under UV radiation has been reported. It was found that the pitting resistance 304 steel increased under UV radiation in 3.5w% NaCl.

4.1. Ultraviolet Radiation and cathodic protection

Photocathodic protection depends on the intensity of UV radiation. In gulf region, the maximum average U.V. radiation of 3.7w/m2 was recorded in Riyadh (Saudi Arabia) [19]. The monthly average UV radiation to global radiation is 0.034± 0.001. In Tokyo, Japan, the maximum UV radiation of 3.4mw/cm2 was recorded and many successful outdoor trials have been made.

5. DESIGN OF PHOTOCATHODIC PROTECTION SYSTEM

The cathodic protection design based on photoanode is still in developmental stage [7]. From a broad range design consideration, the system is based primarily on a photoanode compartment containing an indium tin oxide glass plate coated with TiO2.

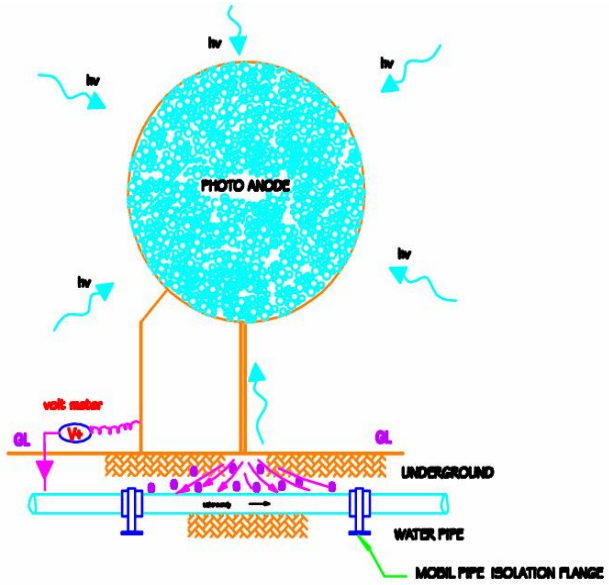

Fig. 5. Design of photo-cathodic protection system.

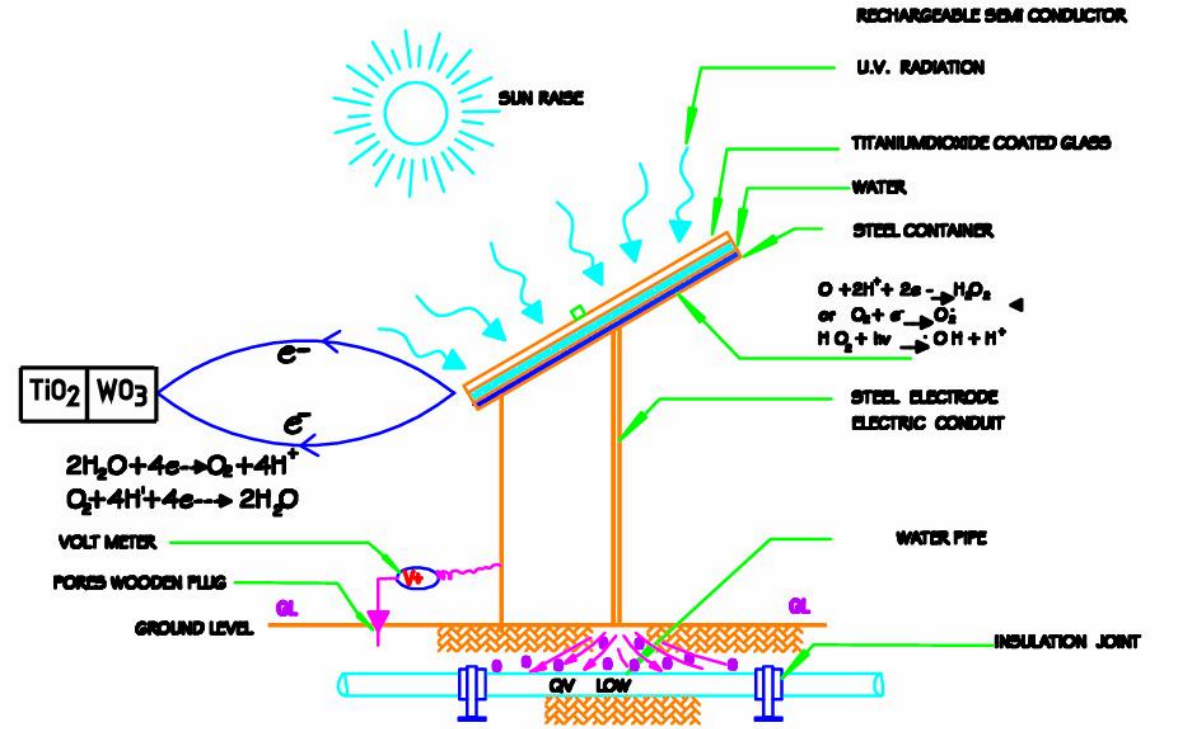

Fig. 6. Details of the proposed design of photocathodic protection system.

Pure water or a formate solution serves as a hole scavenging media to prevent the recombination of holes and electrons. It is observed that H2O2 reduced back to water. Fig. 5 and 6 illustrate the working and dual functioning of TiO_2 semiconductor anode under UV radiation.

$$H_2O_2 + 2h_{vb} \rightarrow O_2 + 2H^+$$
$$H_2O_2 + 2H^+ + 2e_{cb}^- \rightarrow 2H_2O$$

A steel support is connected to the photoanode assembly and fixed at a ground level. Electrons are released from the compartment to be protected. A PVC salt bridge is connected from the photoanode compartment to the ground [5]. An electron pool made by coupling TiO2 coating with WO3 coating is attached to the photoanode (Fig. 6), so that the electrons are collected for the day and released and merged in the electron pool. It is stated that charged WO3 coating could protect stainless steel even in the absence of sunlight (UV radiations). The principle is shown in Fig. 7. The electrons originally enter the structure from the ground level and act in a manner similar to the conventional cathodic protection system. The cathodic protection measurements are same as in conventional systems. A prototype is being developed at KFUPM.

The principal advantage of this novel system is that it is easier to maintain anode above the ground level and external power or intervention is needed. This system offers the unique advantage of environmental cleaning by superoxide and hydroxyl radicals upon been acted by UV radiations.

$$O_2 + e^- \rightarrow \bullet O_2^-$$
$$H_2O + h_{vb}^+ \rightarrow \bullet OH^+ + H^+$$
$$2(\bullet OH) \rightarrow H_2O_2$$

This creates a photocatalytic effect as shown in Fig. 8. For photocatalytic degradation, TiO2 and SnO2 couple may also be used (Fig. 9). All electronic and electrical devices such a photoelectron detector and ammeter are attached through a copper wiring.

$$T_iO_2 \xrightarrow{UV} T_iO_2^X(e^- + h)$$
$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$
$$WO_3 + xe^- + xNa \rightarrow Na_xWO_3$$

Despite some shortcomings, the system offers potential advantages such as the use of maintenance free non sacrificial anodes, eliminating the need for a periodic replacement of anode. One of the greatest advantages of the system is that it is a system which offers cathodic protection and environmental cleaning effects. These are the true assets of the system.

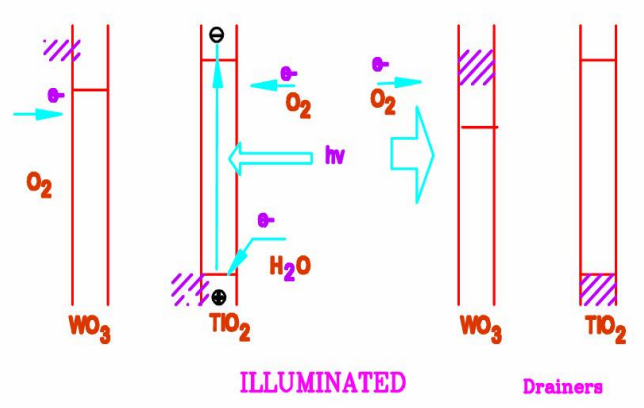

Fig. 7. Storing of reductive energy by WO_3 in NH_4Cl solution [5]

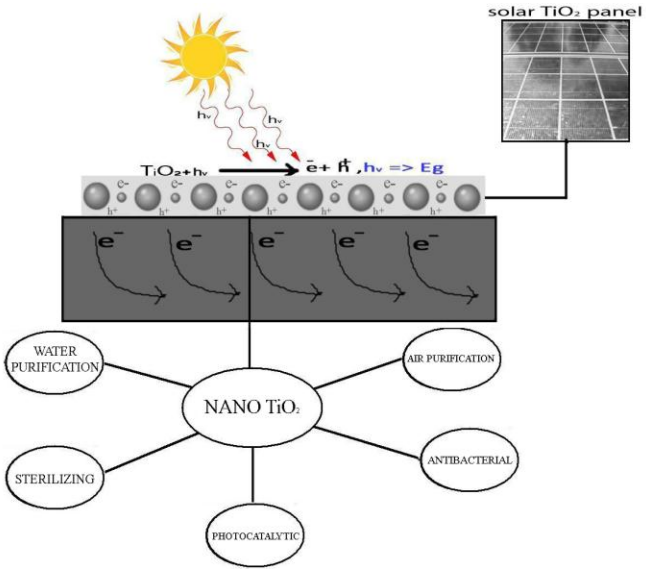

Fig. 8. The Photocatalytic Effect.

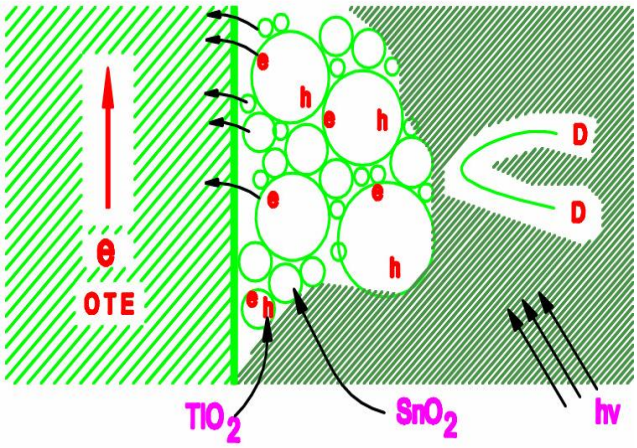

Fig. 8. Idealized illumination of photoinduced charge separation in composite semiconductor [7].

6. CONCLUSION

Steel can be catholically protected by using a TiO2 (n-type semiconductor) based photo-electrochemical system. The photoanode is made by depositing TiO2 using sol-gel technique and placed in water or formate (hole scavenging) medium under UV radiations. This photoanode supplies electrons to the steel by shifting its potential at more negative values depending on PH, electrolyte concentration and UV light intensity. The system is, in a way, similar to conventional cathodic protection system, with the added advantage of eliminating the need for periodic replacement and maintaining an external power. The system also acts as environmental cleaner because of the products such as OH- and O2- radicals. It has been claimed that a TiO2 - WO3 system is capable of storing energy at daytime and release it in the dark in the absence of light, which overcome the limitation of the system in the absence of UV radiations at night. This photo-induced CP system looks environmentally attractive and technically promising, however, more research is required before it can replace the existing CP systems.

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Intesar Ahmed received Phd Electrical Power Engineering from University of Adelaide, South Australia and M.Sc. in Electrical Power Engineering from University of New South Wales, Sydney, Australia in 2007 and 1994 respectively. Currently he is the Head of Renewable Energy and Power Systems research group in Department of Electrical Engineering, COMSATS Institute of Information technology, Lahore Pakistan. He has been involving in various research projects relating to online condition monitoring of electrical machines, power electronics, and study of multiple faults in electric machines via signal processing techniques.

Dr. Zaki Ahmad obtained his Ph.D. from the University of Leeds in Metallurgy. He joined the Mechanical Engineering department of King Fahd University of Petroleum & Minerals in 1980 as an associate professor. He specializes in the field of corrosion engineering and development of alloys for industrial and marine environment. He has a distinguished teaching and research career in highly reputed institutions in Germany, UK and USA. He is a fellow of Institute of materials, and Institute of Metal Finishing (UK) and a member of Education group of European Federation of Corrosion. He is actively engaged in research. He developed a new aluminum bronze with Metallgessellschaft A.G. Germany and modified alumininum alloys with GKSS, Germany. He is working currently on the corrosion mechanism of Al-SiC composites and effect of Scandium on Al-Mg alloys for transport industry. His major interests are in the area of new alloy development, Al-SiC composites, and corrosion sensors. He established several corrosion laboratories in Iran, Germany, and Saudi Arabia. The Corrosion Laboratory at KFUPM is a centre of excellence of which he is the director. He has been the principal investigator of several International Projects with Germany, Austria and U.K. He has participated in several Industrial Projects.

Faheemudin Patel is with Mechanical Engineering Department, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia. He completed MS Mechanical Engineerinf from KFUPM in May 2006. His research interests include Testing, Analysis and Characterization of Materials and Composites, Tribology, Nano Technology, Processing and Characterization of Polymers

Muhammad Shuja Khan completed MS degree in Electronic Engineering from Ghulam Ishaq Khan Institute (G.I.K.I.) of Engineering. Science & Technology, Swabi Pakistan and B.Sc. in Electrical (POWER) Engineering from University of Engineering & Technology, Lahore Pakistan in June 2009 and July 2007 respectively. Currently he has been serving his duties as Lecturer in Department of Electrical Engineering, COMSATS Institute of Information technology, Lahore Pakistan since August 2009. His research interests include design and modeling of M/NEMS devices, M/NEMS fabrication techniques, Microsystems including different Energy Harvesting Technologies and investigation of multiple faults in Machines. He was awarded Higher Education Commission Pakistan Indigenous Fellowship Award for his MS studies at G.I.K.I. 2007-09. He was also awarded two International Travel Grants for presenting his research papers in ICSCT 2009 and ICMENS 2010 held in South Korea and China respectively.