INVESTIGATION ON THE PROPERTIES OF ANODIZIED ALUMINIUM NANO POROUS NETWORK FOR HYDROGEN STORAGE APPLICATION

Kishore. M. J, Annatha Kumar T

Dept. of. Mechanical Engineering, Thiagarajar College of Engineering, Madurai, Tamilnadu, India
Dept. of. Mechanical Engineering, Thiagarajar College of Engineering, Madurai, Tamilnadu, India

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Abstract - *Anodic aluminum oxide was reported at first time more than fifty years ago. Since that it has attracted scientists and engineers' attentions in many fields. In this study, anodized nanoporous aluminium sheet was prepared from a thin aluminium sheet of dimension 10*10*1 mm by developing nano pores over the surface of aluminium by anodization process at room temperature under the influence of parameters such as electrolyte ratio, electrode distance, anodizing voltage, anodizing current and duration time. Here the usage of Teflon beaker plays a vital role as electrolyte bath because of its anticorrosive and inertness property. The prepared anodized nanoporous aluminium sheets is then undergone into different characterizations in order to assess it's suitability for hydrogen storage application. This includes surface morphology by Scanning Electron Microscopy (SEM), the crystalline structure by X-Ray Diffraction (XRD), The composition and structure of the oxide layers (Al2O3) by Fourier transform IR (FTIR) spectroscopy and existence of potential well by Photoluminescence (PL).*

***Key Words*: Nanoporous, Hydrogen Storage, SEM image, Aluminium**

1.INTRODUCTION

In present days , storage of energy became a limited resources and rise in different environmental calamities , pushes to find a different mode of energy for the future generation. Hydrogen is a perfect substitute for energy converters thanks to its high efficiency and essential role in reducing pollution . The ignition of hydrogen without using any apparatus releases useful thermal energy. When an IC engine is used to burn the hydrogen , produced mechanical energy can be exploited. Moreover, since hydrogen are often easily converted to its original material by any combustion process, it are often used as an environment-friendly fuel that doesn't interfere with natural cycles, and is emerging as an important material in various fields of applied science. In the utilization of hydrogen as a fuel, its storage and release are important steps. Nano-scale materials are a natural choice as hydrogen storage materials, thanks to fast kinetics of absorption and desorption and enhanced surface and sub-surface storage of hydrogen. It is also evident that Nanopores have drawn a lot of attention these years because of their molecular biological use. The nanopores fabricated in solid state is the most useful one. Many techniques for the fabrication of solid-state nanopores, such as ion beam sculpting and high energy electron beam, have been represented. Recently, two dimensional (2D) materials such as graphene have been reported to be used in the nanopore fabrication. Many nanofabrication methods reported can only fabricate one nanopore at a time and use expensive instruments such as TEM and FIB. A nanopore array can be fabricated by using electrochemical etching after defining etch pits by electron beam lithography (EBL), but EBL is expensive and time-consuming. A cost to efficient and convenient method called shrinking nanopore was published. It is supported the step coverage feature of PECVD. By this method, a large nanopores array can be fabricated at one time but in the process of AAO, the morphology of the nanopore is like hourglass. Anodic alumina (AAO) templates with highly ordered nanoporous structure were fabricated by means of the electrochemical anodization under the constant anodic voltage and electrolyte temperature. Comparing to others, this process is more cost-efficient and convenient. Further it is known as a versatile and inexpensive platform for constructing multitude Nanostructures (Ghodratollah Absalan, 2017). It only needs a preformed micro hole array to urge the nanopore array. AAO mask with the hole size under 10 nm can be obtained, which is smaller than the minimum size of the original mask. This nanopores array can be used for fabrication of quantum dots, separation of materials and treatment of environmental pollution. Actually, there are two different types of AAO: the nonporous barrier oxide and the porous oxide. Porous anodic alumina is formed via an electrochemical process (anodization).Anodic treatment of aluminum was intensively investigated to obtain protective and decorative films on its surface. More recently, applications of porous alumina with an enormous area and a comparatively narrow pore size distribution are exploited. Nowadays, porous alumina is one among the foremost prominent template materials for synthesis of nanowires or nanotubes with monodisperse controllable diameter and high aspect ratios. In this current work, we have proposed a novel strategy to store hydrogen in a anodized Aluminium associated with nanoporous network.

2. Need for Hydrogen storage

Hydrogen holds considerable promise as a fuel of the longer term. Storage of hydrogen in materials has attracted considerable attention within the past few decades and multiple classes of materials are investigated during this regard. This includes Nanostructured materials like carbonaceous materials (e.g. carbon nanotubes, carbon nanofibers & graphene), nanoparticles (e.g. Mg, Pd, Pt), nanostructured bulk materials (e.g. ZK60 Mg Alloys) and nanohybrids. The following table shows some of the existing materials for storing hydrogen.

In addition to this, liquid hydrogen, compressed hydrogen and hydrogen physisorption are some other techniques which are incorporated for storing hydrogen. However, their extensive use has thus far been limited by major scientific challenges. The storage methods for gaseous and liquid hydrogen present a risk of explosion at room temperature. Metal hydride alloys are capable of storing hydrogen at pressures below 20–40 atm. They are costly and weight too much while only storing ~4 wt.%, which is lower than gasoline or diesel (17.3 wt.%). Thus, in order to resolve all the above specified issue, spongy metallic nanoporous anodized aluminium foil is the most prompted storage system for hydrogen gas.

3. Proposed Methodology

Fig 1, below shows the main block diagram of anodization of aluminium sheet and its characterizations.

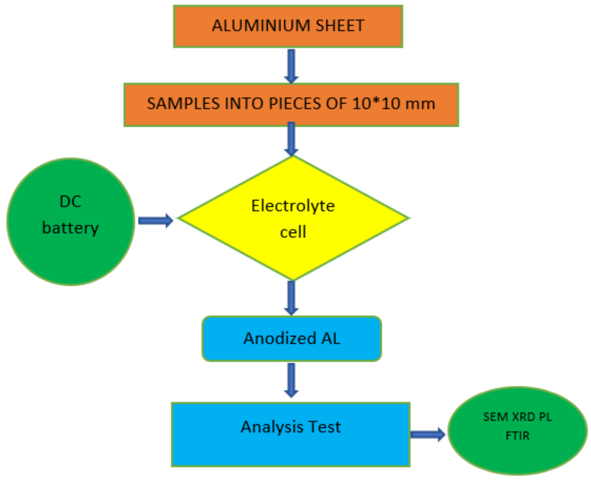


Fig 1 - Block Diagram

4. Requirement of Components

Aluminium sheet (10*10*1) mm, Platinum electrode. Teflon beaker-100ml, Ethanol 500 ml. Hydrofluoric acid 500ml, Distilled water 1000ml, Voltmeter-1.08 v, Ammeter-300 mAmps., DC source battery. Rheostat adjustable. Connecting junction cables. Butter sheet paper as required.

5. Experimental Setup

An cell is an electrochemical cell that drives a non-spontaneous redox reaction through the appliance of electricity. In our set up, we used DC battery source with fixed voltage of 1.08 V and ammeter with current intensity ranging from 0 to 300mA is used for the experimentation. Adjustable rheostat is used to vary the current intensity as per the levels of parameter required. The Teflon beaker of 100ml which is an electrolytic bath in our setup. Teflon is selected because it unreactive to any components and concentrated acids. The electrodes are Aluminium sheet (10*10 *1mm) is an anode and platinum(5*5*0.5mm) is a cathode in our experiment. The electrolyte solution which comprises of hydrofluoric acid, ethanol, distilled water in the ratios of 1:2:3, 2:2:3, 1:4:3 of 100ml solution.

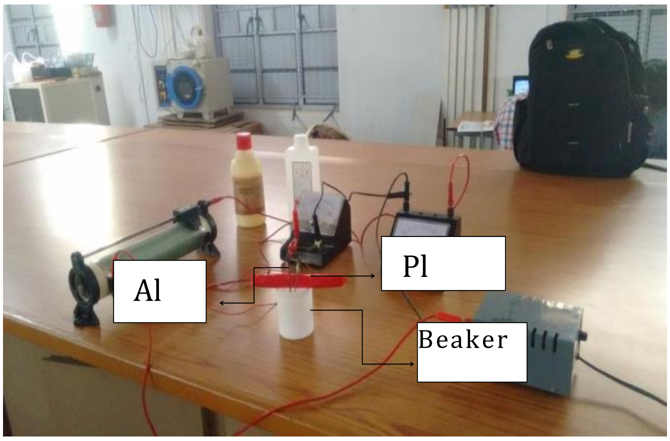


Fig 2 - Experimental setup

6. Experimentation

6.1 Anodization Process

Anodizing is an electrolytic passivation process wont to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called anodizing because the part to be treated forms the anode electrode of an electrical circuit. The anodized aluminium layer is grown by passing an immediate current through an electrolytic solution, with the aluminium object serving because the anode (the positive electrode). The current releases hydrogen at the cathode (the negative electrode) and oxygen at the surface of the aluminium anode, creating a build-up of alumina .Anodization process is employed to generated nanopores network on the surface of aluminium sheet. Hydrofluoric acid is used as etching agent to remove the atom from the surface of aluminium sheet.

Table 1- Electrolytic bath elements

ANODE	**ALUMINIUM SHEET**
CATHODE	**PLATINUM**
ELECTROLYTE	**HYDRO FLUORIC ACID : ETHANOL: DISTILLED WATER**

1. Electrolytic bath - Teflon beaker unreactive to solution and rinsing by distilled water.
2. Anodic cleaning by alcohol-ethanol for 1 min to clean the surface ofaluminium.
3. Cathodic cleaning by alcohol-ethanol for 5 mins to remove the surface impurities of platinum electrode.

Test samples were optimized by L9 orthogonal array in order to meet out the requirements. Test samples are cleaned and anodization process is carried out in a Teflon electrolytic bath. The electrolyte concentration ratio of (HF:C2H5OH; H2O) is taken in 100ml of Teflon beaker. Both the electrodes are immersed in the beaker and electric source is given with standard voltage of 1.08 v and current intensity. The process is continued for 30 minutes etching duration, after that test sample is taken and wrapped in butter sheet to unexposed to the atmosphere.

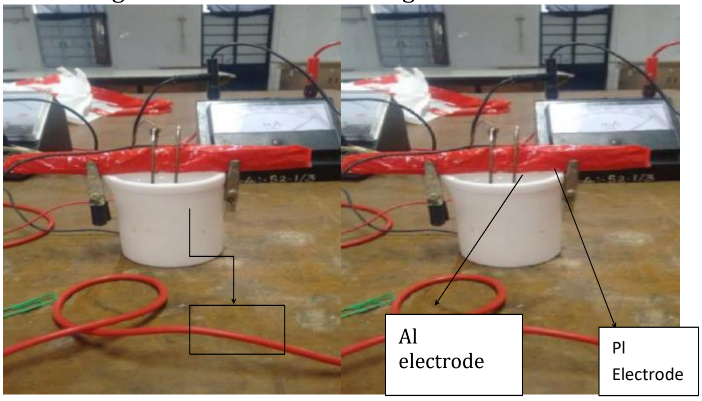


Fig 3 - Electrolytic chamber

The electrolyte solution which is 100ml consist of HF, Ethyl Alcohol and Distilled water in the ratio of - 1:2:3, 2:2:3,1:4:3. The current intensity for the anodization process varies from 200mA,250mA,300mA and the electrode spacing distance are 8mm,10mm,12mm. The effect of concentration of hydrofluoric acid in the anodization process is studied under the SEM image of test samples and influence of electrode spacing distance is also considered for the study. The following levels of parameter are incorporated in anodization technique to study the variation of structural properties of nanopores network generated on the aluminium.

6.2 Anodization reaction

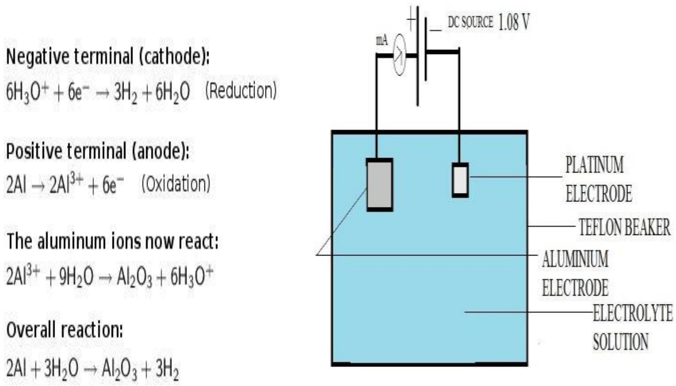


Fig 4- Schematic view of anodization setup

6.3 Design of Optimization

Design of optimization is the process of finding the best design parameters that satisfy project requirements. The Taguchi method involves reducing the variation in a process through robust design of experiments. Orthogonal arrays are special standard experimental design that requires only a small number of experimental trials to find the main factors effects on output. The parameter optimization process of the Taguchi method is based on 7 steps of planning, conducting and evaluating results of matrix experiments to determine the best levels to control parameters. The eight steps are given as follows: -

 Identify the performance characteristics to optimize and process parameters to control
 Determine the number of levels for each of the tested parameters.
 Select an appropriate orthogonal array and assign each tested parameter into the array.
 Conduct an experiment randomly based on the arrangement of the orthogonal array.
 Analyze the SEM image for each combination of tested parameters.
 Find the optimal level for each of the process parameters to generate nanopore network.
 Conduct the confirmation experiment to verify the optimal process parameters.

The levels of each Parameters is three and parameters to be optimized are as follows:

Table 2 : Process parameters and their levels

parameters	level-1	level-2	level-3
current (mAmps)-A	200	250	300
concentration ratio-B	1:2:3	2:2:3	1:4:3
electrode distance (mm)-C	8	10	12

Table 3: Taguchi design (L9 orthogonal array)

	current-mA	concentrtion ratio-ml	electrode distance-mm
EXPERIMENTS	A	B	C
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Table 4 : No of experiments and level of parameters

	LEVELS	LEVELS	LEVELS
EXPERIMENTS	CURRENT (mA)	CONCENTRATION RATIO (100ml)	ELECTRODE DISTANCE (mm)
1	200	1:2:3	8
2	200	2:2:3	10
3	200	1:4:3	12
4	250	1:2:3	10
5	250	2:2:3	12
6	250	1:4:3	8
7	300	1:2:3	12
8	300	2:2:3	8
9	300	1:4:3	10

1. Current intensity
2. Concentration ratio in ml
3. Electrode spacing distance in mm.

Based on the parameters and levels of parameters, we choose L9 orthogonal array to conduct the experiments

6.4 Test for Analysis

The experiments as per optimization are done to nine test samples. The test samples are prepared and given for the following characterization.

1. **PL-** Photoluminescence test is used to find the potential well in the anodized aluminium sample and to conform the quantum confinement effect for hydrogen atom storage.
2. **FTIR-**Fourier-transform infrared spectroscopy test is used to find strength of AO bond in the test samples.
3. **SEM-** it is the test used to conform the nanopore network formed on the surface of anodized aluminium sheet.
4. **XRD-** it is the test used to find the base structure of aluminium oxide formed on the surface of aluminium and to conform the aluminium FCC structure.

7. Results and Discussions

7.1 Scanning Electron Microscope (SEM) Analysis

 The SEM plane view image of AAO fabricated by anodizing the 99% Al at different concentration ratio.
 The image reveals that the pore configuration for different concentration ratio.
 AAO was also synthesized at room temperature to understand the effect of optimizing parameter.
 The image at 2:2:3 is slightly more regular than (1:2:3, 1:4:3, 1:2:6) ratios.

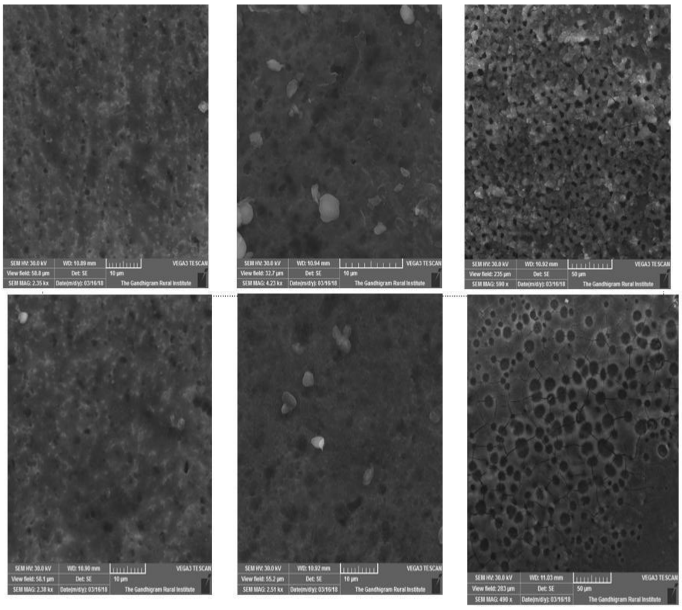
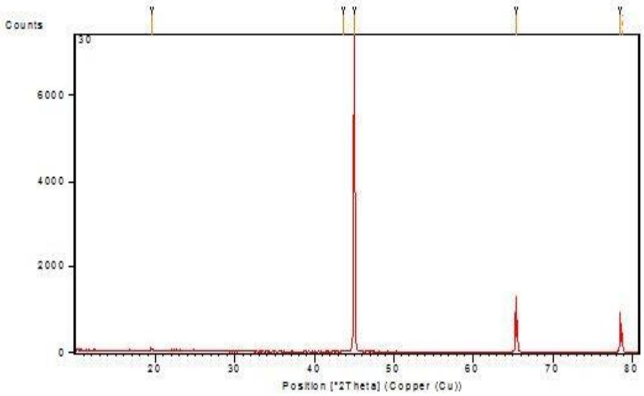
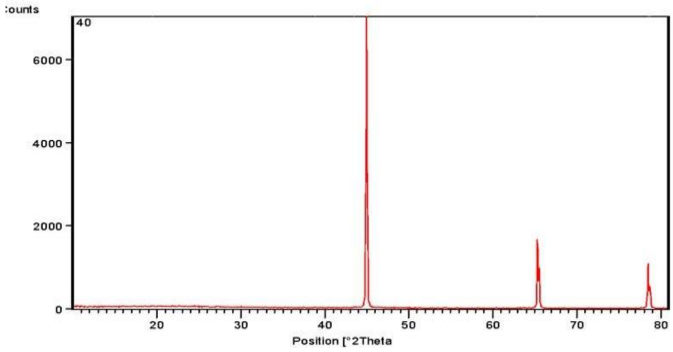


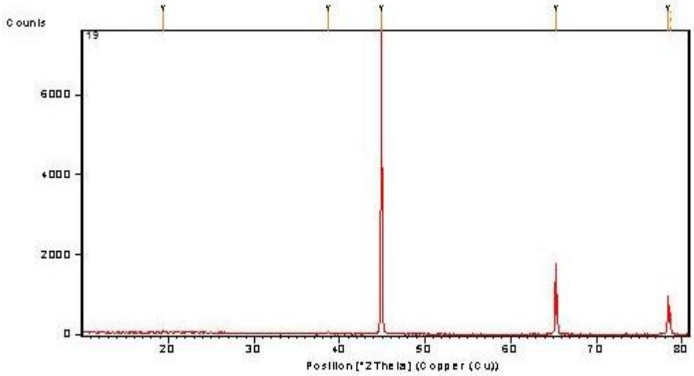
Fig 5- SEM images

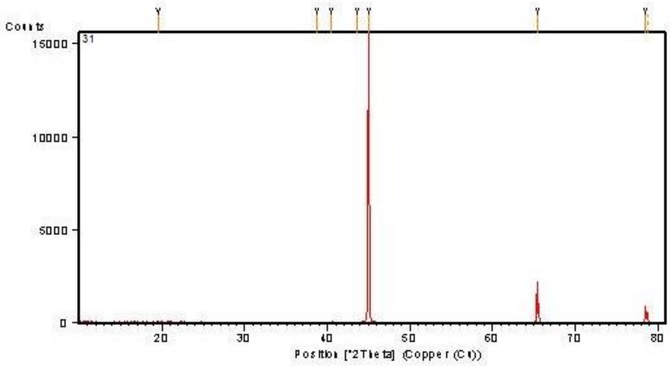
7.2 X-Ray Diffraction Analysis

- The X-ray diffraction pattern of aluminium and anodized aluminium samples are shown
- From the diffraction pattern, it is noticed that the Al and Al2O3 phases are present in the anodized sample.
- This infers that after anodization, the porous Al2O3 layer was formed on the substrate.
- In figure, the aluminium peaks that appeared at 2θ = 44.48, 64.88 and 78.03 confirmed the cubic structure of Al substrate.
- After anodization, tetragonal Al2O3 peaks were observed at 2θ =38.29. The peaks of the re-anodized sample which occurred at 2θ=38.32 indicates the tetragonal structure of Al2O3 as shown in figure below









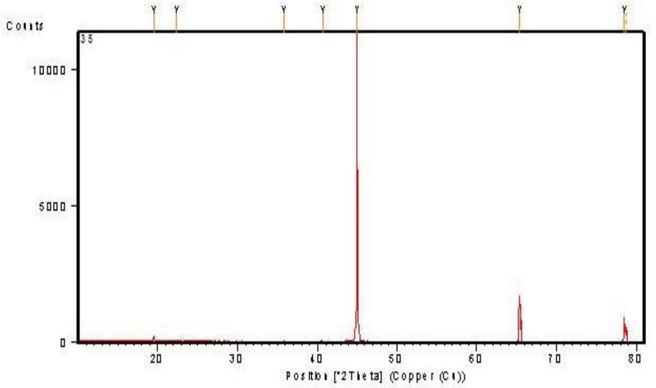
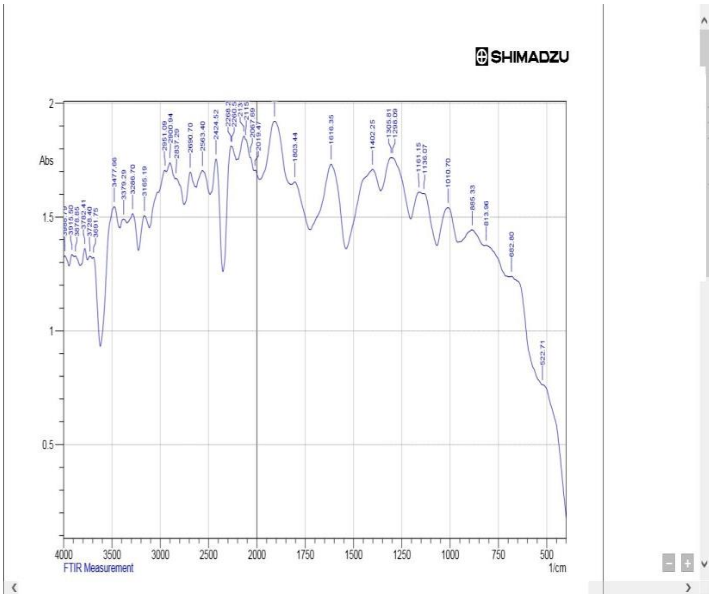
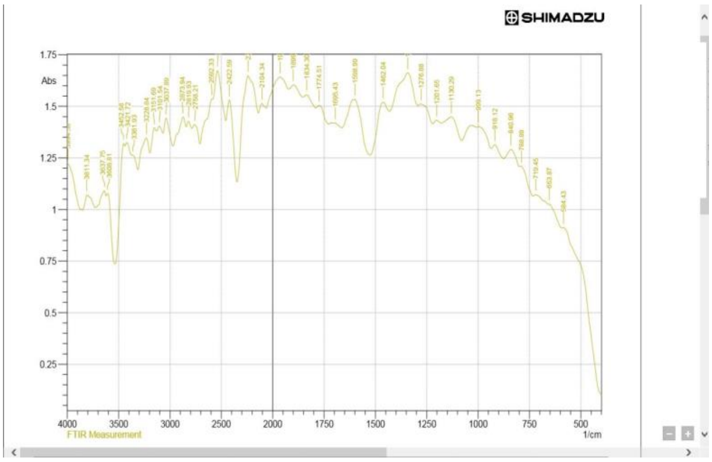


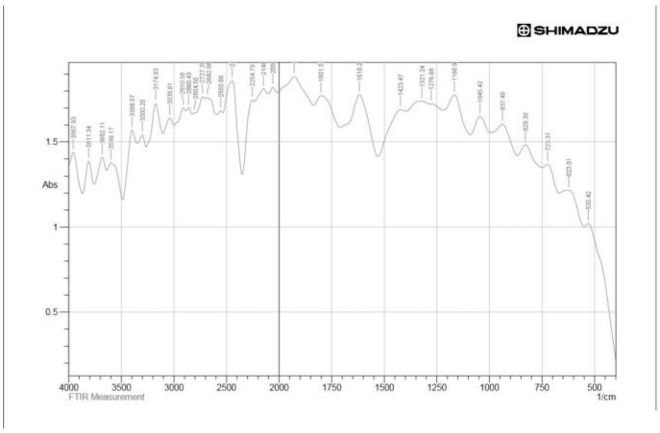
Fig 6 – XRD images

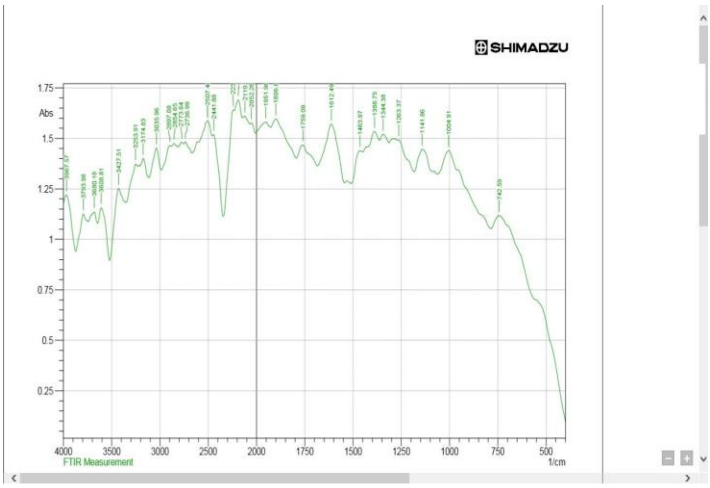
7.3 Fourier Transform Infrared Spectroscopy Analysis

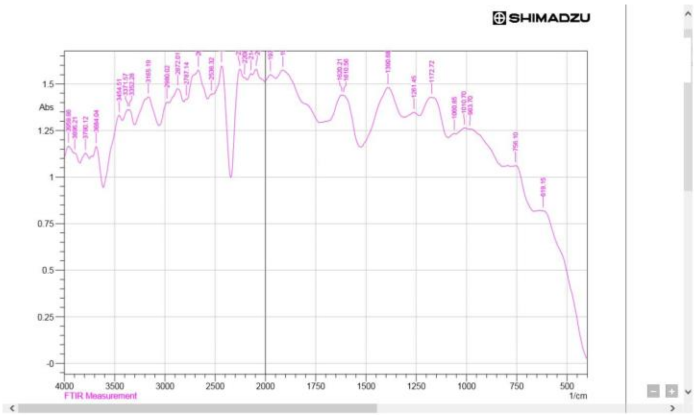
- Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas.
- An FTIR spectroscopy gives the peaks on the aluminium sample.
- FTIR spectra of anodized aluminium metal shows absorbance bands at peaks located at 1345cm-1 ,732cm-1 reflect Al=O,Al-O stretch bands.
- Aluminium occupied 3 different structure AlO_6 ,AlO_5, AlO_4.
- AlO_6 - 500-750cm-1 ,350-450cm-1
- AlO_5 -750-850cm-1 ,250-300cm-1
- Amorphous aluminium oxide occurs at 500-900cm-1 .











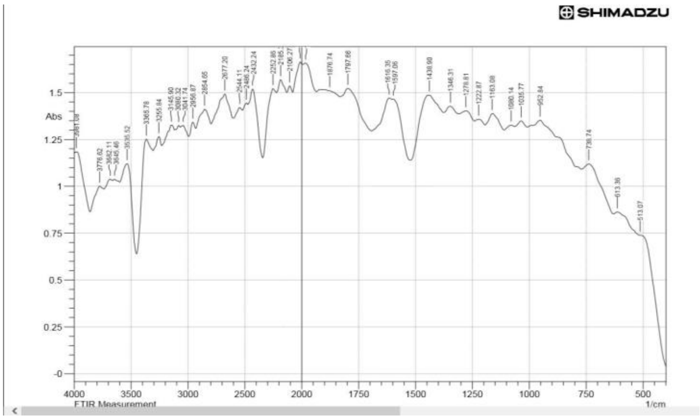


Fig 7 – FTIR Images

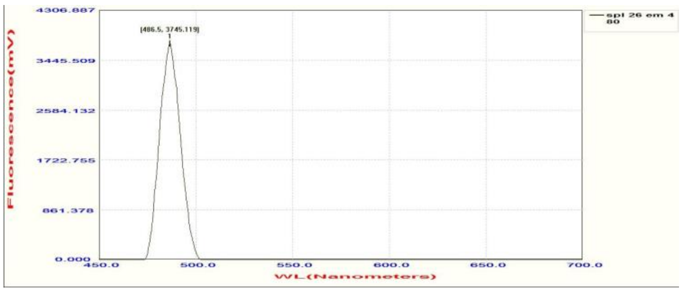
7.4 Photoluminescence Analysis

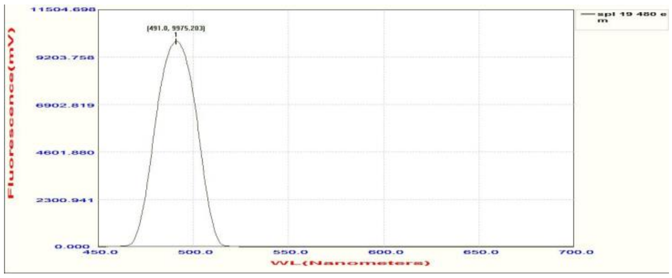
Photoluminescence is light emission from any form of matter after the absorption of photons (electromagnetic radiation). In which excitation wavelength for the sample is fixed as 480nm.

Emission for the corresponding samples are represented in the image with peak wavelength. The difference between excited and emission wavelength give rises to the quantum confinement effect. In our test sample all sample exhibit phase shift of 10nm wave number which indicates existence of potential well in nanopores.

7.4.1 Quantum Confinement Effect

- The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron.
- To understand this effect, we break the words like quantum and confinement, the word confinement means to confine the motion of randomly moving electron to restrict its motion in specific energy levels(discreteness) and quantum reflects the atomic realm of particles.
- So as the size of a particle decrease till we a reach a nano scale the decrease in confining dimension makes the energy levels discrete and this or widens up the band gap and ultimately the band gap energy also increase.





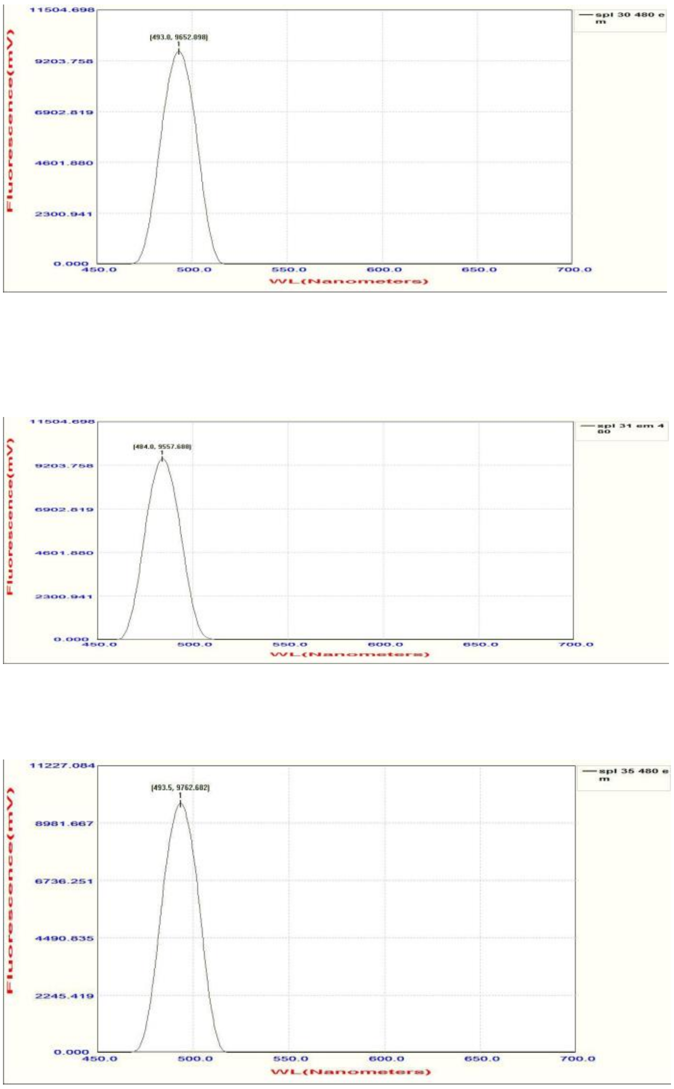


Fig 8 – PL Images

8. CONCLUSIONS

SEM- concludes the nanopore network structure is generated.
PL- concludes the existence of potential well which give rise to storage of hydrogen atom.
FTIR- concludes the existence of Al2O3 is formed the surface.
XRD- concludes the base structure of AL which is FCC in nature.
According to our objective, we generated the aluminium nanopores network and its properties where discussed above and PL results paved the way to store hydrogen atom which is interpreted by quantum confinement effect.

8.1 Advantages

Advantage of this method is nanopores is formed on the aluminium sheet, which is a new way of storing hydrogen.
Though it is a bulk material, no of nanopores formed is higher.
Time taken for anodization process is less when compared with existing methods.

8.2 Future Scope

The future work of this project is to store the hydrogen atom in the nanopores formed on the aluminium sheet. Which can be done by injecting the hydrogen gas and sealing is done advance technique. The conformation of storage of hydrogen gas is done by separate weighing of nanoporous aluminium sheet and hydrogen loaded aluminium sheet.

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