NEWSLETTER

ENERGY RESEARCH CENTER

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COMSATS INSTITUTE OF INFORMATION TECHNOLOGY LAHORE

Contents

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ERC Activities

Workshop on Energy Efficiency and Conservation/Energy Audit

COMSATS Energy Research Center in Collaboration with Punjab Energy Efficiency and Conservation Agency (PEECA) arranged one-day Training Workshop on Energy Efficiency Calculation Tools at CIIT IRCBM seminar room on 11th May, 2017. The key objective of the seminar was to create awareness among the industrialist, faculty members, students and impart training on energy efficiency and conservation of various equipment including pumps, motors, boilers, furnaces etc. The workshop was attended by CIIT Faculty, Engineers from Industry, Punjab Agriculture Department and students of EE department.

Mr. Khalid Saeed, Head ERC, inaugurated the session with his welcome remarks. He explained the significance of Energy Efficiency and Conservation and its impact at global level. Mr. Khalid Saeed put emphasis for adopting energy efficiency and conservation practices as demand side management in Pakistan to supplement the additional power generation being planned. He also appreciated the efforts of Punjab Energy Efficiency and Conservation Agency (PEECA) for creating awareness on energy efficiency related issues in the province.

The training lecture was delivered by Mr. Salman Butt (Certified Energy Auditor) which covered the following topics:

Introduction to Energy Management System (ISO 50001), Basic Requirements of ISO 50001 & other related international standards

Description:
Complete Introduction to Energy Management Systems (ISO 50001) was given along with the brief introduction to the other implementing ISOs. The comparison of ISO 50001 was made with the other important ISOs like

- ISO 9001 (quality),
- ISO 14001 (environment) and
- ISO 50001 (energy)

Some key features of the existing ISO 50001 were described in detail. In continuation to the ISOs comparison, Five major ISO brands were discussed, which include:

- **Democratic** → one country – one vote
  Each country is on an equal footing to influence the direction of ISO's work
- **Voluntary** → non governmental organization
  ISO standards are voluntary: ISO itself does not regulate or legislate
- **Market-driven**
  ISO only develops standards for which there is a market requirement
- **Consensus** → state of the art
  ISO standards are based on international consensus by requiring a periodic review of its standards at least every five years
- **Globally relevant** → are relevant everywhere
  ISO standards are technical agreements which provide the framework for compatible technology worldwide

Characteristics and families of ISO 50001 were also discussed that includes following major points.

Characteristics:

- Imposes "DATA" oriented management practices, thus focuses on performances
- Defines organizations and companies to have a well-recognized framework for integrating energy efficiency into their management practices
- Properly run operational management system that promotes sustainable business development
- EnMS is about business development
- Produce the best quality product on account of least energy consumption

ISO Families:

- **ISO 50001:2011** Energy Management Systems – Requirements with guidance for use
- **ISO 50002:2014** Energy audits - Requirements with guidance for use
- **ISO 50003:2014** Energy management systems - Requirements for bodies providing audit and certification of energy management systems
- **ISO 50004:2014** Energy management systems - Guidance for the implementation, maintenance and improvement of an energy management system
- **ISO 50006:2014** Energy management systems - Measuring energy performance using energy baselines (EnB) and energy performance indicators (EnPI) - General principles and guidance
- **ISO 50015:2014** Energy management systems - Measurement and verification of energy performance of organizations - General principles and guidance

While concluding the discussion of ISO 50001, Mr. Salman summarized some key elements of the ISO 50001 implementation that are:

- Set an energy policy

- Name an energy team
- Conduct an energy review
- Establish an energy baseline
- Establish energy objectives and targets
- Establish an action plan
- Implement the action plan
- Check and improve performance
- Monitor, document and report all the above

Energy Efficiency in Motors, Energy Performance of motors, Motor Energy Efficiency Self-Assessment Tool

Description:
A detailed discussion on Energy Efficiency in motors along with the numerical exercises was done during the sub section of Energy Efficiency in motors. Mr. Salman Butt elaborated Power calculations tools that are necessary for calculating motor efficiency. The characteristic curve of electric motors, its efficiency voltage and current ratings were discussed in details.
Motor losses, class of motors in terms of its efficiency and some key features related variable frequency drives were also discussed in detail.

Energy Efficiency in Pumps, Energy Performance of Pumps, Pump Energy Efficiency Self-Assessment Tool

Description:
Introduction to Pumps, its working and utilization in different fields like industry, domestic sector were discussed. According to the speaker pumps are considered as a heavy load which requires efficient operation. Different types of pumps and associated power ratings were also discussed in detail.
Mr. Salman identified some key parameters associated with the utilization of pumping that needs to be taken care of while operating pumps in any vicinity which are given as under.

- Average pumping efficiency in manufacturing plants can be less than 40 %
- With 10 % of pumps operating below 10 % efficiency.
- Oversized pumps and the use of throttled valves were identified as the two major contributors to the loss of efficiency.

- Energy savings in pumping systems of between 30 % and 50 % could be realized through equipment or control system changes.
- A pump's efficiency can also degrade during normal operation due to wear by as much as 10 % to 25 % before it is replaced.
- Efficiencies of 50 % to 60 % or lower are quite common.

Energy Efficiency in Melting Furnaces, Energy Performance of Melting Furnaces, Energy Efficiency Self-Assessment Tool and Energy Efficiency in Steam Boilers, Energy Performance of Steam Boilers, and Boilers' Energy Efficiency Self-Assessment Tool were also briefly discussed in the technical session.

The workshop participants also discussed the energy efficiency and conservation measures to be taken in daily routine along with the focus on utilizing energy efficient devices. In Pakistan, majority of the people are unaware of energy efficient devices and are still using the old inefficient sub-standard devices. It was stated that industries can overcome the Energy deficit by applying ISO 50001 standards and by simply going through the detailed energy audits. Some success stories of Energy Audits of Industries in Pakistan while implementing ISO 50001 standards and their fruitful impacts were also highlighted in the discussion.

Energy efficiency procedures as well as software related to energy management and Self-assessment tools for identifying the energy losses of motors, pumps, boilers etc. were of particular interest to the Industry, Engineers from Agriculture Department and CIIT EE Faculty. The Chemical Engineers participated in energy auditing of boilers and furnaces and showed interest to work on software /energy management system for further training of CIIT students.

The second session of the workshop was based on the calculations tools used for energy efficiency, conservation and energy audits. A detailed calculation tools were discussed along with the techniques that can be used for effective energy audits.

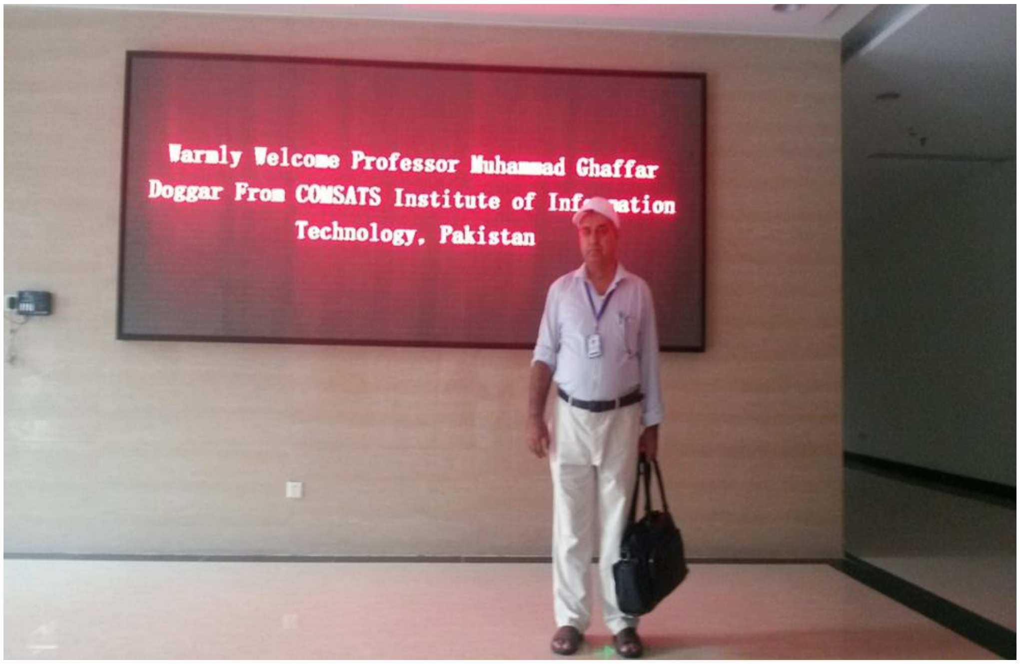
The session was attended by the faculty members of various departments of COMSATS IIT, students and industrialist. The workshop session was an open discussion session where all the attendees actively participated. Head of various faculties (Chemical, Electrical Engineering Departments) and Head Academics and Research attended the workshop and appreciated the efforts of ERC for conducting such an informative session, they also put emphasis on conducting such events on regular basis so as to create awareness and develop skills among the students and faculty members.

It was also proposed that PEECA will invite CIIT Faculty in similar programs to be launched in future as well. The Industry and Agriculture Engineers requested to arrange for practical training sessions on site, in field, for which large scale gathering of engineers shall be assured. For joint training programs on energy efficiency topics shall be proposed by Industry and Agriculture Department engineers.

Mr. Khalid Saeed presented vote of thanks to all the attendees of the seminar and urged to implement ISO 50001 standards within the campus while collaborating with the relevant departments in his concluding remarks.

Progress on the Project "Basic Research and Capacity investigation For Distributed Bio-Energy Utilization via Thermo-Chemical Conversion"

The project entitled "Basic Research and Capacity investigation For Distributed Bio-Energy Utilization via Thermo-Chemical Conversion" was approved under Pak China Cooperation: Joint Research Projects between Pakistan Science Foundation (PSF) and National Natural Science Foundation of China (NSFC), at the cost of Rs. 8.5536 million with an implementation period of 36 months. The starting date of the project is 15th December 2016. As part of the project implementation activities, the Principal Investigator (CIIT ERC) visited Guangzhou Institute of Energy Conversio China Academy of Sciences Guangzhou on 31.5.2017 to 7.6.2017 for project initiation meetings and to prepare plans for its implementation.



Dr. Muhammad Ghaffar Doggar held meetings with CoPrincipal Investigator and research team of Biomass Gasification Project at Guangzhou Institute of Energy Conversion (GIEC) and discussed the project implementation plan, construction of equipment, training of manpower and testing and demonstration of equipment in Pakistan. Presentations were also given by both sides about the project activities and implementation plans. It was agreed that design of the system shall be fixed bed type and it will be designed and developed by Chinese experts. Training of CIIT manpower shall be conducted after its design is finalized and construction sites yet to be decided. For construction of the system both options (in China and Pakistan) are under consideration. Issues of supply of raw material and requirement of supporting equipment during testing and its arrangements were also highlighted. It was agreed that CIIT shall conduct testing of equipment in Pakistan under the supervision of Chinese experts. Dr. Doggar also visited Biomass Gasification Plant which was designed and installed by GIEC researchers in 2015 at Lei Yun Pharamaceuticals Industry in Yunfu district. Meetings on biomass gasification project were held with GIEC researchers, PI and team members in which discussions were again held on the implementation of project and relevant issues. A presentation on biomass energy resource potential in Pakistan was also made. Individual meetings were also held with President GIEC (Dr. Haibin Li) and experts of Biogas energy (Dr. Xialong Kong), solar energy (Dr. Wang Xianglong, Dr. Huang Leia) and geothermal energy (Dr. H. Li) and it was discussed that joint proposals shall be developed in future. Dr. Muhammad Ghaffar Doggar also held meetings with energy experts (Prof. Qing Hua Wu Head, and Dr. Web Hu Tang vice Dean) School of Electric Power Engineering, South China University of Technology, Guangzhou. The experts are working on smart energy grids and RE integrated management systems. Chinese experts were willing to develop joint projects under PSF and China NSFC call for proposals which have been issued on 01.06.2017. Dr. Doggar Also visited Prof. Xie Jun, Director New Energy Materials and Bio Technology Group, South China Agriculture University and discussed options for collaboration to develop joint projects on energy technologies.

ERC to Establish State of the art Labs under project of Advanced Technology Training Center at Knowledge Park, Muridke

ERC plans to establish state of the art conventional and renewable energy labs under approved project of Advanced Technology Training Center at Knowledge Park, Muridke. The Project is a part of efforts to improve access to health and education services, inculcate sustainable growth and promote entrepreneurship in order to move towards becoming a knowledge based economy. It will be financed from the PSDP provision of the Higher Education Commission. In line with the objectives and the goals of the Vision 2025, the project is of immense importance for the country and merits its inclusion in the current priorities of the higher education sector plans. The purpose of the project is to develop infrastructure, human resource and support research facilities in an area targeted by the Government for promotion of research, development and technology incubation.

The project is proposed to be included in the PSDP of current year at a total cost of Rs.2940.341 Million. The project shall be completed in 36 months. ERC shall develop 8 state of the art labs (list given below) under the project. Theses labs cover major research areas of conventional/renewable energy. A part from development of labs, other necessary infrastructure like, class rooms, seminar rooms, faculty hostel, office and transportation etc. are the integral part of the PC-1.

ERC Labs to be developed

1 Bio Energy Lab

2 Spectroscopy Lab

3 Advanced Fuel Cell Lab

4 Advanced Energy Storage Lab

5 Simulation and Computational Lab

6 Solar PV and Thermal Testing Lab

7 Energy Audit Lab

8 Hydel Energy Lab

Professor Jean Louis Marty (University of Perpignan, France) visits Energy Research Center (ERC), COMSATS Lahore

Professor Jean Louis Marty (Biosciences and Environment), University of Perpignan, France visited Energy Research Center on 25th April, 2017 and held meeting with Mr. Khalid Saeed, Head ERC. He discussed about the proposals of collaboration between ERC and Promes Renewable Energy Research Center and Promes Renewable Energy Laboratory for joint research and training of faculty members.Professor Jean Marty introduced the University of Perpignan and Promes Renewable Energy Laboratory and highlighted the core activities of research and academic programs. Mr. Khalid Saeed briefed, on-going research activities and future plans. It was agreed to introduce to each other the faculty and researchers working on Renewable Energy of both institutions to interact and collaborate for joint research and other programs of mutual benefits.

Participation in Seminar on Energy Efficiency for Sustainable Future

ERC officials Mr. Fawad Azeem and Mr. Faisal Farooq, Lecturer ERC attended Seminar on Energy Efficiency for Sustainable Future arranged by Punjab Energy Efficiency and Conservation Agency (PEECA) on 22 May, 2017 at Avari Hotel Lahore. A large number of delegates from public and private sector including business personnel, academicians, industrialist and policy makers attended the seminar. Major areas covered during the seminar were, general energy conservation and efficiency, power factor, LED lighting, Energy Services Companies (ESCOs) model, 3 star label fans and energy efficient building codes (ECBC). The purpose of the seminar was to sensitize relative stakeholders about energy efficiency and conservation measures initiative and educate them to create balance between demand and supply of energy in the country for sustainable future

Participation in Seminar on Building the Future Together

Dr. Muhammad Ghaffar Doggar, PSO, ERC attended a seminar on Building the Future Together arranged by Punjab Energy Efficiency and Conservation Agency PEECA on 6th May, 2017 at Pearl Continental Hotel Lahore. The core objectives of the seminar were to deliberate on consultation on Review & Modification of Building Codes of Pakistan-Energy Provisions 2011 specific to Punjab Region, importance of Building Energy Codes to design professionals and allied stakeholders and to develop partnership among design professionals, Material Manufacturers and Code Enforcement agencies. The seminar was attended by the large number of public and private sector, industries, academic institutions and other relevant departments.

COMSATS ERC to Work for Academia-Industry Research and Development Linkage

CIIT ERC and EE engineers visited Monnoo Industries on 25th May, 2017. The objective was to develop collaboration between Monnoo Industry and CIIT to work on joint energy efficiency and renewable energy projects. Mr. Tahir Mehmood, Technical Director Monnoo Industries Lahore, introduced the industrial units, its processes, products and equipment. CIIT team along with Mr. Tahir also conducted the tour of the industry and saw the equipment and its functioning on site. It was agreed that CIIT experts will conduct feasibility study on energy efficiency for replacing motors, pumps and introducing solar drying systems for air / liquid drying with all expenditures to be borne by the client. It was also agreed that detailed TORs shall be settled in further meetings between the Heads of CIIT and Monnoo Industries Group

Research Articles

CathodicTitania Nanotube Arrays as Anode Material for Lithium-ion Batteries

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Abstract

The titanium dioxide nanotube arrays (TNAs) have been synthesized at cathode and anode via standard electrochemical method for their subsequent use as anode material for lithium-ion batteries (LIBs). The TNAs fabricated at cathode have higher Ti^{3+}in comparison to TNAs at anode, which was confirmed by using X-ray photoelectron spectroscopy and Raman spectrometry. Moreover, the lattice parameters of cathodic-TNAs are estimated via Rietveld refinement of X-Ray diffraction, which also conform Ti^{3+} doping and insertion of protons (H^+). The electrochemical impedance spectroscopy hints an increment in the electronic conductivity of TNAs fabricated at cathode. As a result, high reversible areal specific capacity (~ 385.5 µAh cm^{-2} at 100 µA cm^{-2}) with excellent rate capabailityare acquired by utilizing TNAs fabricated at cathodeas anode material in LIBs.

Keywords: Titanium Dioxide Nanotube Arrays, Electrochemical Properties, Anode Material, Lithium-ion Batteries

1. Introduction

The development of next-generation energy storage devices is inevitable to meet the challenges of electronics and portable gadgets. The interest is increasing in the development of new nano materials that can overcome the intrinsic limitations of high volume changes of the active materials, high internal resistance, low cycle stability, side reactions and safety issues. Titanium dioxide (TiO_2) is one of the promising anode materials due to its inexpensive availability, thermal stability, chemical stability, low volume expansion and low possibility for lithium dendrite formation.

Bulk TiO_2material has poor transport characteristics owing to its limited electronic conductivity and slow lithium-ion diffusion. Therefore, decrease of grain size to nano-scale, i.e. nano-particles, nano-porous structure, and nano tubes arrays, is proved to be an effective strategy by enhancing the contact surface areas between active materials and electrolyte, and short ening the lithium-ion insertion/extraction paths. Transportation of lithium ions and electrons for TiO_2 electrodes has been the topics of the extensive research in recent years. Different strategies have been adopted to enhance the electrochemical properties of TiO_2, such as surface modification with conductive (carbon) coating, annealing in the different atmosphere and ionic doping. Ren *et* *al*. prepared Ti^{3+} doped TiO_2 by controlled solvo-thermal process at low temperature and achieved the specific capacity of 202.1 mAh g^{-1} at 100 mA g^{-1}. They also reported high-rate charge/discharge capability and cyclic stability at 3000 mA g^{-1}.Liu *et al*., synthesized Ti^{3+} doped TiO_2 nano tube arrays by annealing in CO atmosphere that exhibited excellent lithium ion insertion/de-insert ion performance with an initial discharge capacity of 101 mAh g^{-1} at a high current density of 10 Ag^{-1}. Lu *et al*. reported creation ofTi^{3+}in TiO_2nanotube arrays by annealing in a hydrogen atmosphere and achieved high rate capability due to high electronic conductivity. However, to the best of our knowledge the electrochemical properties of cathodically reduced TNAs are rarely explored.

Herein, we adopted a facile cathodic reduction strategy to prepare Ti^{3+}doped TNAs which enhanced the electronic conductivity of TNAs after Ti^{3+}doping and output results are similar to the previously reported literature. Furthermore, cathodic-TNAswere used as anode material in LIBswith exciting improvement in the specific capacity and rate performance.

2. Experimental details

2.1 Synthesis

The titania nanotube arrays electrode (anodic-TNAs) was fabricated by an odization of titanium foil. First of all, 99.7% pure titanium foil (thickness ~ 0.125 mm, Sigma Aldrich) was degreased by sonication in acetone for 10 mins. It is again put in ethanol solution and sonicate for 10 mins. At the end, titanium foils were sonicated in deionized water for 5 mins and dried in air. Electrochemical anodization experiments were conducted at a constant potential difference between electrodes with a DC power supply (DH1722A-2 110V/3A). The electrolyte solution was composed of 0.3 wt. % NH_4F and 2 vol. % water in ethylene glycol (99.8%, anhydrous). All experiments were performed at room temperature. Titania nanotube arrays (anodic-TNAs) were grown at 50 V for 6 hours and nanotubes layer was removed as reported. Now anodic-TNAs were re-grown at same potential for 2 hours and annealed at 450 °C in air for 2 hours to transform from amorphous to anatase.

Electrochemical reduction technique was adopted for Ti^{3+}doping of anodic-TNAs with minor changes in the experiment. The electrochemical cell for anodization consisted of Ti foil as working electrode and a platinum foil as the counter electrode in a two-electrode cell. The experiment was carried out in two electrode system similar to anodic oxidation with polarity reversal. The electrochemical reduction was carried out for 10 minutes at 4 V cathodic potential in the supporting electrolyte of 1M $(NH_4)_2SO_4$solution at room temperature. After electrochemical reduction process cathode washed with deionized water several times.

2.2 Characterization

The surface and cross-sectional morphologies of anodic-TNAsand cathodic-TNAswere characterized using Field Emission Scanning Electron Microscopy (FE-SEM LEO 1530).Average nanotube dimensions were also determined by SEM and TEM. Phase purity of both samples was characterized using X-ray powder diffraction (Rigaku D/max) with Cu Kα at wavelength λ=0.15 nm.To calculate the crystal lattice parameters of samples, XRD patterns were analyzed viaRietveld refinement by profile matching method using Fullprof suite program.X-ray photoelectron spectrometry (Escalab-250Xi, Thermo Scientific, USA) was utilized for observation of thechemical state of surface atoms.To remove the oxidized top surface layer of the anodic-TNAs and cathodic-TNAs, theArgon sputtering for few minutes was employed before analyzing Ti^{3+} in the bulk phase. XPS fitting was performed via Avantage Thermo Scientific^{TM}. Thestructural analysis was performed by Raman spectroscopy (Renishaw-HR800).

2.3 Electrochemical characterization

Lithium storage performance ofanodic-TNAshas been evaluated using Li|anodic-TNAs or cathodic-TNAshalf-cells of type 2032-coin cell, assembled in anargon filled glove box usingconductive-carbon and binder-free electrodes. A celgard 2300 polypropylene separator soaked with a liquid electrolyte of 1 M $LiPF_6$ dissolved in a 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) was placed between the electrodes. The cells were galvanostatically charged and discharged between 1-2.5 V (*vs.* Li/Li^+) at current density of 100 μA cm^{-2}.All the potentials in this paperrefer to potential versus Li/Li^+.

The galvanostatic discharge/charge measurements were carried out by battery testing system (LAND CT-2001A Instrument, Wuhan, PRC) at 100 μA cm^{-2} for 100 cycles. The electrochemical impedance spectroscopy (EIS) measurement was recorded using electrochemical workstation (CHI660C, CH Instruments, Shanghai, PRC) at 5 mV s^{-1} between 0.01 Hz-100 kHz. EIS measurements were performed after 100 cycles under the 100 μA cm^{-2} current density between potential windows of 1-2.5. Open circiut potential for anodic–TNAs and cathodic-TNAs are 2.073 V and 1.839 V, respectively.

3. Results & discussion

The morphology of anodic-TNAs and cathodic-TNAsis characterized by using SEM (Fig. 1 (a)). The top (Fig. 1 (a)) and lateral view (insetFig. 1 (a)) showthat the TNAsare uniform in size and oriented vertically.

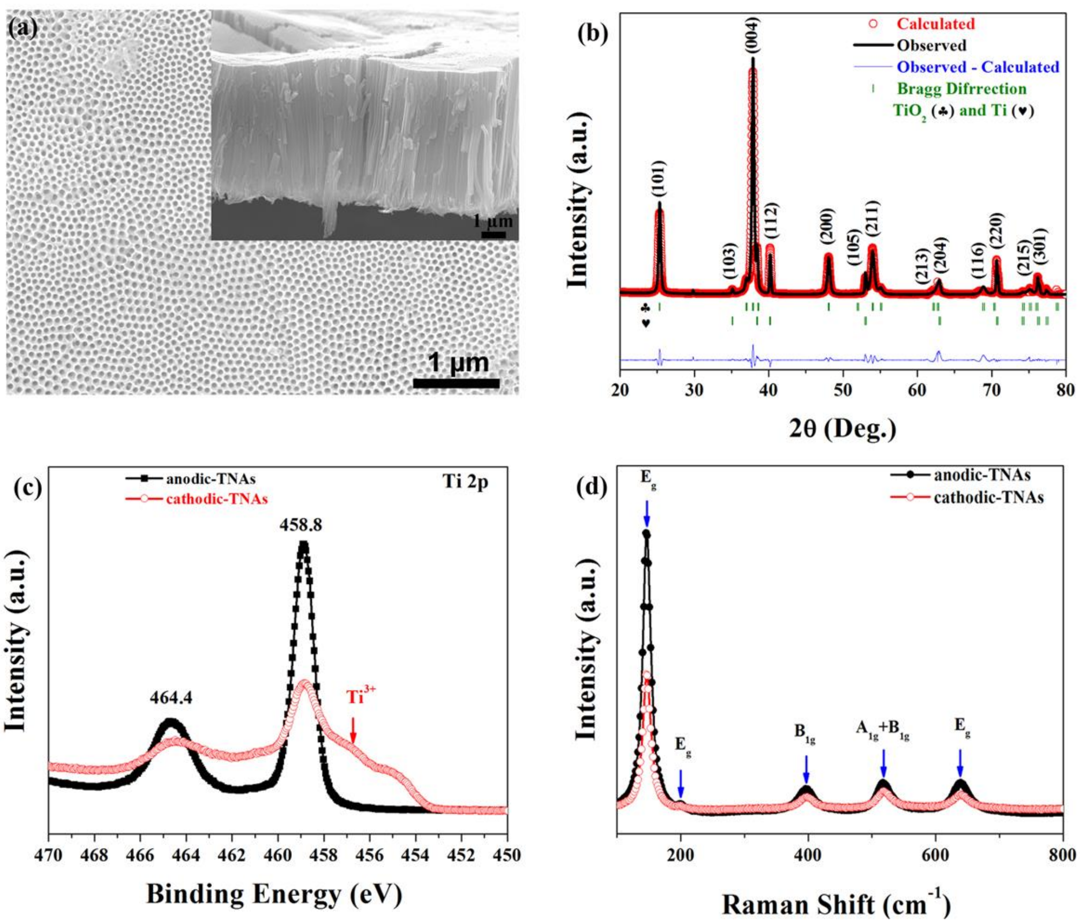


Fig. 1 (a) SEM images of TNAs(b) Observed, calculated and difference patterns of Retvield refinement of X-Ray diffraction data. The vertical green lines are Bragg reflections of anatase TiO_2 and Ti substrate. (c) High Resolution XPS of Ti 2p (d) Raman spectrum of the anodic-TNAs and cathodic-TNAs.

The average diameter, wall thickness and tube length of anodic-TNAs are 110 nm, 15nm, and 6.04 µm, respectively. Moreover, average diameter, wall thickness and tube length of cathodic-TNAs are70 nm, 17 nm, and 5.42 µm, respectively.

XRD patterns of anodic-TNAs and cathodic-TNAs, shown in Fig. 1 (b), indicate that TNAs were anatase TiO_2 with a space group of $I4_1$/amd (JCPDS NO. 21-1272). Other strong peaks originated from titanium substrate (JCPDS NO. 44-1294). In comparison with anodic-TNAs, no significant changes in XRD patterns have been observed after Ti^{3+}doping. The reflections for anatase TiO_2 centered at 25.3°, 36.9°, 37.8°, 48.0°, 53.9°, 55.1° and 68.8° can be clearly observed, which are indexed to (101), (103), (004), (200), (105), (211) and (116) planes, respectively.

Further secondary phases such as rutile and reduced species of TiO_2 are not observed. To calculate the crystal lattice parameters of samples by Rietveld refinement using Fullprof suite program, the experimental data obtained from XRD was plotted with the WinPLOTR program and the angular positions of the peaks were obtained with the same program. The reference file (.CIF, Crystallography Input File) was obtained from Inorganic Crystal Structure Database (ICSD). The refinement was carried out using fullProf program by profile matching routine between reference file and experimental data. The Bragg peaks were modeled with pseudo-Voigt function and the background was estimated by linear interpolation between selected background points. The Rietveld refinement is showing obvious differences in a, b and c lattice parameters of anodic-TNAs and cathodic-TNAs. Change in the lattice parameter altered unit cell volume, which may alter the electrochemical properties. The phenomenon of crystal lattice expansion after ionic doping has also been observed, which is consistent with the earlier reports. The lattice parameters for anodic-TNAsand cathodic-TNAs calculated by Rietveld refinement method showed in Table 1.

Table 1. Refined structural parameters for the anatase TNAs before and after self doping.

Lattice Parameters (Å)	**(JCPDS # 21-1272)**	**Anodic-TNAs**	**Cathodic-TNAs**
a	3.7852	3.78219	3.78516
c	9.5139	9.49350	9.49779

X-Ray photoelectron spectroscopy is helpful to confirm Ti^{3+}doped chemical state. XPS is performed to study the chemical composition and oxidation state of titanium in the anodic-TNAs and cathodic-TNAs before and after doping of species. It is well known that the Ti^{3+} species on TiO_2 surface oxidized back very easily to Ti^{4+} by oxygen in theair. The XPS only probes the surface composition of the material. So material's bulk composition analysis is of vital importance. The argon sputtering treatment at high energy for few minutes was employed to remove the top surface layer of the TiO_2 under high level vacuum conditions before XPS measurement was conducted and Ti^{3+} was probed under high vacuum.TheTi 2p spectra for cathodic-TNAs shows Ti $2p_{3/2}$ and $2p_{1/2}$ peaks centers at 458.8 and 464.6 eV, respectively. There are no peaks observed for Ti^{3+} for anodic-TNAs. While in the case of cathodic-TNAs, Ti 2p spectrum shows the presence of Ti^{3+} at 456.9 (Fig. 1(c)) as reported in the literature.

Raman spectra of anodic-TNAsand cathodic-TNAs(Fig. 1 (d))confirm anatase phase according to the peaks centering at 146 cm^{-1}(E_g),200 cm^{-1}(E_g), 398 cm^{-1}(B_{1g}), 517 cm^{-1}(A_{1g}), 519 cm^{-1}(B_{1g}) and 640 cm^{-1}(E_g). Even though Raman spectroscopy has been conducted under same conditions, peak intensities of cathodic-TNAsare lowerthan that of anodic-TNAs and peaks are broader, which are the same as reported. The FWHM of the main characteristic peak (E_g) 146 cm^{-1} for anodic-TNAs and cathodic-TNAs was measured to be 13.84 and 14.34 cm^{-1}, respectively. This decrease in intensity and broadening in peak width can be attributed to the coupling of defects to the stoichiometric bulk, formation of Ti^{3+} and oxygen vacancies.

During electrochemical cathodic reduction protons (H^+) or cations presents in the electrolyte may be intercalate in anodic-TNAs to compensate charge in TiO_2 lattices. This proton H^+ uptake played major role to accumulation charges in TiO_2. Literature showed that electron accumulation with the help of different measurements techniques. The study elucidated electron accumulation in nano structured TiO_2 in contact with acidic aqueous electrolytes is quantitatively accompanied by charge compensating proton (H^+) adsorption or intercalation according to following equation:

$Ti^{IV}O_2 + e^- + H^+ \leftrightarrow Ti^{III}(O)(OH)(1)$

The proton up taking might change crystal structure and as a result conducting properties of anodic-TNAs. Furthermore, electron accumulation in Ti^{3+} doped TNAs is related to charge compensation by counter ions. The insertion of H^+ and cations intercalation is also conformed in XRD and Raman as we find structure changes. This proton and cations produced changes in structure might enhance electrochemical properties of LIB (Fig. 2).

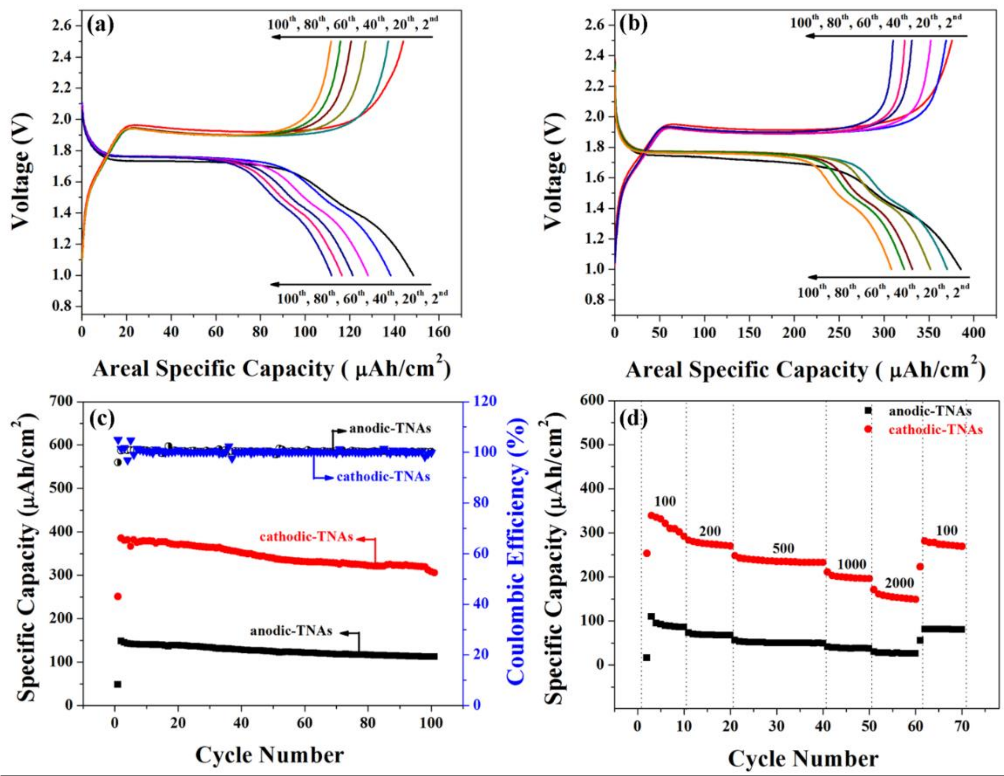


Fig. 2 Comparison of electrochemical properties of anodic-TNAsand cathodic-TNAs. The galvanostatic charge/discharge curves for different cycles at 100 µA cm^{-2} (a) anodic-TNAs (b) cathodic-TNAs(c) cyclic performance and coulombic efficiency (d) rate capability at the potential of 1-2.5 V.

The different galvanostatic charge and discharge curves of anodic-TNAs (Fig. 2 a) and cathodic-TNAs(Fig. 2 b) between the potential window of 1-2.5 V exhibit typical voltage profiles of anatase TiO_2 having flat charge and discharge plateaus. The plateau depicts transition of phase between tetragonal and orthorhombic upon Li insertion/deinsertion into/from anatase TiO_2 as similar to earlier reports.The cyclic capacity for2nd, 20th, 40th, 60th, 80th, and 100th discharge ofanodic-TNAsis 148.4, 138.3, 128.1, 121.3, 116.4, 111.8 µAh cm^{-2}, respectively. The 1st discharge capacity of anodic-TNAs is very low 48 µAh cm^{-2}(Fig. S4). The cyclic capacity of 2nd, 20th, 40th, 60th, 80th and 100th discharge of cathodic-TNAs is 385.5, 370.3, 351.7, 331.6, 322.4, and 308.2 µAh cm^{-2}, respectively.

The cycling performance and coulombic efficiency of anodic-TNAs and cathodic-TNAsat current density of 100 µA cm^{-2} are shown in Fig. 2 (c). The capacity for cathodic-TNAsis three times high eras compared toanodic-TNAs. Both electrodes exhibit excellent cycle stability over 100thcycles. Anodic-TNAshas 148.4 µAh cm^{-2} for 2nd cycle and 111.8 µAh cm^{-2} at 100thcyclehave capacity retention 75 % with a capacity loss rate of 0.33 % per cycle. While cathodic-TNAs has 385.5 µAh cm^{-2} for 2nd and 308.2 µAh cm^{-2} for 100th cycle have capacity retention of 80 % with a capacity loss rate of 0.25 % per cycle. The higher capacity fading rate is attributed to more lithium ion insertion which may be a reason of more strain and led towards the microstructure disintegration. Even thoughareal capacity of cathodic-TNAs (308.2 µAh cm^{-2}) after 100 cycles is three times higher than anodic-TNAs (111.8 µAh cm^{-2}), the average coulombic efficiency over 100 cycles is more than 100 % for both anodic-TNAs and cathodic-TNAs.

Fig. 2 (d) depicts the rate performance of anodic-TNAs and cathodic-TNAs in the light of power density. Cathodic-TNAs exhibits higher reversible areal capacities of 311, 280, 233, 201, 156, and 280 µAh cm^{-2} at current density of 100, 200, 500, 1000, 2000 µA cm^{-2} and recover ingrate of 100 µA cm^{-2}, respectively. Anodic-TNAs shows reversible areal capacities of 89, 68, 51, 37, 27, and 81 µAh cm^{-2} at current density of 100, 200, 500, 1000, 2000 µA cm^{-2} and recovering rate of 100 µA cm^{-2}, respectively. Cathodic-TNAs shows 90% of initial capacity at 100 µA cm^{-2} when the current density is reversed back to 100 µA cm^{-2}, whereas anodic-TNAs exhibited 91% of initial capacity under the same condition. Cathodic-TNAs shows significantly improved rate performances compared to those of anodic-TNAs at all rates. The higher reversible capacities and better cycle performance are evidence of better electrochemical properties which may be attributed to the following reasons. Firstly, Ti^{3+} doping, oxygen vacancies, and protons H^+ in TiO_2jointly enhance electronic conductivity of material and reduce Li^+/electrons recombination time. Secondly, changes in lattice parameters lead to the expansion of unit cell which not only buffered the volume changes during the lithium insertion but also weakened the Li–Li interaction and allowed more lithium to intercalate.

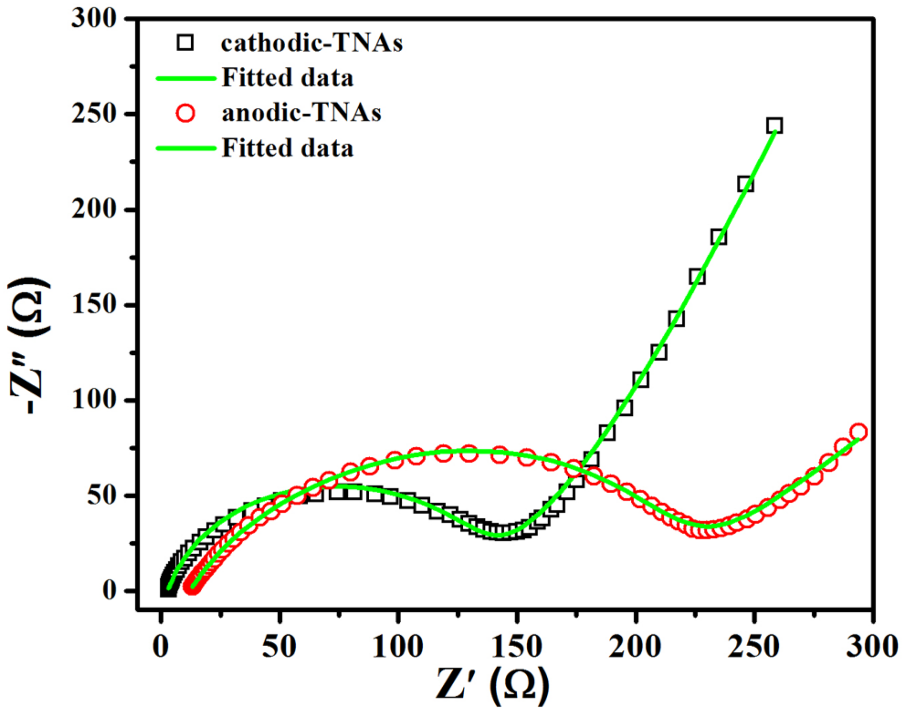


Fig.3 EIS of anodic-TNAs and cathodic-TNAsat 5 mV s^{-1}in the range 0.01 Hz ~100 MHz.

Effect of cathodic reduction at anodic-TNAs is studied by electrochemical impedance spectroscopy (EIS) (Fig. 3). The Nyquist plots have an intercept at high frequency, followed by a depressed semicircle in the intermediate frequency region, and a slope line in the low-frequency range. The detailed analyzed results of anodic-TNAsand cathodic-TNAsare summarized in Table2.

Table 2. Analysis results of EIS simulations from Fig. 3.

Electrode	**R_s (□□**	**R_{ct}□□□**	**W (□)**	**n**	**C (μF)***
anodic-TNAs	12.24	210.6	0.0058	0.7064	4.39
cathodic-TNAs	2.643	117.5	0.0025	0.855	2.88

- Calculated capacitance from experimental values using equation$C = (CPE \times R_{ct})^{1/n}/R_{ct}$.

Where R_s, R_{ct}, W, n and C are electrode/electrolyte bulk resistance, active materials/electrolyte charge-transfer resistance, Warburg impedance (Li^+ diffusion rate in the host material under semi-finite conditions), n is degree of deviation with respect to real capacitanceand calculated capacitance, respectively. The real capacitance value was calculated from the Constant Phase Element (CPE) from the equation above. The CPE, Rc, Rct, and W were calculated from semi-circle fitting in ZView software. Following values of Rs,Rct, W, and C of anodic-TNAs decreased from 12.24 to 2.643 Ω,210.6 to 117.5 Ω,0.0058 to 0.0025 Ω, and4.39 to 2.88 µF, respectively for cathodic-TNAs. The reduction in resistance values predicted the increase in electronic conduction. Meanwhile, at same experimental conditions and electrolyte, R_s and R_{ct} could be used to evaluate the electronic conductivity and the Li^+ ion diffusion capability through the solid-electrolyte interface layer, respectively. Therefore, self doping via cathodic reduction improve electronic conductivity as R_s decreases after self doping and Li^+ ion diffusion was enhanced which facilitate fast kinetics of electrochemical reactions. As a result, higher specific capacity and excellent rate capability have been achieved in LIBs for which cathodic-TNAs were used as anode material.

4. Conclusions

The cathodic reduction of anodic-TNAs in an acidic aqueous electrolyte which produce Ti^{3+}doping and oxygen vacancies, that is, persist electron accumulation accompanied by proton H^+intercalation, as a result, electronic conductivity was enhanced. The areal specific capacity of cathodic-TNAs (385.5 µAh cm^{-2})enhanced three times as compared to anodic-TNAs(148.4µAh cm^{-2}).High Rate capability at 2000µA cm^{-2} has been achieved for cathodic-TNAs. Coulombic efficiency for both samples is 100 %.The electrochemical properties enhancement was attributed to Li ions and electron accelerated transport together with reduced recombination time as well as improved electron injection due to Ti^{3+} doping. The changes in lattice parameters expand unit cell which may reduce Li-Li interaction. Cathodic-TNAs maybe a promising anode material for lithium ion batteries.

Energy-Pakistan

350 MW Bhikki Power Plant Inaugurated

Regasified Liquefied Natural Gas based Bhikki thermal power plant, near Sheikhupura inaugurated on 19th April, 2017 for producing 350MW against 720MW in the first phase.

The plant has an overall capacity of generating 1200 MW of electricity. The plant will start adding 750MW electricity in the national grid by March next year while it will start fully generating 1200 MW by December next year. The plant will save one hundred billion rupees to the national exchequer.

The Bhikki facility will be the country's first power plant to run on imported supplies of LNG. It is projected to generate up to 1,180 MW the equivalent power needed to supply approximately 2.5 million Pakistani homes – once it starts combined cycle operations later this year.

Trial run of first phase of Bhikki plant has been continued and it would become functional by the first week of May.

Pakistan to produce 2,050MW wind power

Wind power generation capacity in Pakistan increasing rapidly as 13 projects with a cumulative installed capacity of around 650 MW have been installed and commissioned whereas 25 projects with cumulative capacity of around 1400 MW are in various stages of implementation.

Pakistan is developing wind power plants in Jhimpir, Gharo, Keti Bandar and Bin Qasim in Sindh as the cheap and environmental-friendly wind energy is gaining popularity. Alternative Energy Development Board of Pakistan has identified two wind corridors (of Jhimpir and Gharo) in the province of Sindh while the estimated potential for these two corridors is more than 50,000 MW. The National Electric Power Regulatory Authority (NEPRA) has granted another generation license to wind power plant. The NEPRA granted generation license to the Iran-Pak Wind Power (pvt.) Limited (IPWPPL) for its wind farm with installed capacity of 49.50 MW located at Tapo Junqshahi, District Thatta, Sindh.Main sponsor of the project include SUNIR (Iran Power & Water Equipment and Services Export Company) of the Islamic Republic of Iran whereas the minor sponsors include the Planet Group and the Tufail group of Pakistan. Energy Department of Government of Sindh issued Letter of Intent (Lol) for development of the project and also allocated to the sponsors 1250 acres of land in the Jhimpir wind corridor at Deh Kohistan 7/3 Tapo Jungshahi, Taluka & District Thatta, in the province of Sindh for setting up an approximately 50.00 MW generation facility/Wind Power Plant/Wind Farm.

Net metering in Pakistan consumers now can sell extra electricity to the power distribution companies

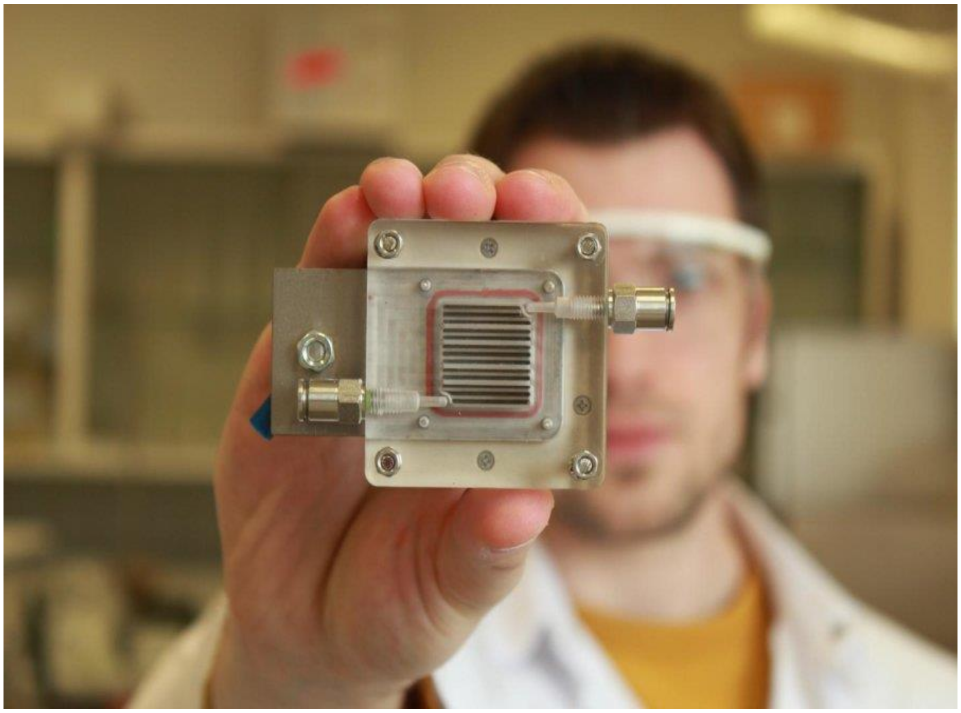
The novel idea to sell extra electricity by the consumers to the power distribution companies at lucrative rates has become materialized as the Islamabad Electric Supply Company (IESCO) has started awarding net-metering connections having 1.8 megawatts accumulative capacity to purchase surplus electricity. The consumers now can sell extra electricity to the power distribution companies at off peak rates which they could generate easily through the solar and wind systems. Instead of staying just as consumers, the clients of the power distribution companies have been provided an opportunity of selling the extra electricity. Following successful models of several western and eastern countries, the NEPRA has introduced this net-metering system to facilitate power-producing customers and helps to overcome the unending power deficit in the country. IESCO is the first power distribution company which has offered opportunities to customers to generate electricity through solar panels and sell their extra electricity. The other DISCOS in the country are also expected to implement the new scheme soon. IESCO has got encouraging response from the general public and 40 connections of net metering had been energized in a short time including the Parliament House, Pakistan Engineering Council and so on while many such requests were under process. All customers having three phase connections can avail IESCO's net metering facility and one window system is now fully functional for net metering where customers can submit their applications and have free net metering connection in just three to four weeks A system having the capacity to generate one kilowatt (kW) electricity, would have the cost around Rs 120,000, while the system for three to five kW would be sufficient for an average house.

Energy around the World

New Technology Generates Power from Polluted Air

Researchers have succeeded in developing a process that purifies air and, at the same time, generates power. The device must only be exposed to light in order to function. Researchers from the University of Antwerp and KU Leuven (University of Leuven), Belgium, have succeeded in developing a process that purifies air and, at the same time, generates power. The device must only be exposed to light in order to function.

A small device with two rooms separated by a membrane," where air is purified on one side, while on the other side hydrogen gas is produced from a part of the degradation products. This hydrogen gas can be stored and used later as fuel, as is already being done in some hydrogen buses. “In this way, the researchers respond to two major social needs: clean air and alternative energy production. The heart of the solution lies at the membrane level, where the researchers use specific nanomaterial. The catalysts are capable of producing hydrogen gas and breaking down air pollution. In the past, these cells were mostly used to extract hydrogen from water. Researchers have now discovered that this is also possible, and even more efficient, with polluted air."

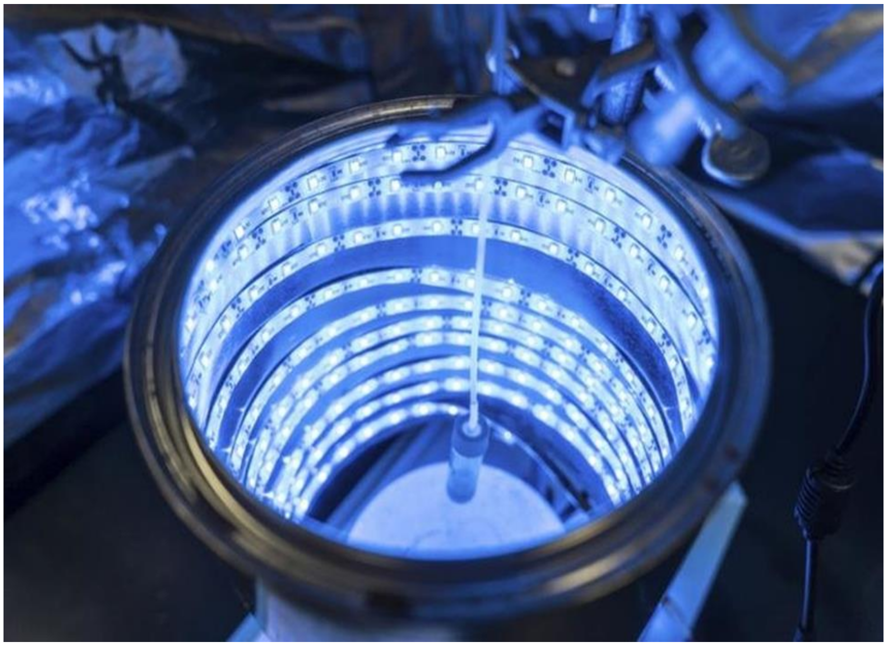


It seems to be a complex process, but it is not: the device must only be exposed to light. The researchers' goal is to be able to use sunlight, as the processes underlying the technology are similar to those found in solar panels. The difference here is that electricity is not generated directly, but rather that air is purified while the generated power is stored as hydrogen gas.

Record New Renewable Power Capacity Added Worldwide at Lower Cost

As clean technology costs continue to fall, the world added record levels of renewable energy capacity in 2016, at an investment level 23 percent lower than 2015, new UN-backed research shows. As the cost of clean technology continues to fall, the world added record levels of renewable energy capacity in 2016, at an investment level 23 per cent lower than the previous year, according to new research published by UN Environment, the Frankfurt School -- UNEP Collaborating Centre and Bloomberg New Energy Finance (BNEF). Global Trends in Renewable Energy Investment 2017 finds that wind, solar, biomass and waste-to-energy, geothermal, small hydro and marine sources added 138.5 gigawatts to global power capacity in 2016, up almost 9 per cent from the 127.5 gigawatts added the year before. The added generating capacity roughly equals that of the world's 16 largest existing power producing facilities combined. Investment in renewable capacity was roughly double that in fossil fuel generation; the corresponding new capacity from renewable was equivalent to 55 per cent of all new power, the highest to date. The proportion of electricity coming from renewable excluding large hydro rose from 10.3 per cent to 11.3 per cent. This prevented the emission of an estimated 1.7 gigatonnes of carbon dioxide. The total investment was $241.6 billion (excluding large hydro), the lowest since 2013. This was in large part a result of falling costs: the average dollar capital expenditure per megawatt for solar photovoltaic and wind dropped by over 10 per cent. "Ever-cheaper clean tech provides a real opportunity for investors to get more for less," said Erik Solheim, Executive Director of UN Environment. "This is exactly the kind of situation, where the needs of profit and people meet, that will drive the shift to a better world for all." New investment in solar totaled $113.7 billion, down 34 per cent from the record high in 2015. Solar capacity additions, however, rose to an all-time high of 75 gigawatts. Wind made up $112.5 billion of investment globally, down 9 per cent; wind capacity additions fell to 54 gigawatts from the previous year's high of 63 gigawatts. While much of the drop in financing was due to reduced technology costs, the report documented a slowdown in China, Japan and some emerging markets, for a variety of reasons. Renewable energy investment in developing countries fell 30 per cent to $117 billion, while that in developed economies dropped 14 per cent to $125 billion. China saw investment drop 32 per cent to $78.3 billion, breaking an 11-year rising trend. Mexico, Chile, Uruguay, South Africa and Morocco all saw falls of 60 per cent or more, due to slower than expected growth in electricity demand, and delays to auctions and financings. Jordan was one of the few new markets to buck the trend, investment there rising 148 per cent to $1.2 billion. The US saw commitments slip 10 per cent to $46.4 billion, as developers took their time to build out projects to benefit from the five-year extension of the tax credit system. Japan slumped 56 per cent to $14.4 billion. Recent figures from the International Energy Agency cited the switch to renewables as one of the main reasons for greenhouse gas emissions staying flat in 2016, for the third year running, even though output in the global economy rose by 3.1%.

Triggering Artificial Photosynthesis to Clean Air



A chemistry professor has just found a way to trigger the process of photosynthesis in a synthetic material, turning greenhouse gases into clean air and producing energy all at the same time. The process has great potential for creating a technology that could significantly reduce greenhouse gases linked to climate change, while also creating a clean way to produce energy. Professor Fernando Uribe-Romo and his team of students created a way to trigger a chemical reaction in a synthetic material called metal-organic frameworks (MOF) that breaks down carbon dioxide into harmless organic materials. Think of it as an artificial photosynthesis process similar to the way plants convert carbon dioxide and sunlight into food. But instead of producing food, Uribe-Romo's method produces solar fuel. The process has great potential for creating a technology that could significantly reduce greenhouse gases linked to climate change, while also creating a clean way to produce energy. It's something scientists around the world have been pursuing for years, but the challenge is finding a way for visible light to trigger the chemical transformation. Ultraviolet rays have enough energy to allow the reaction in common materials such as titanium dioxide, but UVs make up only about 4 percent of the light Earth receives from the sun. The visible range -- the violet to red wavelengths -- represent the majority of the sun's rays, but there are few materials that pick up these light colors to create the chemical reaction that transforms CO2 into fuel. Researchers have tried it with a variety of materials, but the ones that can absorb visible light tend to be rare and expensive materials such as platinum, rhenium and iridium that make the process cost-prohibitive. Uribe-Romo used titanium, a common nontoxic metal, and added organic molecules that act as light-harvesting antennae to see if that configuration would work. The light harvesting antenna molecules, called N-alkyl-2-aminoterephthalates, can be designed to absorb specific colors of light when incorporated in the MOF. In this case he synchronized it for the color blue. His team assembled a blue LED photo reactor to test out the hypothesis. Measured amounts of carbon dioxide were slowly fed into the photo reactor -- a glowing blue cylinder that looks like a tanning bed -- to see if the reaction would occur. The glowing blue light came from strips of LED lights inside the chamber of the cylinder and mimic the sun's blue wavelength.

New Induction at ERC

Dr. Tauseef Anwar, Dr. Tariq Manzoor and Engr. Faisal Farooq have joined Energy Research Center. ERC welcomes all the newly inducted members and looks forward to their active role and contribution in making ERC a center of excellence for research in emerging energy technologies. A brief introduction to the ERC team members is given as under.

 **Dr. Tauseef Anwar**	Dr. Tauseef Anwar has been appointed as Assistant Professor at Energy Research Center Lahore. Dr. Tauseef has completed his PhD from Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China. His research area includes Material Science and Engineering. Currently Dr. Tauseef is working on Lithium Ion batteries and Energy Technology.
 **Dr. Tariq Manzoor**	Dr. Tariq Manzoor has been appointed as Assistant Professor at Energy Research Center Lahore. He is specialized in the area of advanced materials and Computational Solid Mechanics /CFD. He is currently working on Energy, CFD analysis of Flow through porous media, Combustion modeling, crank shaft modeling, DICE MPV design and assembly and copper based alloys.
 **Engr. Faisal Farooq**	Engr. Faisal Farooq has been appointed as a Lecturer at COMSATS Energy Research Center Lahore. Engr. Faisal has completed his BEng in Aeronautical Engineering, University of Glasgow, Glasgow, UK and MSc in Sustainable Engineering: Renewable Energy Systems and the Environment , University of Strathclyde, Glasgow, UK. His research area is related to Microgrids Optimization and Controls.