

DETECTION OF TDI (TOLUENE DIISOCYANATE) THROUGH POLYMERS

Submitted in partial fulfilment of the requirements for the award of Bachelor of
Technology degree in Chemical Engineering

By

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DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF BIO AND CHEMICAL ENGINEERING

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **ABU SAMAQUE** (37190003), **SHAIK MOHAMMED FAZEEL** (37190036) who have done the project as a team, who carried out the project entitled "STUDIES ON THE ISOCYANATE GAS SENSING RESPONSE OF POLYMERS" under our supervision from September 2020 to March 2021.

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Submitted for viva voce Examination held on _____

INTERNAL EXAMINER

EXTERNAL EXAMINER

DECLARATION

I **ABU SAMIQUE (37190003)** hereby declare that the Project Report entitled **“ISOCYANATE GAS SENSING RESPONSE OF POLYMERS”** done by me under the guidance of **Dr. A. Annam Renita** at Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for award of Bachelor of Technology degree in Chemical Engineering.

DATE:

PLACE:

A handwritten signature in black ink that reads "Abu Samique". The signature is written in a cursive style and is placed within a light blue rectangular box.

SIGNATURE OF THE CANDIDATE

DECLARATION

I **SHAIK MOHAMMED FAZEEL (37190036)** hereby declare that the Project Report entitled

“ISOCYANATE GAS SENSING RESPONSE OF POLYMERS” done by me under the guidance of **Dr. A. Annam Renita** at Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for award of Bachelor of Technology degree in Chemical Engineering.

DATE:

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SIGNATURE OF THE CANDIDATE

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ABSTRACT

Toulene diisocyanate (TDI) is a natural compound. Isocyanates are exceptionally responsive and low atomic weight compounds containing the isocyanato group ($-N=C=O$). Work incorporates choice and readiness of directing polymers that are sufficiently delicate to recognize TDI gas on microlevel and fabricate a model for complete examination and testing. Studies on sensor reaction to different centralizations of isocyanate gas by permitting TDI gas to get in contact with the directing polymer in the model. Studies on opposition change because of mugginess. Air examining to test the productivity of model.

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CHAPTER 1

INTRODUCTION

1.1: TOLUENE DIISOCYANATE

Toluene diisocyanate (TDI) is a natural compound with the equation $\text{CH}_3\text{C}_6\text{H}_3(\text{NCO})_2$. Toluene Diisocyanate is a manufactured combination of the 2,4- and 2,6-isomers is an unpredictable, lackluster to light yellow fluid that is dissolvable in numerous natural solvents. These isomers are utilized essentially in the amalgamation of polyurethane froths.

At the point when warmed to decay, toluene diisocyanate transmits harmful exhaust of cyanides and nitrogen oxides. Openness of people to toluene diisocyanate causes tissue disturbance, particularly to the mucous layers, and can create extreme respiratory issues. These isomers are sensibly foreseen to be human cancer-causing agents.

Isocyanates are exceptionally receptive and low atomic weight compounds containing the isocyanato gathering ($-\text{N}=\text{C}=\text{O}$). There are three basic sorts of isocyanates accessible: mono-, di-/tri- and polyisocyanates and among them polyisocyanates are not unstable at room temperature. Toluene Diisocyanates are not referred to happen as common items. They are made by the response of diaminotoluenes with phosgene.

Toluene diisocyanates are created as 2 isomers: 2,4-Toluene diisocyanate (2,4 TDI) and 2,6-Toluene diisocyanate (2,6-TDI). They are economically accessible in 3 isomer proportions:

- >99.5% 2,4-TDI
- 80% 2,4-TDI: 2,6-TDI (most commonly available)
- 65% 2,4-TDI: 35% 2,6-TDI

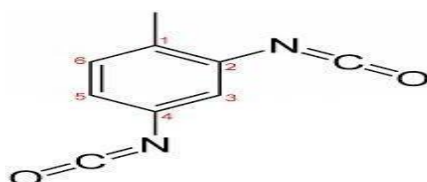


Figure 1.1: TDI structure

1.2: PHYSICAL AND CHEMICAL PROPERTIES

- Chemical Group/family:

Isocyanates

- Form:

Colourless liquid or crystals with pungent odour; turns pale yellow on exposure to air.

- Physical State:

At room temperature, present in the form of liquid or crystals.

- Colour:

Colourless to pale yellow

- Odour:

Distinct pungent, sweet, fruity, odour detectable around 0.7mg/m^3

- Solubility in water and organic solvents:

Soluble in acetone, alcohol, benzene, ethyl acetate, ether, carbon tetrachloride, chlorobenzene, kerosene, and various oils, e.g. Corn oil. TDI reacts with air to produce carbon dioxide.

- Autoignition Temperature:

620°C

- Important Chemical interactions:

They may respond brutally with compounds containing dynamic hydrogen, like alcohols, with the age of sufficient warmth to prompt self-start temperatures and in this manner lead to arrival of poisonous burning items.

Different solvents that should not be blended in with toluene diisocyanates incorporate water, acids, bases, and solid soluble materials like sodium hydroxide and tertiary amines. TDI responds with water and most acids to create polymeric urea.

- Major products of combustion/pyrolysis:

When heated to decomposition, TDI emits toxic fumes of oxides of nitrogen.

- Explosion Limits:

For 2,4-TDI

Concentration : (%v/v)

Lower : 0.9%

Upper : 9.5%

- Boiling Point:

At 760mmHg : 251⁰C

At 10mmHg : 120⁰C for 2,4-TDI

121⁰C for commercial mixture

- Density(g/cm³):

2,4-TDI : 1.22g/ml

- Vapour Pressure:

Pa at 20⁰C : 1.3

- Relative vapour density : 6.0

Flash Point:

Open cup : 135 (2,4-TDI)

Closed cup : 127

If TDI shapes possibly savage polymerisation responses with bases or acyl chlorides, response with water frees carbon dioxide. TDI can respond with alanine. The warmth of this response might be adequate to touch off encompassing combustibles and the actual material.

It responds viciously with amines, alcohols, bases, and warm water, causing blast risks. Solid oxidizers, water, and acids cause froth and splatter. TDI is burnable when presented to warmth or fire. At the point when warmed to deterioration, TDI transmits exceptionally harmful

exhaust of oxides of nitrogen. TDI polymerizes within the sight o soluble base.

1.3: USES

- Used in polyurethane froths, coatings in floor and wood completes, sealers, paints.
- Used as solid sealers for airplane and tank trucks, elastomers in earth pipe seals, elastomers and coatings.
- Effectively utilized as crosslinking specialist for nylon.
- Isocyanates are broadly utilized in enormous amount in numerous modern areas, like car, development and sports. The most generally utilized diisocyanates are 4,4-methylenediisocyanate (MDI), 2,4-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,5-naphthalene diisocyanate (NDI), and p-phenylene diisocyanate (PPDI).
- The limit of isocyanates to frame polymers has been generally misused in industry, especially in the creation of adaptable and unbending froths, polyurethane paints and cements.
- TDI is a receptive transitional and can be utilized in blend with polyester polyols and polyether to deliver polyurethane items.
- Elastomers created from TDI are scraped area and dissolvable safe, and are utilized in cements, covered textures, films, linings, dirt line seals, and in grating wheels, and other mechanical things.

1.4: HISTORY OF TDI AT SPACESTATION

Toluene diisocyanate is progressed during extension of diminishing expert in the last mixing communication of the powers. Recognizing evidence and fragile estimation of airborne isocyanates is of basic importance in workplace. NIOSH limit is 5 ppb and MSDS limit is 10 ppb for time weighted ordinary of isocyanate center during 8hrs work move.

The model by and by being utilized at ISRO space station is a paper-tape for which the

assessments of center depicted are not exact and people at work saw it from smell. The area of available entirety ought to be conceivable by covering of unstable motion pictures on substrate using methodologies like turn covering, plunge covering, electrochemical declaration. Smoothing out of thickness of small film on terminals by changing the centralizations of polymer answers for be covered and other covering factors.

Receptiveness to even a restricted amount of isocyanates can make unsettling influence the eyes and skin and besides lessened lung work when taken in as gas, steam, buildup or airborne. The most broadly perceived unpleasant prosperity influence related with isocyanate receptiveness is asthma in light of refinement.

This derives that the area of isocyanate compounds in a workplace is significantly expected to keep a secured work space and shield the experts from opposing prosperity impacts.

The bleeding edge being created of engineered finders for compound battling subject matter experts and for toxic current manufactured substances is towards multifunctional, low power consuming and adaptable devices, which can be used for biological checking by fast and strong way.

The piece of engineered sensor advancement is essential when developing the fragile and misleadingly specific helpful size pointers for these applications. The conservative size identifiers ordinarily apply assortments of engineered sensors like electrochemical sensors similarly as surface acoustic wave (SAW) sensors or resistor-type sensors reliant on metal oxides or polymers.

1.5: OBJECTIVES

- Studies on sensor response to various concentrations of isocyanate gas.
- Studies on resistance change due to humidity.
- The polymer coated substrates are set in contact with the TDI gas by passing the gas onto the substrates and testing the substrates for changes after certain interval.
- Development of Prototype for enabling a complete setup to analyse the detection properties of polymers coated on substrates

1.6: INTRODUCTION OF POLYMERS

Polymers are materials made of long, reiterating chains of atoms. The materials have exceptional properties, dependent upon the sort of particles being invigorated and how they are supported. A couple of polymers bend and stretch, like flexible and polyester. Others are hard and extraordinary, like epoxies and glass. More broad capacities, as expansive examinations actually have maintained can be identified with polymer covered sensors.

1.6.1 : CONDUCTING POLYMERS

Driving Polymers are those polymers with framed plans. Driving polymers have been used in view of their conductivity, similitude and simplicity processability. Also, differentiated and regular metal or semiconductor materials, driving polymers are more biocompatible.

These central focuses make coordinating polymers more interesting to planning researchers. The association of coordinating polymers can be refined by electrochemical polymerisation, which is more clear than traditional compound mix. The applications recall the use of driving polymers for biosensors, neural terminals, drug movement and bio actuators.

The advancement of driving polymers prepared for an immense assessment development on these new materials to research their potential for the affirmation of characteristic contraptions and optoelectronics to fight with their inorganic accomplices. Coordinating polymers work at room temperature and have incredible affectability and reproducibility.

Common semiconductors build up another class of materials including little particles and polymers with semiconducting properties. Over the span of late numerous years, characteristic semiconducting polymers like polyaniline, poly(3,4-ethylenedioxythiophene), polythiophene, polyacetylene, polypyrrole, polyindole, polycarbazole, etc have been getting extending. Coordinating polymers address a focal class of regular materials with help the resistivity towards external lifts.

1.6.1.1 : SELECTIVITY

Many Conducting polymers, for instance, trans-Polyacetylene, Polythiophene, Poly(p-phenylene), Poly (p-phenylene vinylene), Polyaniline, Polypyrrole, Polycarbazole, etc

exist out of which 3 polymers specifically Polythiophene, Polyaniline and Polycarbazole are picked for ID and examination of TDI reliant on their reactivity and affectability.

1.6.2 : POLYCARBAZOLE

Polycarbazole is a determined in term of carbazole. Polycarbazole is an electrically directing polymer acquired by the polymerization of carbazole. It is a tricyclic structure, comprising of a six-membered benzene rings melded on one or the other side of a five-membered nitrogen-containing ring. Electrochemical polymerization and testimony of natural semiconductor. i.e., polycarbazole on ITO-covered glass substrate, is performed utilizing an electrochemical workstation.

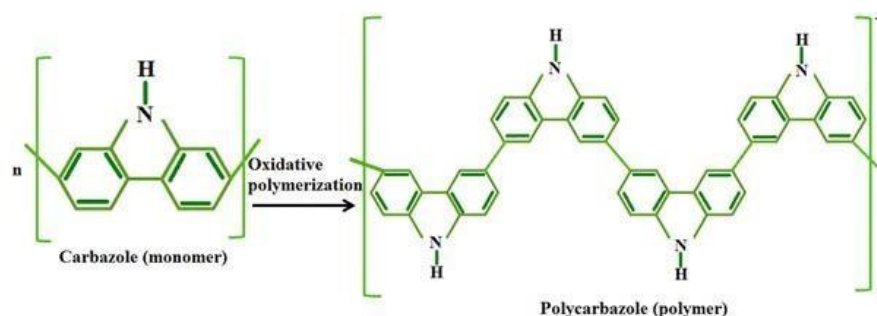


Figure1.2: Polycarbazole Structure

1.6.2 : POLYANILINE

Polyaniline (PANI) is the first among conducting polymers to be used in practice, as an antistatic coating and corrosion inhibitor, due to its high chemical stability, nontoxicity, good process ability, and stable intrinsic redox state derived from the imine groups of the PANI chain. PANI a well-known conducting polymer, play a major role in gas sensing applications due to the ease of synthesis and its potential to detect various gases . PANI can exist as two different emeraldine classes of compounds. Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Amongst the family of conducting polymers, polyaniline is unique due to its ease of synthesis, environmental stability and simple doping/dedoping chemistry. Although the synthetic methods to produce polyaniline are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex.

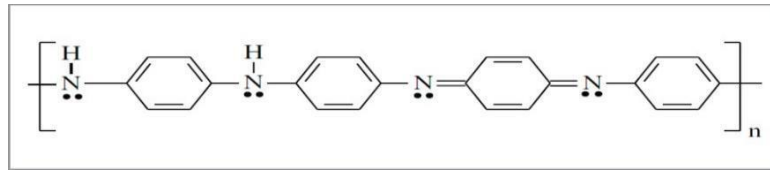


Figure1.3: Polyaniline Structure

1.6: SUBSTRATE

Substrate is the parent or base material to which a covering is applied or the material whereupon an interaction is led. A substrate can be almost any kind of material, including metals, plastics and pottery. Regular metals that go about as substrates whereupon coatings are applied include: Steel, Aluminum, Copper, Zinc combinations, Galvanized steel.

1.7.1 : FTO COATED GLASS SUBSTRATE

FTO covered glass substrate is a solitary side Fluorine doped tin oxide covered soft drink lime glass. The resistivity of the covering 0varies from 4 ohms/cm sq. to 150 ohms/cm sq. It is a solitary side covered TOC. The conductive layer thickness is in the scope of 10 nm to 300nm. The dimness is under 1. The thickness of the glass substrate is 0.7mm and 1.1mm. It is a solitary side covered helpful glass. It significantly used in the touch screen, sun powered cell, EMI protecting, Solar board and considerably more. FTO covered conductive glass likewise knows conductive glass substrate.

1.7.2 : METAL SUBSTRATE

Common metals that act as substrates include:

- 1.7.2.1 Steel
- 1.7.2.2 Aluminium
- 1.7.2.3 Galvanized Steel
- 1.7.2.4 Zinc alloy

1.7 .3: COATING

A coating is a covering that is applied to the surface of the substrate. In the case of corrosion protection, the coating is applied to protect the substrate, but the coating may be decorative as well.

1.8.1 : COATING TECHNIQUES

- SPIN COATING
- DIP COATING
- DROP CASTING
- ELECTROCHEMICAL DEPOSITION

1.8.1.1 : SPIN COATING

Spin coating is the least difficult strategy for manufacturing a film on a substrate. Meager oppose layers for photolithography are covered with this procedure. The twist covering measure begins with the weakening of the material to be kept in a dissolvable. The arrangement is accordingly apportioned on the substrate surface. The wafer is then turned at a high velocity.

The thickness of the film is dictated by the turning speed, surface strain, and consistency of the arrangement. The dissolvable is eliminated somewhat during the turning cycle because of dissipation and mostly by ensuing preparing at raised temperatures.

1.8.1.2 : DIP COATING

Plunge Coating is quite possibly the best cycle in which the substrate is drenched in a fluid and lifted out of the arrangement at a pre-set speed constrained by a persistent engine. The arrangement substrate is submerged in the answer for successful development of the material. When the material is kept then the substrate can be taken out by dissipation which will result the thickness of the layer are one of a kind.

The significant powers that are utilized for the plunge covering measure are power of idleness, gooey drag, gravitational power, and surface pressure. The benefits of plunge covering are minimal effort and layer thickness can be effectively changed.

1.8.1.3 : DROP CASTING

For little substrates (~1 cm²), a simple and tuneable statement strategy is drop-projecting

– spreading a nanoparticle scattering over a substrate and permitting it to dry under controlled conditions, for example pressing factor and temperature.

On a basic level, film thickness relies upon the volume of scattering utilized and the molecule fixation, the two of which can be handily fluctuated. There are additionally different factors that influence the film construction, for example, how well the dissolvable wets the substrate, vanishing

rate, slender powers related with drying, and so on For the most part, it is attractive to utilize solvents that are unpredictable, wet the substrate, and are not powerless to thin movies instabilities(de-wetting).

1.8.1.4 : ELECTROCHEMICAL DEPOSITION

Electrochemical statement technique is quite possibly the most valuable ways to deal with get ready nanostructured ORR electrocatalysts. Utilizing this strategy, the designs, shapes and sizes of the electrocatalysts can be controlled on the outside of leading materials by changing the states of electrochemical testimony.

Besides, in the electrochemical statement strategy, there is another valid statement, no covering reagent or surfactant or other scattering specialist is engaged with the electrodeposition technique.

Electrochemical statement ends up being quite possibly the most advantageous and solid strategy for developing natural slight movies on directing surface for making electronic gadgets.

1.8.2 : PRECAUTIONARY MEASURES

When covering a substrate, one ought to guarantee that:

- The substrate surface ought to be spotless and liberated from soil and oil.
- If there's a covering effectively on substrate, it ought to be liberated from surface scratches, covering gab or covering deformity. These deformities can prompt ill-advised covering.

- The substrate is cleaned well utilizing ethanol arrangement and cleaned with a tissue to guarantee its neatness.
- The uncoated substrate ought to be level to dodge issues, for example, covering dot unsettling influences, twist and pressure control issues.

1.9 : INTRODUCTION TO SENSOR

Headway of gas identifying device is the sincere prerequisite for scaled down, solid, minimal effort, reduced electronic sensor methodology for a wide extent of employments, for instance, air quality checking, clinical diagnostics, control of food quality or wellbeing of mechanical cycles and natively constructed security framework.

Gas sensors are basically comprised of two kinds:

- (i) Gas sensors dependent on natural leading polymers
- (ii) Gas sensors produced using inorganic metal oxides.

Gas sensors create utilizing natural leading polymers, [for model, polyaniline (PANI), poly(3,4-ethylene-dioxythiophene)(PEDOT), polypyrrole, polythiophenes (PTs) etc.] of desired usefulness and conductivity continue improving gas distinguishing execution.

The utilization of inherently leading polymers as detecting components in synthetic sensors is a serious zone of examination because of their high changes of electrical or optical when presented to assorted sorts of gases or fluids. Every sensor was uncovered consistently and haphazardly to the test fumes in a wide fixation range. Gas sensors regularly depend on observing the immediate change in their electrical properties in light of the collaboration with analyte atoms.

Synthetic sensors dependent on movies can be required to improve the affectability, selectivity and reaction time in view of the slenderness and the exceptionally requested constructions of the touchy layers.

1.10.1 : SEM (Scanning Electron Microscopy)

An examining electron magnifying instrument (SEM) is a sort of electron magnifying lens that produces pictures of an example by checking the surface with an engaged light emission. The electrons collaborate with molecules in the example, creating different signs that contain data about the surface geology and organization of the example.

The electron shaft is checked in a raster examine design, and the situation of the pillar is joined with the power of the distinguished sign to deliver a picture. In the most widely recognized SEM mode, optional electrons radiated by particles energized by the electron shaft are distinguished utilizing an auxiliary electron finder (Everhart-Thornley identifier).

The quantity of auxiliary electrons that can be recognized, and subsequently the sign power, depends, in addition to other things, on example geology. SEM can accomplish goal better than 1 nano meter.

Examples are seen in high vacuum in regular SEM, or in low vacuum or wet conditions in factor pressure or ecological SEM, and at a wide scope of cryogenic or raised temperatures with particular instruments

1.10.2 : FTIR (Fourier Transform Infrared Spectroscopy)

Fourier Transform Infrared Spectroscopy is a method used to acquire an infrared range of retention or emanation of a strong, fluid or gas. A FTIR spectrometer all the while gathers high-ghastly goal information over a wide unearthly reach. This gives a huge benefit over a dispersive spectrometer, which estimates force over a tight scope of frequencies all at once.

The objective of FTIR is to gauge how much light an example assimilates at every frequency. The most clear approach to do this, the "dispersive spectroscopy" procedure, is to focus a monochromatic light shaft at an example, measure the amount of the light is assimilated, and rehash for each extraordinary frequency.

1.10.3 : RAMAN SPECTROSCOPY

Raman Spectroscopy is a spectroscopic strategy routinely used to choose vibrational

strategies for particles, though rotational and other low-repeat techniques for systems may moreover be taken note. Raman spectroscopy is usually used in science to give a hidden finger impression by which molecules can be perceived.

It is a kind of inelastic light scattering, where a photon empowers the model. This excitation puts the iota into a virtual energy state for a short period of time before the photon is delivered.

CHAPTER 2

LITERATURE SURVEY

Direct Determination of isocyanates and Amines as Degradation Products in the Industrial Production of Polyurethane-covered Wire. Isocyanates and amines were taken apart in the workplace environment during the making of polyurethane-covered wire (Christina Rosenberg, JULY 1984). The unforeseen development and characterisation of polymeric based distinguishing devices, primarily focussed on making novel quick materials subject to driving polymer coatings saved money on foam substrate. (Brady, Kate Lau, 2005). Test depiction of electrochemically polymerized polycarbazole film and examination of its direct with different metals contacts (Aditi Srivastava, P. Chakrabarti, November 2017). Follow assessment of isocyanate gas in present day airs using gas chromatography and electron get acknowledgment. A gas chromatographic technique for the follow examination of isocyanates in current conditions has been made. (G.Skarping, C.Sango, 1980). Direct distinguishing proof of ultralow follow proportions of isocyanates in air using a fluorescent shaped polymer A fluorescence material polymer containing the pentiptycene and tetraphenyl ethylene units associated by acetylene was mixed for direct area of isocyanates in air (Khama Rani Ghosh, 2014). Evaluation of Total Isocyanate-in-Air Method Using I-(2Methoxyphenyl) piperazine and HPLC. (David A Bagon, Charles J Warwick, April 2013). Confirmation of Airborne Isocyanates Generated During the Thermal Degradation of Car Paint in Body Repair Shops. (Michael Boutin, Andre Dufresne, September 2005). Confirmation of Toluene Diisocyanate in Air Using Micro Liquid Chromatography With UV-Detection. An ordinary system using small scale LC for the confirmation of toluene diisocyanate (TDI) in air is presented. Follow examination of amines and isocyanates using gas slim gas chromatography and specific area, Determination of free fragrant amines using free nitrogen explicit revelation. (M. Dalene, 1985). Receptiveness to 2,4-and 2,6-toluene diisocyanate (TDI) during production of versatile foam: affirmation of airborne TDI and urinary 2,4-and 2,6-toluenediamine (TDA). Word related receptiveness to 2,4-and 2,6-toluene diisocyanate (2,4-and 2,6-TDI) was assessed during the making of versatile foam. (Ari Hirvonen, Hannu Norppa, June 2001). Chipped away at Sample Handling Procedure for Checking Industrial Isocyanates in Air. Another testing methodology was proposed by Keller and Sandridge (5) using PNBPA subordinates, in which investigating time was decreased to two minutes or less. (Jeffrey D. Graham, 1980). An Improved High Pressure Liquid Chromatographic Method for the Determination of Isocyanates Using "Nitro Reagent". The

chromatographic issues related with plenitude derivatizing subject matter expert, in the conventionally used HPLC technique for affirmation of isocyanates have been murdered. (Daniel. C. Hakes, Glenn. D. Johnson, 1986). Beat Ion Mobility Spectrometer for the Detection of Toluene 2,4-Diisocyanate in Ambient Air. Molecule adaptability spectrometer with a nonradioactive ionization source that can be worked in beat mode, which offers the advantage of introducing defer times after the ionization was used. (Wolfgang Baether, Stefan Zimmermann, 2012). Looking at of Isocyanates in Air In current tidiness and clinical assessments remembering the assessment of isocyanates for air, a need exists to choose centers all through moving time periods at levels down to low ppb ranges. (R. L. Sandridge, Jiirgen Keller, 1979). Confirmation of Isocyanates in Air by Liquid Chromatography with Fluorescence Detection. (Richard D. Smith, Allen L. Johnson, 1980). Small scale affirmation of TDI in Atmosphere. The composing has been developed primarily for the confirmation of isocyanates in commonly thought plans (Kalman Marcali, 1956). Association and Preparation of Polythiophene Thin Film by Spin Coating Method. Polythiophene (PT) Nanoparticles have been incorporated by oxidative emulsion polymerization of Thiophene monomer inside seeing copper nitrate catalyzed. (Dr. S. Sakthivel, A. Boopathi, 2014). Joined use of downsized non-standard longing type molecule flexibility spectrometer (IMS; implied as molecule convenientce cell, IMCell) and metal oxide semiconductor (MOS) gas sensor for recognizing unsafe substance exhaust in a predictable 1–2 l/min flow-through structure. (Mikko Utriainen, 2003). Use of Tryptamine as a Derivatizing Agent for Airborne Isocyanate Determination. Appraisal of Total Isocyanates Analysis by High-execution Liquid Chromatography With Fluorescence and Amperometric Detection. (Weh S. Wu, Robert E. Stoyanoff, 1990). Quartz-improved photoacoustic spectroscopy (QEPAS) sensor has been made for the sensitive disclosure of ethylene (C₂H₄) at 10.5 μ m using an unending wave scattered analysis quantum course laser. (Zhen Wang, Zhili Li, 2016). Significantly Sensitive and Selective Chemiresistor Gas/Vapor Sensors subject to Polyaniline Nanocomposite (Sadananda Pandey). ZnO nanoarchitectures: Ultrahigh fragile room temperature acetaldehyde sensors. (Ganesh Kumar Mani, John Bosco Balaguru, 2015).

An assessment concerning the usage of electrochromic polymers in optical gas sensors. A gas sensor subject to the circuit of electrochromic polymers into an optic device is depicted. (B. Kondratowicz, R. Narayanaswamy, 2001). Regio customary polythiophene field-sway semiconductors used as substance sensors . Dissolvable alkyl-and alkoxy-subbed regiochemically defined polyterthiophenes are used as powerful layers in identifying characteristic thin films semiconductors (OTFTs). (L. Torsia, A. Tafuria, 2003)

CHAPTER 3

AIM AND SCOPE

The point of the work incorporates determination and planning of leading polymers that are adequately delicate to recognize TDI gas on microlevel and fabricate a model for complete investigation and testing.

Objectives:

- Design of a chemiresistor (sensor array and integrated circuit).
- Coating of thin film on ITO coated glass substrate.
- Optimisation of film thickness by varying the concentration of polymer solution to be coated.
- Studies on sensor response to various concentrations of isocyanate gas by allowing TDI gas to get in contact with the conducting polymer in the prototype.
- Studies on resistance change due to humidity. Air sampling to test the efficiency of prototype.

Scope:

- Studies on sensor response to various concentrations of isocyanate gas.
- Efficient detection of Toluene diisocyanate gas using the built sensor for accurate concentration

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1 COLLECTION OF MATERIAL

- Thiophene
- Carbazole
- Tetrabutylammonium perchlorate (99%)
- Methylene Chloride (99%).
- Distilled Aniline
- Concentrated Sulfuric acid
- Demineralised water
- Potassium Dichromate
- Methanol
- Sodium Dodecyl sulphate
- Hydroxyl peroxide
- CopperNitrateTrihydrate catalyst
- Sodium Hydroxide
- Chloroform
- N-Methyl-2-pyrrolidone

4.2 POLYMER PREPARATION

4.2.1 PREPARATION OF POLYCARBAZOLE

Materials Required: Carbazole (95%), Tetrabutylammonium perchlorate (99%), Methylene Chloride (99%).

Procedure:

1. First, ITO covered glass was cleaned with CH_3CO using righteousness wipes or sensitive development free material.
2. Meanwhile, a liquid plan of 10% NaOH was set up in 250 ml estimating glass which

was warmed to 55 °C.

3. After that ITO-covered glass substrate was dunked in NaOH answer for 3 min.
4. Then, the substrate was flushed in deionized (DI) water for around 1 min. Quickly, it was cleaned dry with an uprightness wipe to thwart water spots.
5. Polycarbazole is fused by oxidative polymerization of carbazole in the dichloromethane (CH_2Cl_2) medium using tetrabutylammonium perchlorate ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}(\text{ClO}_4)$) as an oxidant.
6. This test was performed using electrochemical workstation.
7. Carbazole monomers used in electrochemical polymerization are fragrant heterocyclic regular blends.
8. It has a tricyclic structure, including two six-membered benzene rings merged on either side of a five-membered nitrogen-containing ring.
9. It can be oxidized at commonly low anodic potential, generally at 1.3 V.
10. For electrochemical proclamation of polycarbazole film, it is critical to set up the reaction answer for be used as the electrolyte in the electrochemical workstation.
11. The reaction game plan was set up by dissolving 60 mM carbazole monomer and 0.1 M tetrabutylammonium perchlorate (TBAP) in dichloromethane.

12. The ITO-covered glass target substrate was mounted as the working terminal. The two coordinated cycles, i.e., polymerization of carbazole monomer and electrochemical explanation of polycarbazole on the ITO-covered glass substrate, were performed simultaneously using electrochemical workstation.

13. In this test, the ITO-canvassed glass substrate fills in as a working terminal (WE). The platinum terminal, which closes the circuit way, fills in as the counter anode (CE). Ag/AgCl which measures the voltage between the electrolyte and WE (ITO-covered glass substrate) limits as the reference terminal (RE).

14. After the declaration of the polycarbazole film of the ideal induced thickness over ITO-covered glass substrate, the model was disposed of from the plan and dried for film depiction measure.

15. The electrochemical system is enjoyed over substance strategy, in light of the fact that, in the electrochemical method, one can modify properties of the common

semiconducting film by changing conditions like oxidation potential, dissolvable center, oath time, electrolyte type.

16. Low-cost creating, basic assembling techniques diverged from inorganic devices, light weight, and closeness with versatile substrates are a bit of the invigorating features of regular equipment.

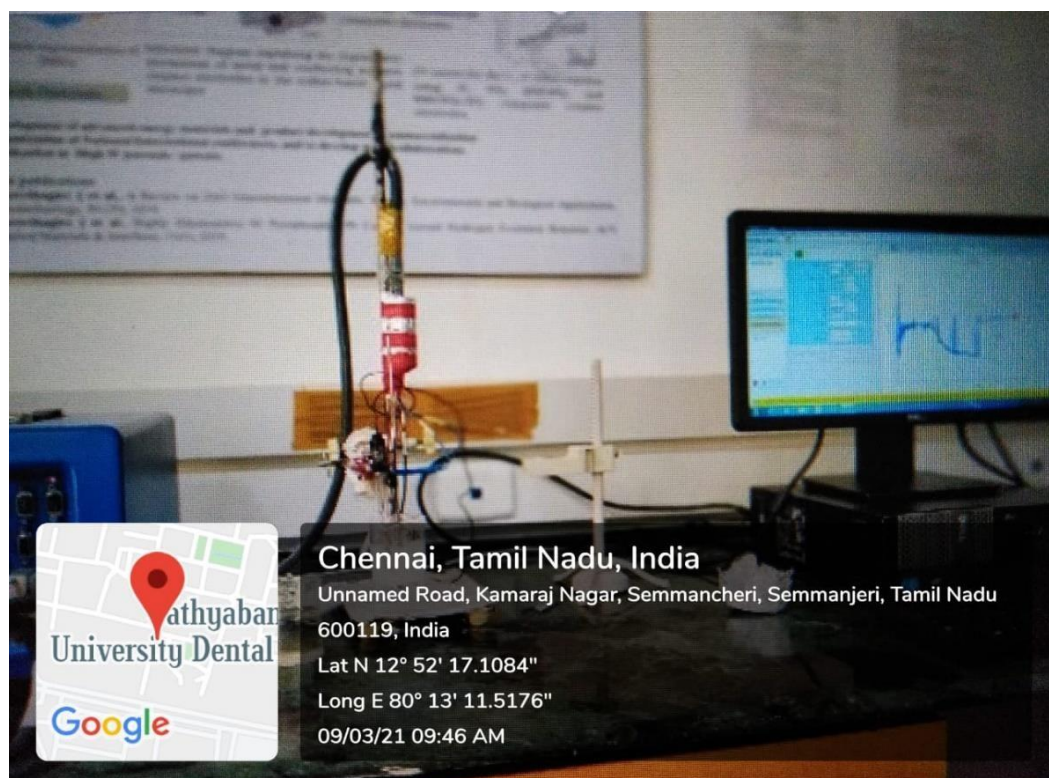


Fig 4.1: Electrochemical Workstation



Fig 4.2: Reaction solution



Fig 4.3: Coat on Metal Substrate

Note:

Electrochemical Workstation empowers Polymerisation of carbazole monomer and concurrent coating on substrate. The whole gear is fixed with appropriate associations and the polymerisation is observed utilizing screen and as the monomer gets polymerised it gets covered on the metal substrate at the same time.

- Using this method, the structures, shapes and sizes of the coat, can be controlled on the surface of conducting materials by altering the conditions of electrochemical deposition.
- The thickness of the film is varied by altering the voltage conditions and time.



Fig 4.4: Film on S.S. substrate



Fig4.5: Film on Glass substrate

4.2.2: PREPARATION OF POLYANILINE

Polyaniline shows electrical as well as optical property changes when it is in contact with oxidant/reductant gas. These materials offer the possibility of control of sensitivity to chemical vapours by modification of their chemical structures.

They are also very useful because they can be used at room temperatures and deposited on different substrates including flexible ones.

Such sensors offer advantages over the other ones in monitoring in a variety of industrial process control, Environmental concerns, Biomedical research and automotive industries.

Materials Required: Distilled Aniline, Conc. Sulfuric acid, DI water, Pottasium Dichromate, Methanol.

Procedure:

- Add 17.7ml of DI water and 2.3ml of sulfuric acid in a beaker and stir it for 10min.
- Add 4.5ml of aniline dropwise in acid to get a white precipitate and stir for 20min.
- Add 0.9g of Potassium Dichromate in 25ml of DI water and add this makeup solution dropwise to aniline makeup solution and stir for 2hrs resulting in a dark green precipitate.
- Filter and wash with DI water and also with methanol, precipitate is collected and dried for 14hrs results in solid Polyaniline.

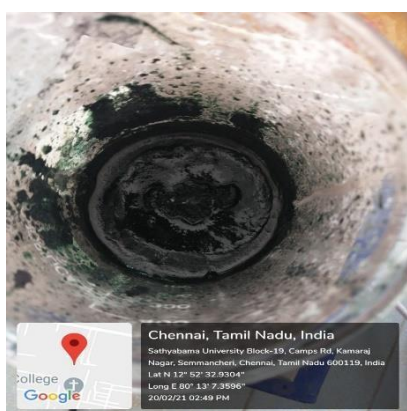


Fig 4.6: Aniline Mixture



Fig 4.7: Polymer solution

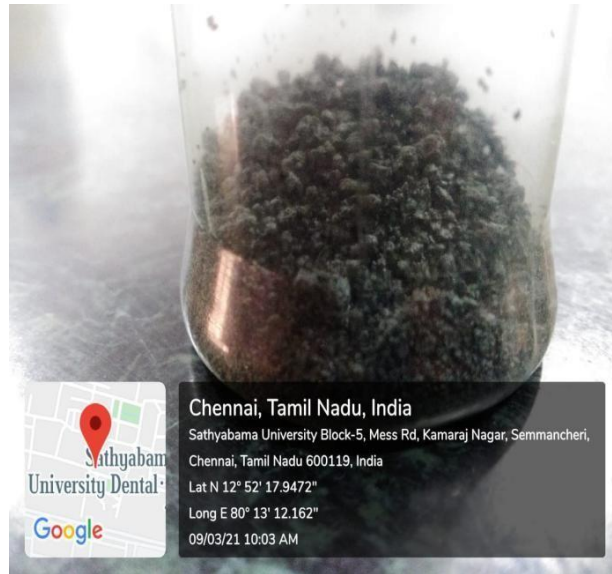


Fig 4.8: Solid Polyaniline

4.3: POLYMER COATING ON THE SUBSTRATE

Techniques used:

1. Spin Coating:

- Spin Coating is a strategy used to deposit uniform slight movies onto level thin flim. Normally a modest quantity of covering material is applied on the focal point of the substrate, which is either turning at low speed or not turning by any means.
- The substrate is then pivoted at a fast to spread the covering material by diffusive power. The machine utilized for this reason for existing is known as a spin coater or just a spinner.
- Rotation is continous while the liquid twists off the edges of the substrate, until the ideal thickness of the film is accomplished. The applied dissolvable is generally unstable, and at the same time vanishes.
- The higher the angular speed of turning, the more slender the film. The thickness of the film additionally depends consistency and convergence of the arrangement and dissolvable.



Fig 4.9: Spin Coater

4.4: PREPARATION OF POLYMER SOLUTION

- Dissolve 0.1g of Polyaniline powder arranged in 5ml of N-Methyl-2-pyrrolidone
- The blend is took into account sonication for a time of 30min for complete disintegration.
- The polymer arrangement got is put away under low temperatures to maintain a strategic distance from undesired responses and store the properties of polymer.
- The arranged polymer arrangement is covered on glass and Steel substrate utilizing turn covering
- Heat of 120'C is provided utilizing an electric warmer for 10min to covered film.
- Thin Polyaniline films were kept from a synthetic arrangement on the glass substrates. The thickness was about 100nm.
- The films were dried in a radiator as referenced in an oxidant air.
- The got composite coatings of thickness 21 μ m showed a communicated green tone and their electrical conductivity is considered as factor for detecting.
- These materials offer the chance of control of affectability to explicit gases by alteration of their synthetic constructions.

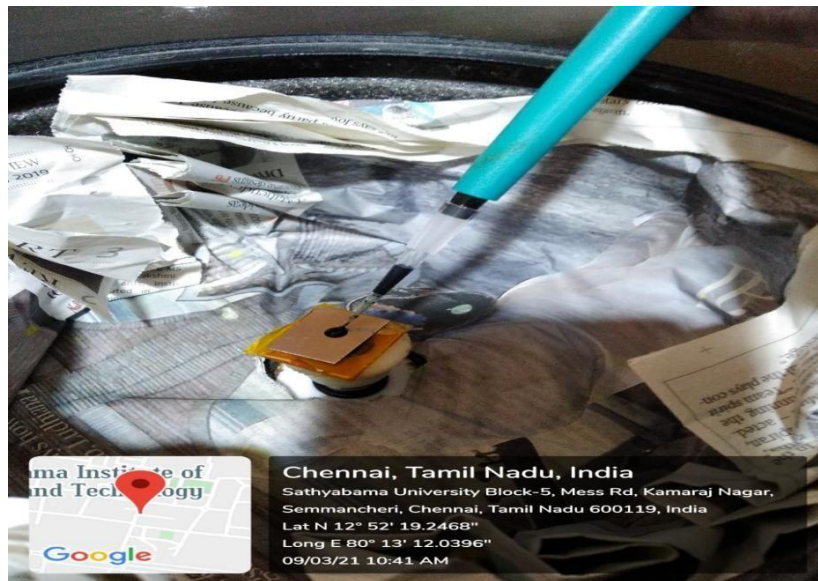


Fig 4.10: Polyaniline coat Process



Fig 4.11: Spin coating

Spin Coater Protocol Sequence:

Table 4.1: Glass substrate (ITO coated)

Quantity	Rpm	sample	Substrate
100	3000	1	Glass
100	2000	2	Glass
70	1000	3	Glass
70	500	4	Glass

Table 4.2: Metal substrate (S.S)

Quantity	Rpm	Sample	substrate
140	400	1	S.S
140	Drop casting	2	S.S
70	Drop casting	3	S.S
70	Drop casting	4	S.S

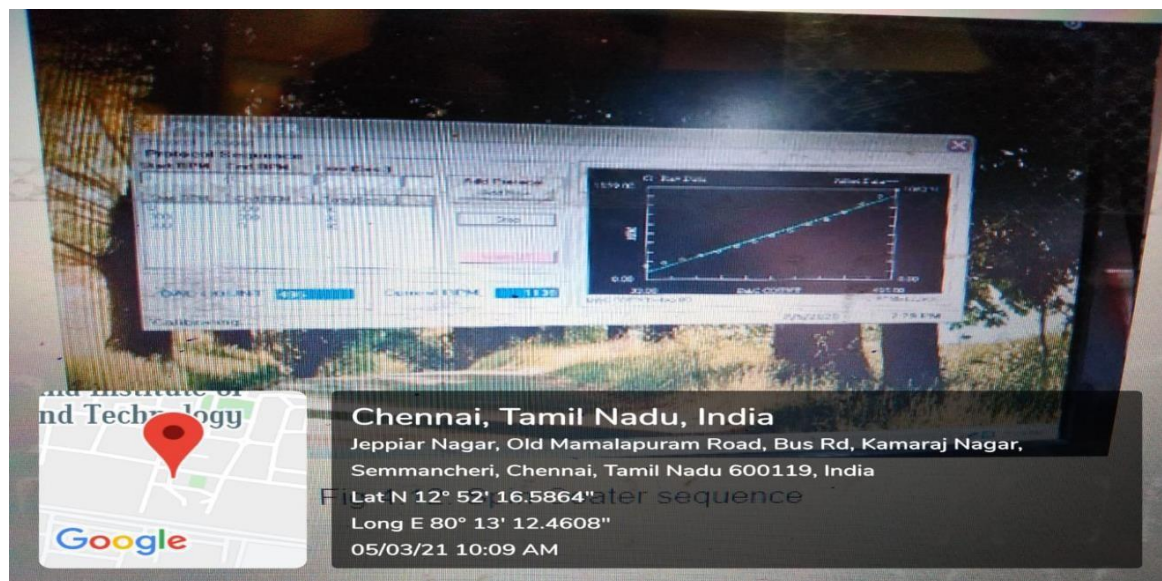


Fig 4.12: Spin Coater sequence

- Coating on the S.S substrate was done at low rpm for enhanced thickness of required film. The Film coating was not uniform at low rpm and took much time to settle.

1. Drop Casting:

- In this method, the coat arrangement is dropped on to substrate to be covered and heat is provided to the substrate on which covering is to be finished.
- Heat provided prompts the dissolvable vanishing spontaneously and substrate is permitted to chill off subsequent to dropping and settling of coat.
- The polymer coat totally settles down of suitable thickness is shaped.
- In rule, film thickness relies upon the volume of scattering utilized and the molecule focus, the two of which can be effectively changed. There are additionally different factors that influence the film design, for example, how well the dissolvable wets the substrate, dissipation rate, narrow powers related with drying, and so on
- The procedure is extremely straightforward as far as utilization and misuse of material is negligible.
- There are additionally different factors that influence the film substrate such how well the dissolvable wets the substrate, vanishing rate, hairlike powers related with drying, and so on
- Generally, it is alluring to utilize solvents that are unstable, wet the substrate, and are not powerless to thin movies instabilities(de-wetting).
- Water will in general be a helpless dissolvable for drop projecting because of the low fume pressing factor and low fume pressing factor and huge surface strain. Now and again liquor can be utilized instead of water, while natural solvents like hexane, toluene or halogenated solvents are frequently excellent decision for coat arrangement.
- In our examination, N-Methyl-2-pyrrolidone was utilized as a dissolvable for setting up the polyaniline polymer combination.



Fig 4.13: Polymer Solutions

4.5: CHARACTERISATION AND ANALYSIS

The polymer got was tested and examined utilizing different procedures like SEM (Scanning Electron Microscopy), FTIR (Fourier Transform Infrared Spectroscopy), Raman spectroscopy. These strategies recognize the exactness of the yield dependent on its surface morphology and different components present



Fig 4.14: Drop Casting

4.6: GAS SENSOR

A gas detector is an equipment that recognizes the presence of gases in a area , frequently as a component of a security framework. This kind of hardware is utilized to recognize a gas break and interface with a control framework so a cycle can be naturally closed down.

A gas indicator can sound an alert to administrators in the zone where the hole is happening,

allowing them the chance to leave.

Gas identifiers can be utilized to distinguish ignitable, combustible and poisonous gases, and oxygen exhaustion.

This kind of gadget is utilized generally in industry and can be found in areas, for example, on oil rigs, to screen make measures and arising advancements like photovoltaic.

Headway of gas distinguishing device is the sincere necessity for scaled down, dependable, ease, minimal electronic sensor systems for a wide extent of employments.

4.7 : GAS SENSING EQUIPMENT:

4.7.1 : SENSING ELEMENT

- Gas detecting properties of the detecting component for the most part rely upon the surface morphology, grain size, Porosity, thickness of the material utilized for detecting.
- Conducting polymers represent a central class of natural materials with support the resistivity towards outer boosts.
- Gas sensors are basically comprised of two sorts:
 - (i) Gas sensors dependent on natural directing polymers
 - (ii) gas sensors produced using inorganic metal oxides.
- Gas sensors create utilizing natural directing polymers of pined for usefulness and conductivity continue improving gas recognizing execution.
- They are some of the time discovered to be unsteady and show helpless affectability because of the enormous partiality of leading polymers toward unpredictable natural mixtures (VOCs) and dampness present in the climate.
- These gas sensors work at high temperatures ($\sim 300\text{--}400^\circ\text{C}$), consistently provoking to pattern float and oxidation of analytes.

- The gas sensing components utilized for recognition of TDI are leading polymers due to their high affectability in changes of electrical and optical properties on openness to gases and fluids.
- The leading polymers considered are:
 - (i) Polycarbazole
 - (ii) Polyaniline
- PANI a notable leading polymer, assume a significant part in gas detecting applications because of the simplicity of blend and its capability to distinguish different gases.

4.7.2 : *SENSOR APPARATUS*

- The chemical detection comprises of independent glass vessels mounted and manufactured as per the sort and states of utilization.
- i Gas compartment:
 - A round bottom flask with a level lower part of volume 100ml is utilized. Its cap is changed so that it has some space for permitting the gas to move through a little cross-segment.
 - The top knob is planned so that it forestalls such a spillage of gas just permitting it to course through the little opening in center.
 - The top shutting knob is a mounted cone connector empowered with an open and close valve to empower or deter the stream when vital.

- The fluid type of TDI accessible is kept in this vessel and its connector is associated with different vessels through a line.



Fig 4.15: Gas vessel

i Polymer Holder:

- The holder includes a glass tube shaped compartment with tube length around 10cm and an opening in cross segment of 3-3.5cm distance across.
- The lower part of the compartment is made level to empower balance and contains a sum of four openings.
- The top opening in the center is of greater breadth and is covered with an elastic plug of same size and is made to guarantee impermeable and no spillage is seen up to 98%.
- The vaporous type of TDI is gone through the opening on left side through the line and is permitted to fall on the polymeric detecting material inside the vessel.
- The opposite side of the holder has arrangement for two outlets with a one side valve to guarantee legitimate release whenever required.
- The polymer covered on the substrate either metal or glass is held between the wires associating the working cathode in the electrochemical workstation.
- The polymer substrate is carried down alongside the wires encased by the stopper at

the top. The snugness of the stopper guarantees the wires are held tight over the base in the holder.

- The substrate is held tight so that the vast majority of zone is available to fall in contact with the passed TDI gas and the



Fig 4.16: Polymer chamber

i. Workstation:

- In this experiment, the ITO-covered glass substrate fills in as a working anode (WE). The platinum terminal, which shuts the circuit way, functions as the counter anode (CE). Ag/AgCl which quantifies the voltage between the electrolyte and WE (ITO-covered glass substrate) capacities as the reference electrode (RE).
- The Working electrode is the detecting substrate and consequently the gas is permitted to interact with it and is seen throughout a period breaking point of 5min and stream is halted and substrate is observed throughout the timeframe.
- The analysis is directed powerfully as the odds for desorption of gas is more whenever left for a great deal of time.



Fig 4.17: Sensing Apparatus Overview

Working:

- The fluid type of TDI around 5ml is taken in the vessel designed reasonably to hold and move the gas through the lines.
- The Boiling Point of TDI is around 2510C and the vessel holding fluid TDI is warmed to around 240-2500C to permit vaporization of fluid TDI to vaporous state to permit it for detecting.
- First, to settle the sensor and measure the pattern of the sensor we went dry air through the chamber for 50s.
- The disintegrated TDI is permitted to go through the opening fixed tight by fixing the kickoff of line to vessel opening by giving fitting warmth and putting it.
- The gas is given to the compartment in which the substrate covered with polymer is put in and permitted to fall in contact throughout a particular timeframe.
- The Workstation is associated so that the working anode is in contact with streaming gas and individual changes are observed.
- Conducting polymers here act just as dynamic layers. At the point when a fitting

potential is applied on the terminal, the analyte particles are anodic oxidized or cathodic diminished, bringing about a current change.

- The gas course through the substrate is recorded for changes in the substrate surface for change in its properties and adsorption efficiencies are noted.
- Finally, we recycled dry air for another 200s to procure the sensor recuperation and prepare it for the following arrangement of estimations.
- The try was directed twice to notice any progressions and the dataset was partitioned into groups dependent on test led.

4.8: CHARECTARISATION AND ANALYSIS

The recognition tests have been led for both of the polymer substrates and changes should be broke down by taking impedance and cyclic voltammetry characterisation which gives out the electrochemical changes in both the substrates over the time of gas openness. The progressions appeared because of openness of gas is recorded and results are taken.

Impedance is utilized to examine leading polymers. It is utilized to examine the reaction of electrochemical frameworks to sinusoidal bothers about a consistent state or harmony state.

Cyclic Voltammetry is for the most part used to examine the electrochemical properties of an analyte in an answer or of a particle that is adsorbed onto the anode.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 : POLYMER CONFIRMATION AND ANALYSIS

5.1.1 : POLYCARBAZOLE

SEM images:



Fig5.1:Surface Morphology of bare FTO

- The surface morphological images have acquired from Scanning Electron Microscopy (SEM). The surface is checked utilizing a light emission and cooperations produce data about the surface geology and arrangement.

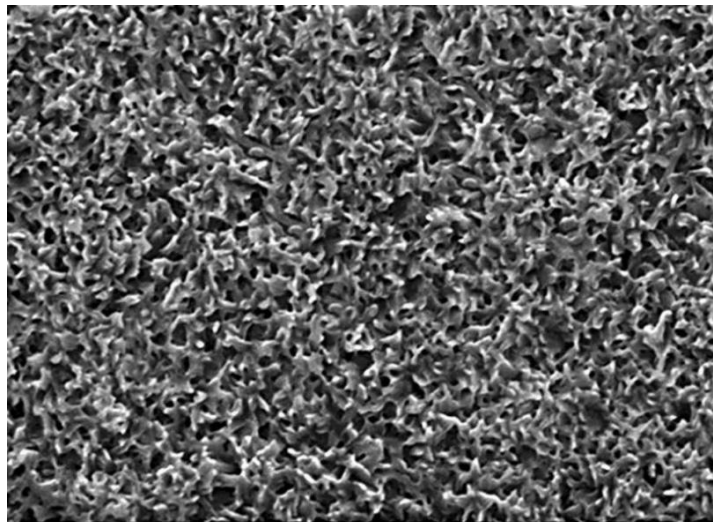


Fig 5.2: Surface Morphology of Electrochemically deposited Polycarbazole on FTO.

- It can be seen from the SEM picture that PCz film shows sinewy constructions that help increment the detecting response, on the grounds that the film has a huge surface zone

to volume proportion. Subsequently, this film can be utilized in detecting applications.

- The SEM investigation has been performed to know the surface morphology and unpleasantness profile of the electrochemically polymerized polycarbazole film on FTOcoated glass substrate. SEM investigation has been performed at 11,000X amplification.
- Figure 5.1 shows surface morphology of exposed FTO, which shows a smooth surface of Indium Tin Oxide. Figure 5.2 shows the surface morphology of electrochemically stored polycarbazole film on ITO-covered glass substrate which affirms the affidavit of polycarbazole film on ITO.
- It can be seen from the SEM picture that electrochemically polymerized film is minimal unpleasant.

Raman Analysis:

Optical Spectroscopy, Raman Spectroscopy specifically give an adaptable non-dangerous instrument to explore slight movies. For example, Raman Spectroscopy empowers one to test low recurrence rudimentary excitations, for example, phonons, magnons and some electronic excitations just as transaction between them.

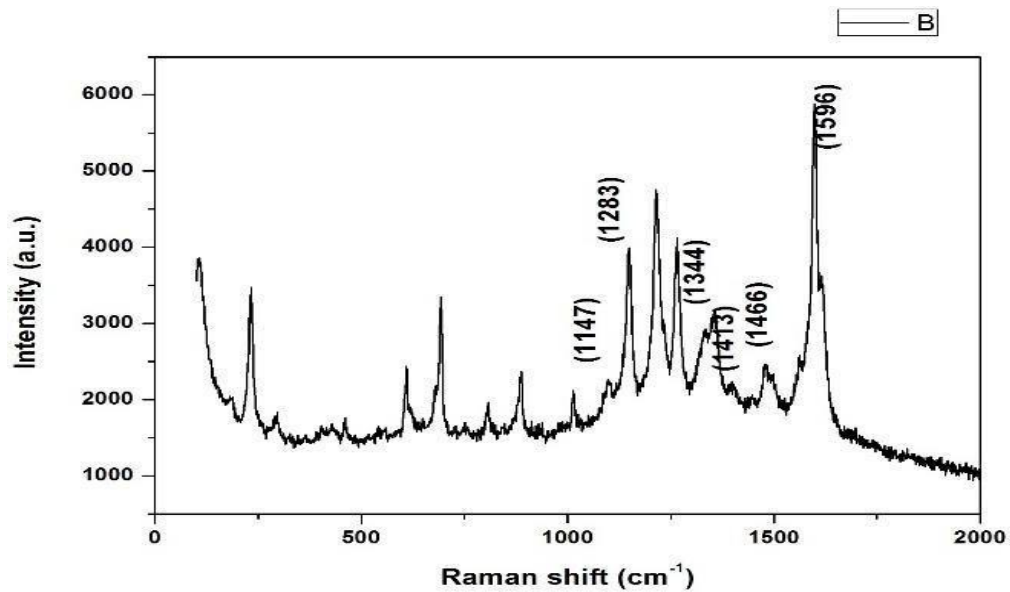


Fig 5.3: Raman Spectrum of sample

Table 5.1: Raman Analysis of Polycarbazole

Wave Number	Bond
1344	C-C
1413	C-N
1546	C=C

- In Raman experiment the laser light is shone upon the film and dispersed light is investigated. Ordinarily, the film is too slight to even think about keeping the light from entering into the substrate.
- In this test we look at the Raman force of polymer film acquired from polymerisation with the reference paper to guarantee its arrangement.
- Formation of Polycarbazole has been affirmed from tops that relate to bonds from Raman examination.
- The separate pinnacles have coordinated with the ones in the reference and securities show bend likewise to construction of polycarbazole.

Cyclic Voltammetry:

An starting quick increment of current shows a consistent and progressive polymer development on ITO-covered glass substrate.

- After that, a consistent current was created, which shows that the developed polymer was conductive, and the obstruction of the polymer was unimportant in this polymerization period.
- The cyclic voltammetry bends of polycarbazole film were gotten in 0.1M tetrabutylammonium perchlorate and dichloromethane arrangement in the scope of – 0.2 V to 2 V at an output pace of 0.100 V/s, under a similar condition for a similar example.

- The cyclic voltammetry displays redox measures with the oxidation and decrease top at 1.1377 and 0.21973 V, separately.
- The response of the extreme cation with different species, for example, revolutionary cation or nonpartisan carbazole monomers prompts the arrangement of the polymer, i.e., polycarbazole.
- The solidness of the polycarbazole film can likewise be checked by these cyclic voltammetry bends.

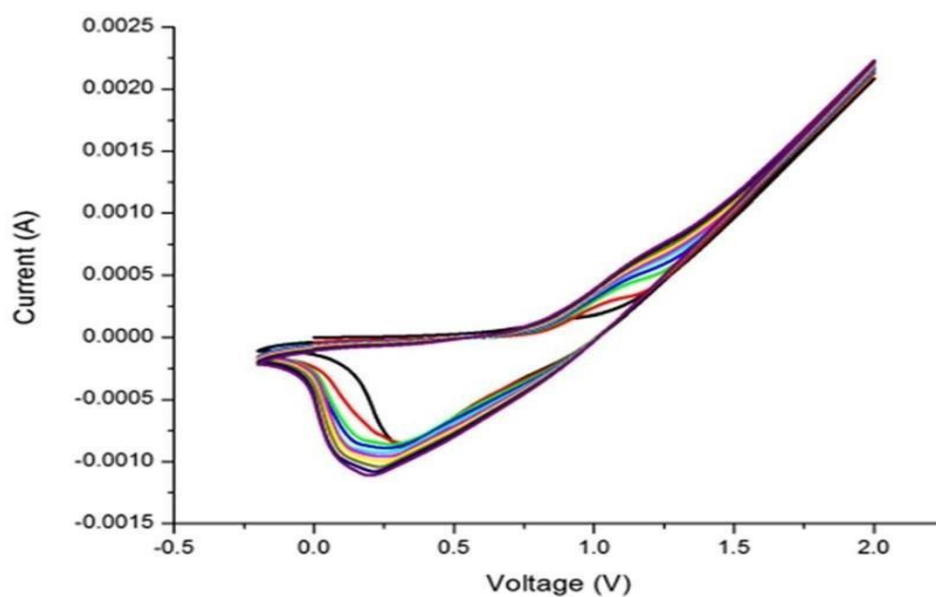


Fig 5.4: Cyclic voltammetry curves of polycarbazole film

5.1.2 : POLYANILINE

SEM images:

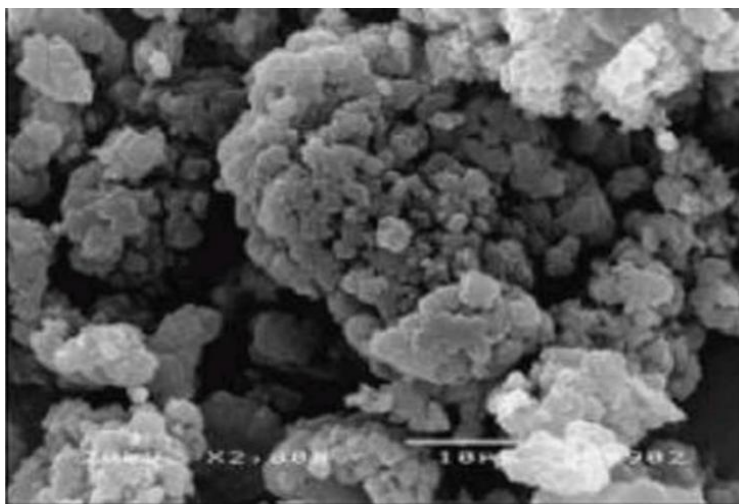


Fig 5.5: Surface Morphological image of Polyaniline

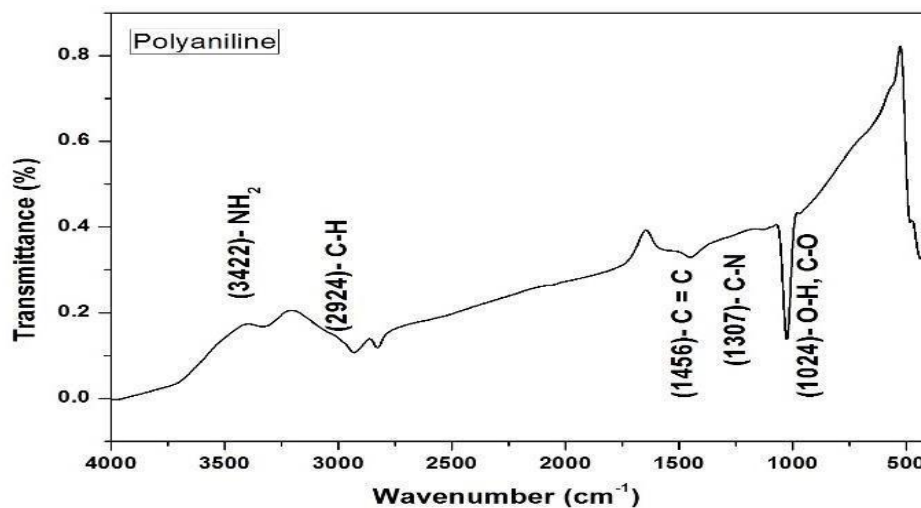
- SEM is seen that as the Polyaniline rate assembles, the partner pathways become progressively thick.
- SEM morphology reveals that the wellspring of high electrical conductivity and incredible optical quality furthermore an improvement in partner pathways overhauls the charge transport and therefore the conductivity.
- Figure 5.6 shows the surface image of Polyaniline procured from SEM examination which depicts a haze like development which is non-uniform and penetrable.

FTIR analysis:

- The hidden examination of the polymer gained by polymerisation measure is performed by infrared spectroscopy.
- IR spectra of solids are for the most part erratic with innumerable zeniths, each contrasting with a particular vibration change.
- A complex reach, things being what they are, to express vibration modes is possible

with the nuclear material. IR spectra are immensely used for straight forward distinctive evidence of unequivocal helpful get-togethers present in the material especially in normal molecules.

- By differentiating the IR bunches recognized in the polymer spectra with those saw in



the reference range, one can get the data about the sub-atomic bond courses of action.

Fig 5.6: Infrared Spectrum of sample

Table 5.2: FTIR results of Polyaniline

Wave Number	Bond
2924	C-H
1307	C-N
1456	C=C
3422	NH-H Stretching

- Formation of Polyaniline has been confirmed by wavenumbers that correspond to various bonds in polyaniline.
- The peaks and respective wave numbers have been verified with the respective reference paper and curves show similar conjugate peaks for various elements.

5.2: FILM ANALYSIS

5.2.1 : POLYCARBAZOLE

Raman Spectroscopy :

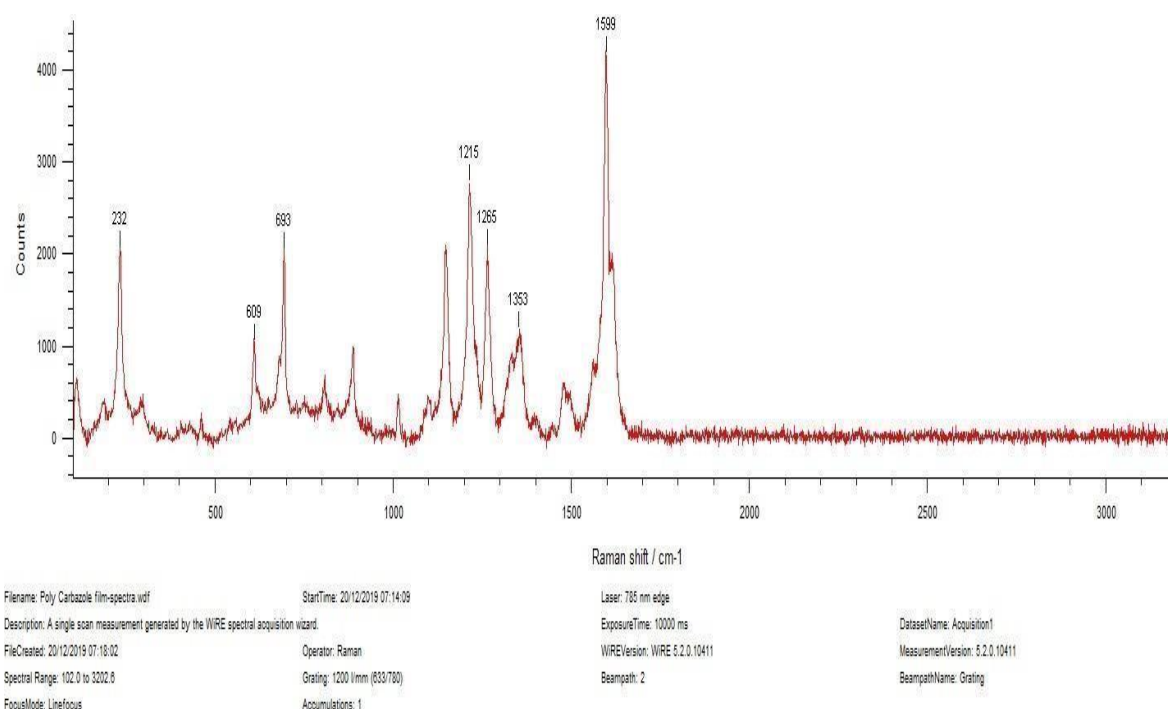


Fig 5.7: Raman image of Polycarbazole film

Table 5.3

Peak no	Centre	Height	Width	Area	Abs.intern	Low edge	High Edge
1	231.979	2068.4	13.8299	79782.2	2105.43	147.1	362.467
2	609.213	857.668	8.2615	46342.1	1087.08	568.75	646.77
3	692.881	1744.92	8.33194	81054.4	2080.6	647.982	733.25
4	1215.39	2411.43	15.97	96439.6	2829.7	1180.24	1242.27
5	1265.49	1688.46	13.8915	66056.64	2199.94	1243.4	1300.55
6	1353.44	1100.6	40.2886	68198.4	1210.55	1301.63	1407.64
7	1598.6	4120.58	15.5492	158823	4237.73	1525.87	1677.3

The table depicts the values of various peaks shown by the characterisation of film under room temperature.

5.2.2 : POLYANILINE FILM

Raman Spectroscopy:

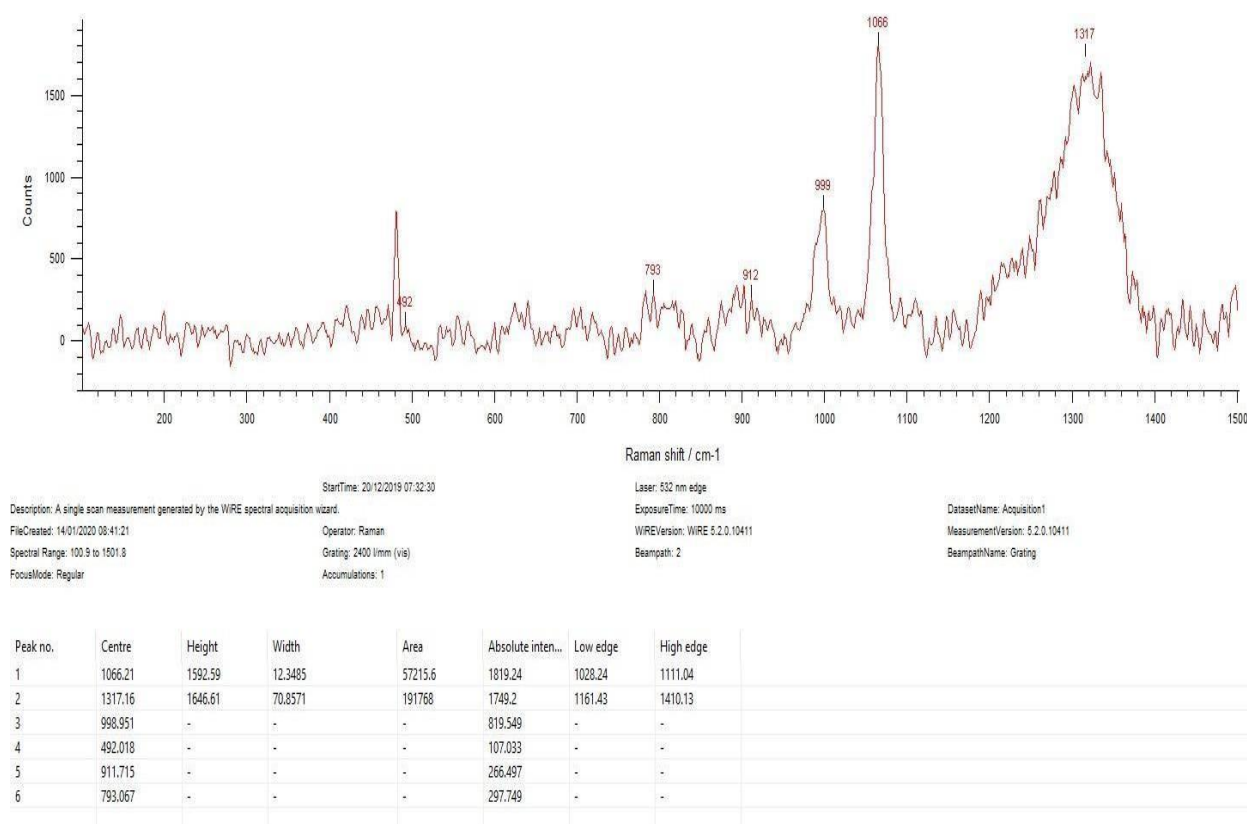


Fig 5.8: Raman image of Polyaniline film

5.3: SENSING PROPERTIES OF POLYMERS

The examination range of Polyaniline film is appeared in figure 5.10. The serious band close to 1500cm^{-1} is doled out chiefly to benzenoid C-C ring extending vibration and a band almost 1600 is ascribed to C=C extending of the polymer chain.

The 1343cm^{-1} band in polymer is additionally doled out to the C-C bond. Specifically, the raman band at 1167cm^{-1} is assignable to the external plane C-H bond.

These outcomes identified with the powers of sub-atomic vibrational groups of the polyaniline test can be related with the variety of polymeric layer thickness.

5.3.1 : IMPEDANCE CURVES

5.3.1.1 : POLYCARBAZOLE

- The analysis is done in the detecting gear as per the cycle referenced by putting the polymer covered substrate in the polymer compartment.
- The gas is passed and the progressions on a superficial level are noted through impedance factor curves.

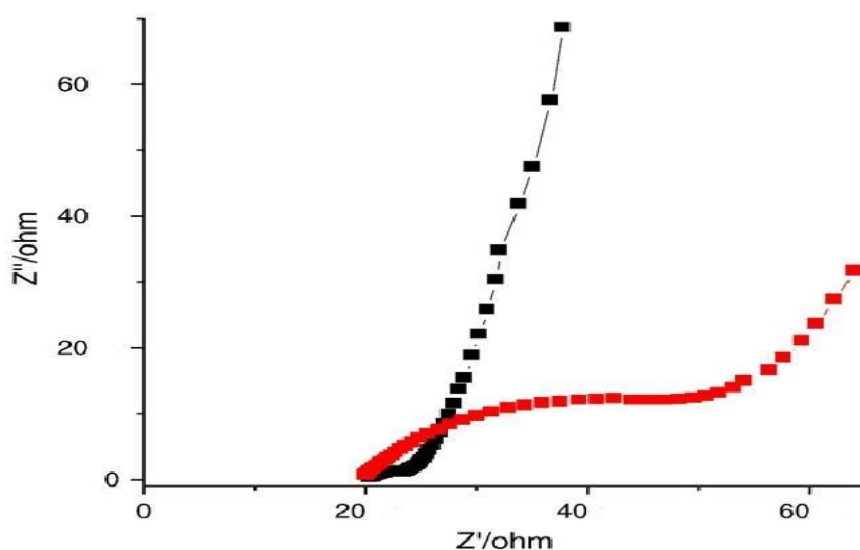


Fig 5.9: Impedance curves of PcZ Film

- Figure 5.11 portrays the outcomes acquired from the impedance study. A primer investigation of the impedance curves showed that the polymer showed critical changes when the gas is passed and showed affectability in discovery.

- The estimations of Z' shows the estimations of genuine impedance and estimations of Z'' on the y hub shows the fanciful impedance.
- The red curve in the figure shows the treated film and dark portrays the untreated one.
- This was ascribed to the high porosity of the polycarbazole films saw by checking electron microscopy. The estimations of impedance show a slow reduction after the openness of substrate to TDI gas throughout some stretch of time

5.3.1.2 : POLYANILINE

- The test is led twice with Polycarbazole and dry air is passed to guarantee that the hardware is prepared for the following arrangement of readings.
- The second arrangement of examinations is done with Polyaniline and the substrate with the polymer coat is set in the chamber. The gas is permitted to go through and comparative impedance investigation is taken.

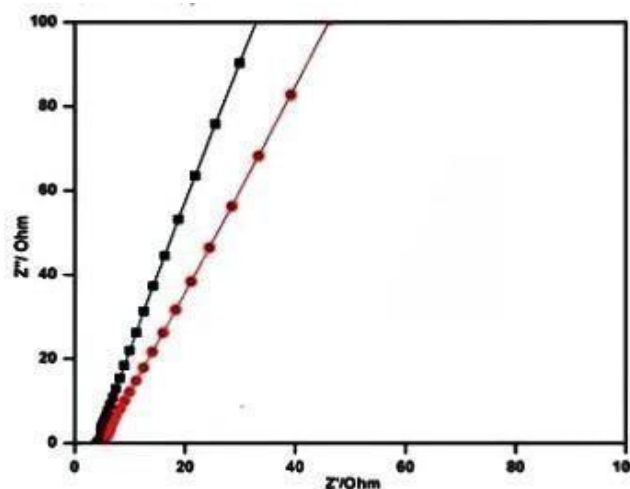


Fig 5.10: Impedance curves of Polyaniline

- Figure 5.12 portrays impedance bends relationship for the frequencies of 120Hz. The red bend shows the treated film after the openness with gases and the dark bend shows the untreated polymer susbtrate.
- From the figure it tends to be seen that the impedance estimation of the polymer films was diminished step by step after a time of openness to gas concerning voltage.

- The estimations of fanciful impedance for both treated and untreated movies continue ascending from the start however the reporter esteems at each point fluctuates showing a few changes generally.

5.3.2 : CYCLIC VOLTAMMETRY

Cyclic voltammetry is a potentiodynamic electrochemical estimation. In a cyclic voltammetry try, the working anode potential is inclined straightly versus time.

- After a set point is reached in a CV investigation, the working electrode is ramped toward the path inverse and gets back to initial potential.
- The potential is estimated between the working anode and the reference terminal, while the current is estimated between the working cathode and the counter electrode.

5.3.2.1 : POLYCARBAZOLE

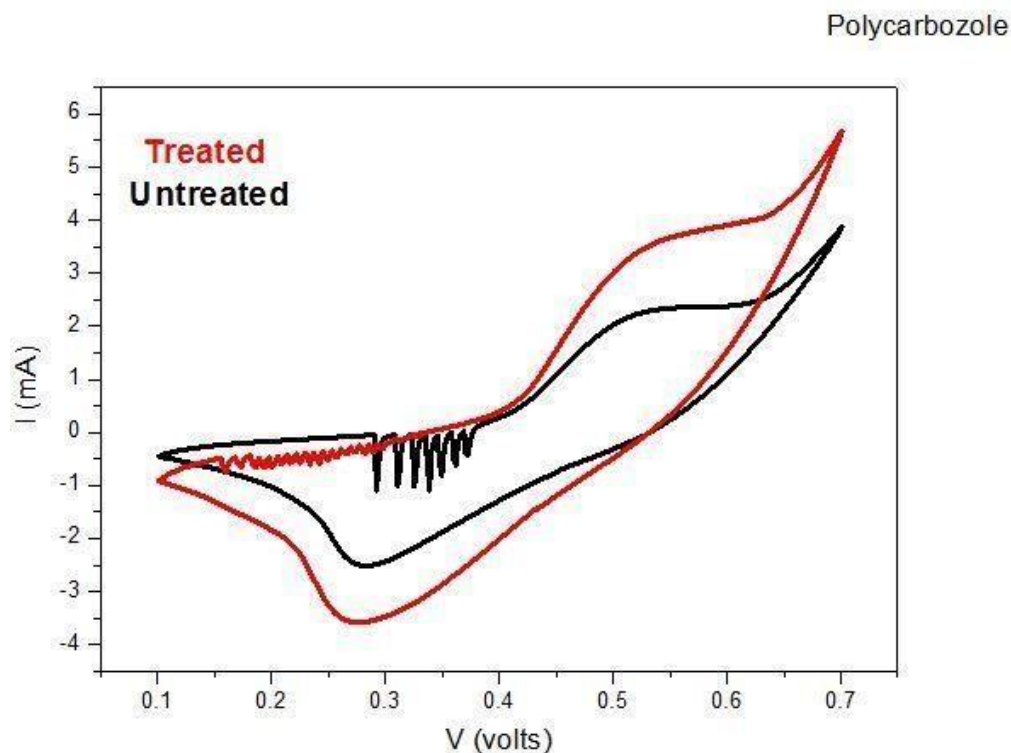


Fig 5.11: CV curves for Pcz

The polymer is sensitive towards a gas detection and the presence of TDI gas can be confirmed.

5.3.2.2 : POLYANILINE

The second set of experiments was conducted with polyaniline in a similar way for cyclic voltammetry characterisation and changes were plotted with current against voltage.

The red curve shows treated polymer substrate and black depicts the untreated curve.

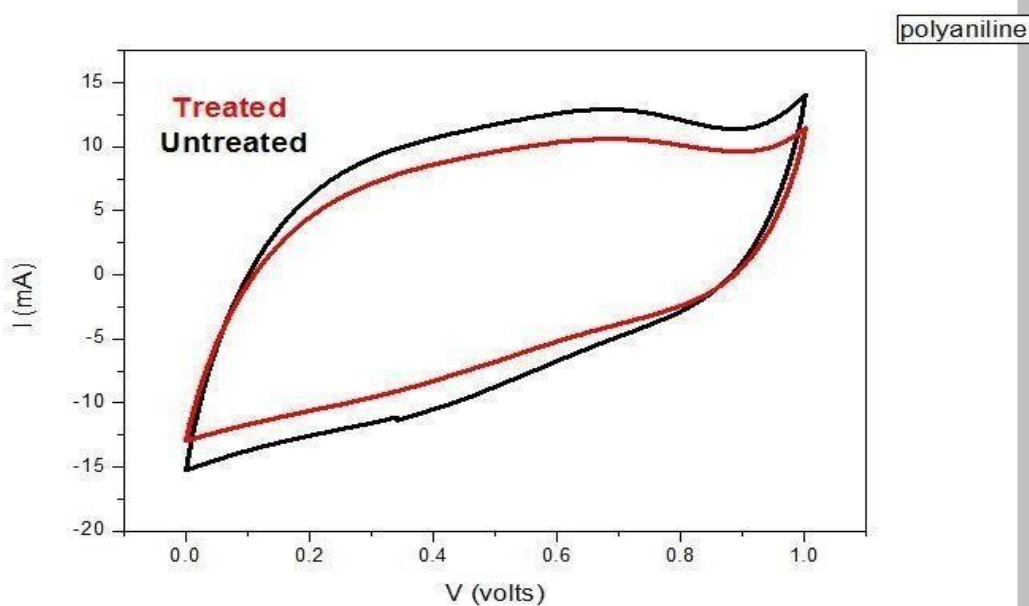


Fig 5.12: CV curves for Polyaniline

From the curves it is significant that Polyaniline films showed affectability towards the gas TDI and presence of gas has been recognized by electrochemical changes.

It very well may be seen that estimations of current w.r.t voltage decline during the openness and the bends appear to converge at starting and the end implying that gas is getting desorbed toward the end stages and polymer is holding its properties.

TDI gas has a perceptible desorption rate and subsequently powerful investigation should be completed.

CHAPTE 6

CONCLUSION

The properties of the gas Toluene Di isocyanate have been dissected and appropriate gas detecting polymers have been taken under investigation. The polymers have been blended utilizing savvy techniques and means. The polymers arranged by different polymerisation methods are covered on the substrates and confirmed for their development by characterisation procedures like SEM, FTIR, Raman Spectroscopy. Polymer arrangements have been orchestrated and are covered on the substrates, for example, metal and ITO covered glass substrates for permitting the electrical conductivity to permit the investigation of changes during adsorption.

Polycarbazole is covered on the substrates by electrochemical testimony and synchronous polymerisation. The thickness of the film is changed by variety of voltammetry attributes. Polyaniline is covered by turn covering and drop projecting and thickness of film is shifted by changing the turn factor and measure of polymer taken.

Artificially kept Polyaniline and Polycarbazole coatings have been utilized as detecting components in the detecting gear for location of TDI and affectability have been explored. The impedance esteems and changes in Cyclic Voltammetry of the examples were assessed under the impact of TDI. From the impedance bends it tends to be seen that the polymer covered on substrates show a critical change in their properties during the time of gas openness.

The estimations of fanciful impedance diminish comparing to each relating line of untreated substrate. The bends in Cyclic Voltammetry likewise show a distinction in their present versus voltage attributes which demonstrates that the polymers are delicate towards the identification of TDI.

REFERENCES

- L. A. P. Kane-Maguire and G. G. Wallace. Synth. Met. 119, 39.
- R. J. Hamers. Nature 412, 489.
- A. G. MacDiarmid. Angew. Chem., Int. Ed. 40, 2581.
- Zi Wang et al. Synthetic Metals 160 (2010) 921– 926.
- Deepali Kelkar and Ashish Chourasia, Journal of Chemistry & Chemical Technology Vol. 5, No. 3, 2011.
- Aurobinda Acharya, Rajkishore Mishra, and G.S. Roy, Armenian Journal of Physics, 2010, vol. 3, issue 3, pp. 195-202.
- Aurobinda Acharya, Rajkishore Mishra, and G.S. Roy, Armenian Journal of Physics, 2010, vol. 3, issue 3, pp. 195-202.
- S. Inaoka, D. Roitman, R. Advincula, Chem. Mater. 2005, 17, 6781.
- P. Taranekar, A. Baba, T. M. Fulghum, R. Advincula, Macromolecules 2005, 38, 3679.
- E. Sahin, P. Camurlu, L. Toppare, V. M. Mercore, I. Cianga, Y. Yagci, J. Electroanal. Chem. 2005, 579, 189.
- Erginer, M. İNDOL -KARBAZOL VE İNDOL -TİYOFEN KOMONOMERLERİNİN SENTEZİ, ELEKTROPOLİMERİZASYONU VE KARAKTERİZASYONU. Istanbul Technical University. Institute of Science and Technology. Department of Chemistry. 2010; Doctoral Thesis.
- Kavanoz M, Sen M, Pekmez N Ö , ELECTROCHEMICAL PREPARATION OF POLY(VINYLFERROCENIUM)-PERCHLORATE- POLYANILINE COMPOSITE MODIFIED PLATINIUM ELECTRODE IN METHYLENE CHLORIDE. Collection of Czechoslovak Chemical Communications. 2011; 76 ,1855-1877.
- Morin J F, Leclerc M. SYNTHESIS OF CONJUGATED POLYMER DERIVED FROM N-ALKYL, 2,7-CARBAZOLES. Macromol 2001; 34: 4680-4682.

LIST OF ABBREVIATIONS

- TDI -- Toluene Diisocyanate
- D.I -- De-ionised
- Pcz -- Polycarbazole
- Pan -- Polyaniline
- CV -- Cyclic Voltammetry
- SEM -- Scanning Electron Microscopy
- FTIR -- Fourier Transform Infrared Spectroscopy
- ITO -- Indium Tin Oxide