Technical Feasibility of Proton Battery with an Integrated MWCNT Electrode

A Dissertation submitted in fulfillment of the requirements for the Degree
of

MASTER OF ENGINEERING
in
Power Systems

Submitted by

Diksha Kapoor
801742008

Under the Guidance of

Dr. Parag Nijhawan	Dr. Amandeep Singh Oberoi
Associate Professor	Assistant Professor
EIED, TIET, Patiala	MED, TIET, Patiala

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

2019

Electrical and Instrumentation Engineering Department
Thapar Institute of Engineering & Technology, Patiala
(Declared as Deemed-to-be-University u/s 3 of the UGC Act., 1956)
Post Bag No. 32, Patiala – 147004
Punjab (India)

DECLARATION

I hereby certify that the work which is presented in dissertation entitled, "**Technical Feasibility of Proton Battery with an Integrated MWCNT Electrode**", in partial fulfillment of the requirements for the award of the degree of Master of Engineering in Power Systems, submitted to Electrical & Instrumentation Engineering Department (EIED) of Thapar Institute of Engineering & Technology (TIET), Patiala is as authentic record of my own work carried under the supervision of **Dr. Parag Nijhawan** and **Dr. Amandeep Singh Oberoi**. It refers others researcher's work which are duly listed in the reference section. The matter contained in this dissertation has not been submitted, neither in part nor in full to any other degree to any other university or institute except as reported in text and references.

Diksha

Date: 8-Aug-2019
Place: Patiala

(Diksha Kapoor)
Roll No.: 801742008

It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

Date: 8-Aug-2019

Parag

(Dr. Parag Nijhawan)
Associate Professor
EIED
TIET,Patiala

Amandeep Singh

(Dr. Amandeep Singh Oberoi)
Assistant Professor
MED
TIET, Patiala

ACKNOWLEDGEMENT

I express gratitude to the Electrical & Instrumentation Engineering Department (EIED) of Thapar Institute of Engineering & Technology, Patiala for giving me the opportunity to work on the thesis project.

I would like to thank Dr. R. S. Kaler (H.O.D. of EIED Department) for his kind support, Dr. Parag Nijhawan (Associate Professor, EIED) and Dr. Amandeep Singh Oberoi (Assistant Professor, MED) for their invaluable guidance throughout my project work and endeavor period has provided me with the requisite motivation to complete my project successfully.

I also present immense gratitude towards Ms Manbir Kaur (Associate Professor, EIED) for her encouragement and support throughout the degree program without which this thesis won't have been possible.

I specially appreciate the help and guidance of my parents and family who supported me in good and bad times both mentally and at emotional level. I would also like to thank my batch mates and friends who shared their low and high points of carrier and made the journey pleasant.

Diksha

Diksha Kapoor

801742008

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION TO PROJECT

CHAPTER 2: LITERATURE SURVEY

CHAPTER 3: FUEL CELL

CHAPTER 4: DESIGN AND WORKING OF EXPERIMENTAL SETUP

CHAPTER 5: RESULT AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Symbol	**Description**
DMFC	Direct Methanol Fuel Cell
MWCNT	Multi Walled Carbon Nano Tube
E-mode	Electrolyses Mode
FC-mode	Fuel Cell Mode
URFC	Unitized Regenerative Fuel Cell
PEM	Proton Exchange Membrane
MEA	Membrane-Electrode-Assembly
NASA	National Aeronautics and Space Administration
PAFC	Phosphoric Acid Fuel Cell
MCFC	Molten Carbonate Fuel Cell
SOFC	Solid Oxide Fuel Cell
AFC	Alkaline Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PB	Proton Battery
GDL	Gas Diffusion Layer
SEM	Scanning Electron Microscopy
EDS	Energy-Dispersive X-Ray Spectroscopy
CHPS	Combined Heat And Power System

ABSTRACT

For sustainable and incremental growth, mankind is adopting renewable sources of energy along with storage systems. Storing surplus renewable energy in the form of hydrogen is a viable solution to meet continuous energy demands. In this thesis the concept of electrochemical hydrogen storage in a solid multi-walled carbon nanotube (MWCNT) electrode integrated in a proton battery is investigated. The method of solid electrode fabrication from MWCNT powder and egg white as an organic binder is disclosed. The electrochemical testing of proton with an integrated MWCNT-based hydrogen storage electrode is performed and reported. Charging and discharging was carried out and results analyzed to ascertain the electrochemical hydrogen storage capacity of the fabricated electrode. The analysis ascertains that maximum of 81.793 mAhg^{-1} can be stored while charging or electrolyser mode of proton battery and energy extracted while discharging or fuel cell mode is 1.358 mAhg^{-1}.Total four charging and discharging cycles were carried out to assess the performance of proton battery. This proves the technical feasibility of proton battery with an integrated MWCNT-based hydrogen storage electrode, which is the first of its kind. This is surely a step forward towards building a sustainable energy economy.

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

The demand of energy for many centuries is being full filled by exhaustible fuels all around the world. This hike in the population and development has lead to tremendous increase in the fossil fuel utilization [1]. International energy agency has reported a rise of 2.3% in energy demand in 2018, which is due to the exceptional performance of global economy and strong heating and cooling needs [2]. Burning of fossil fuel to run engines and machines gives energy plus exhaust. This exhaust contains carbon monoxide, nitrogen oxide, smoke and other particulate matter [3]. The gases released during combustion forms major constituent of green house gases. The increase in green house gases leads to global warming i.e. increase in the temperature of earth. The after effect of excessive greenhouse gas is melting of glaciers and ocean water becoming acidic. The acidic nature of ocean water causes the shells of sea creature to get dissolved affecting marine life [4].

The particulate matter and toxic gases causes air pollution which is causing 1.4 million deaths ever year in world [5]. Hence there is an urgent requirement to shift from conventional source of energy to non conventional sources. Non conventional sources include wind, solar, tidal, geothermal and biomass. The challenge of shifting towards non conventional sources is their intermittent nature. The intermittency of these sources can be removed via use of energy storage system [6]. There are various forms of energy storage system such as mechanical: compresses air energy storage, flywheel and pumped hydroelectric storage, electrochemical: flow batteries and conventional rechargeable batteries, thermo-chemical: solar fuels, electrical: superconducting magnetic energy storage, capacitor and upper capacitor, thermal storage: latent heat, sensible heat storage and chemical hydrogen storage [7].

Hydrogen storage is one of the sustainable, versatile and scalable forms of energy storage [8, 9]. Hydrogen acts as energy carrier capable of replacing petroleum product [10, 11]. However, storing hydrogen in efficient and safe manner still remains a huddle in a way towards development of a sustainable energy alternative.

It also acts as an effective electricity producer via electrochemical reaction in fuel cell [8]. Fuel cell is defined as an electrochemical device that is capable of converting chemical energy of reactants into electrical energy [12]. Fuel cell are of different types such as alkaline fuel cell, solid oxide fuel cell, Phosphoric acid fuel cell, molten iron fuel cell, direct methanol fuel cell (DMFC), direct oxide fuel cell and proton exchange membrane fuel cell [13]. Among all the fuel cells proton exchange membrane fuel cell is quite popular due to its quick starting ability and working at room temperature. Unlike conventional battery, fuel cell does not produce pollution and the by-product of the reaction is water along with electricity. Hydrogen storage can be done in various forms such as liquid at cryogenic temperature, high pressure storage and chemical compound also called as electrochemical storage.

Hydrogen is considered as the cleanest vector of energy hence it has become great interest of research. It can solve the issue of green house gas emission form the vehicles. The main components of hydrogen system are electrolyser, fuel cell and hydrogen storage. The purpose of electrolyser is to split water into oxygen and hydrogen. This generated hydrogen is being feed to the fuel cell that takes oxygen from atmosphere producing electricity along with water and heat. The features of proton exchange membrane hydrogen storage system have been discussed in this section. Hydrogen can be stored in high pressure hydrogen storage, liquid hydrogen, hydrogen sorption in solid state and chemically bonded hydrogen storage liquids.

In high pressure hydrogen, gas is stored under high pressure in pressure vessel. Hydrogen can be formed in 3 ways in compressed form. One of the way is compressing hydrogen gas with multi stage compressor, in second way high pressure electrolysis is done via pressurized water supply, whereas in third hydrogen is produced within cell in pressurized form [14]. In case of cell producing hydrogen, the accumulation of gas leads to increase in gas pressure within cell. In these cells provision of safety valve is there by which gas leaves cell and when pressure reaches desired value gas stored in high pressured cylinder. This method is dependent on the membrane ability because of pressure difference between hydrogen and oxygen side, oxygen side gas diffusion layer supports in mechanical stress withstand.

According to the material strength of storage cylinder elevated pressure of hydrogen along higher volumetric density can be achieved. But increased thickness leads to increase of cylinder mass and decrease in gravimetric densities. Hence for pressurised hydrogen gas storage system, volumetric density increase is compromised in order to achieve required gravimetric density.

Safety is one of the major concerns in case of pressurized storage. As per [14], the hydrogen gas cylinder in future is estimated to have 3 layers: outer layer will withstand mechanical damage and corrosion and the inner layer polymer layer will be filled with carbon fibre. These cylinders would achieve volumetric storage density of 30 Kg/m^3 and up to 6% gravimetric storage density [14].

Liquid hydrogen storage has challenges because of its low boiling point (21.2K) [15]. These challenges include high adiabatic efficiency along with heat insulation method for low temperature and other is expenditure of energy that is required for attaining 21K. As per literature approximately thirty percent of heating value of hydrogen stored is required for hydrogen liquification [16].

In case liquid hydrogen in stored in un-insulated vessel it vaporizes very quickly. The heat transfer to vessel occurs with both thermal conduction and thermal radiation. The pressure inside vessel increases with evaporation of hydrogen. Hence for keeping the pressure of vessel within safe limits it is required to removal gas from the vessel. The main concern with vehicle using this type of storage is removal of gas when unattended especially when the vehicle is confined in garage like closed space [17]. The major challenges in area of liquid hydrogen storage are effective insulation system and high energy expenditure. For light vehicle this type of storage's safety limitation makes it inappropriate for use.

In case of solid state the Hydrogen storage can be categorized into physisorption and chemisorption. In case of physisorption there is presence of weak Van der Waals attraction between host material and hydrogen molecules whereas in case of chemisorption strong chemical bond between host material and hydrogen. This method is superior over cryogenic liquid hydrogen storage and pressurised hydrogen gas storage in term of safety. Chemisorption is in form of chemical compounds which absorb large amount of gases, whereas in case phyisorption faster cycles of desorption/adsorption occurs along with higher efficiency in energy [18]. For storage of hydrogen in solid- state storage carbon materials and metal hydrides has received immense attention. Metal hydride stores hydrogen less than 2wt% of hydrogen [19].

The major disadvantage of metal hydride is that they are quiet heavy as they are made from rare earth metals, hence it is has limitation in achieving high gravimetric energy density. In case of solid state hydrogen one of the promising materials is carbon. Carbon is promising as it is environment friendly, porous easily available, low cost, good chemical stability and low density. It offers wide range of pore size distribution with considerably high internal pore surface area. Carbon material is available with varying surface area and porosity that can be in form of activated carbon, carbon nanotubes and carbon nanofibers.

Initially for chemical bonding of hydrogen Methonal and N-ethylcarbazol (liquid hydrogen storage material) gave promising results. There has been work in the field of liquid phase material with required thermodynamic properties so that hydrogen storage is supported reversibly. Ammonia is also one of the potential hydrogen storage medium that is capable of chemical adsorption of hydrogen. Ammonia decomposition catalyst is used to release hydrogen gas from ammonia gas. The hydrogen releases in this process produces less heat emission and posses better thermodynamic characteristic compared to hydrocarbons. But the main drawback with ammonia is related to apparatus and people safety because it is corrosive and toxic. Hydrogen production is done via chemical reaction followed by recycling and reaction products [20].

This thesis work revolves around electrochemical storage of hydrogen in porous multi walled carbon nano tubes electrode employed within a modified PEM fuel cell and checking life cycle by performing multiple charge discharge cycles. The presented modified PEMFC works on the principle of a conventional battery with an exception that the hydrogen storage in the fuel cell does not get self discharged. Unlike conventional batteries, it does not emit any fumes and is capable of supplying continuous power with potential application in automotive industry and remote area power supply.

1.2 NEED ANALYSIS

Rising level of green house gas and environmental pollution are main concern of this century. Few source of pollution include emission from fossil fuel and lead acid batteries. Fossil fuel causes pollution in form of nitrogen, sulfur and carbon dioxide which are part of green house gas. The increase in level of green house gases lead to melting of glaciers and rise in temperature. Renewable sources of energy can work as a suitable substitute to the conventional sources of energy. However, these sources are intermittent in nature hence require storage system. Storage can be in form of batteries (Lead acid, nickel cadmium, lithium-ion and lithum-polymer). Lithium-based batteries when fully discharged are dumped instead of recycling because of high cost involved and water pollution.

The remedy of this issue lies in the use of hydrogen as the potential candidate for reducing the level of pollution. Hydrogen energy is harnessed by fuel cell in form of electricity, water and energy. A proton battery works as a battery that could store energy in the form of hydrogen in an integrated porous multi-walled carbon nano tube (MWCNT) electrode (the process is called charging) and supply power when required (the process is called discharging). This technology can be used in storage of energy from other renewable source. Fuel cell finds application in cars, hospitals, airport, banks, schools, military bases and homes. It can power almost any machine or device that contains batteries. Companies like Honda, Mercedes, Toyato and Hyudai are manufacturing fuel cell based cars. Countries like Scoltand, England, Germany and Japan are working towards advancement in hydrogen energy. Hence there is a need to enhance and discover ways for hydrogen storage for clear, green and sustainable development.

1.3 AIM AND OBJECTIVE OF THESIS

The aim of the thesis is:

To check the technical feasibility of a proton battery with an integrated multi walled carbon nano tube (MWCNT) electrode for electrochemical hydrogen storage.

Objectives of the thesis are:

1. To select a suitable material for electrochemical storage of hydrogen.
2. Fabrication of solid MWCNT- based electrode for hydrogen storage.
3. Fabrication of a novel proton battery.
4. To perform multiple charging and discharging cycle of fabricated MWCNT electrode in order to check the life cycle of proton battery.

1.4 ORGANIZATION OF THESIS

Chapter 1 consists of introduction, need analysis along with aim and objective of thesis.

Chapter 2 consists of the literature survey along with gap of research.

Chapter 3 contains the details of the fuel cell along with its different types.

Chapter 4 contains the experimental setup and design of proton battery.

Chapter 5 contains the results along with their discussion related to charging and discharging of proton battery with integrated muti walled carbon nano tube electrode.

Chapter 6 consists of the conclusion related to the proposed work along with future scope in this field of research.

CHAPTER 2

LITERATURE SURVEY

In 1839 Sir William Grove invented galvanic cell battery [21]. The battery worked on continuous supply of expensive and rare gases with a short lifetime due to corrosion; hence the concept was not pursued. After 50 years Langer and Mond enhanced Grove's work and developed fuel cell with fifty percent efficiency and power of 1.5 W. Basic principle of fuel cell is release of energy that leads to release of chemical energy with byproducts - hydrogen and oxygen. Burning gas releases heat whereas in case of fuel cell energy is released in form of electric current. There are mainly nine types of fuel cells. These fuel cell are differentiated on the basis of the fuel and electrolyte used [22]. Proton exchange membrane fuel cell is the most commonly used fuel cell as it operates is room temperature and starts quickly.

2.1 CONVENTIONAL HYDROGEN SYSTEMS

A hydrogen system employs an electrolyser, storage unit, photovoltaic cell and fuel cell. Generation of hydrogen in case of conventional system is with the surplus solar energy through electrolysis of water. DC electricity from photovoltaic cell is used to split the water into oxygen and hydrogen. Hydrogen is stored separately which is used in production of water and electricity with the help of a fuel cell. Hydrogen is compressed before storage in order to get higher energy storage density. But when this stored hydrogen is used in fuel cell the pressure is reduced. This type of storage can be utilized as a source of remote area power supply. Fig 2.1 represents conventional hydrogen system.

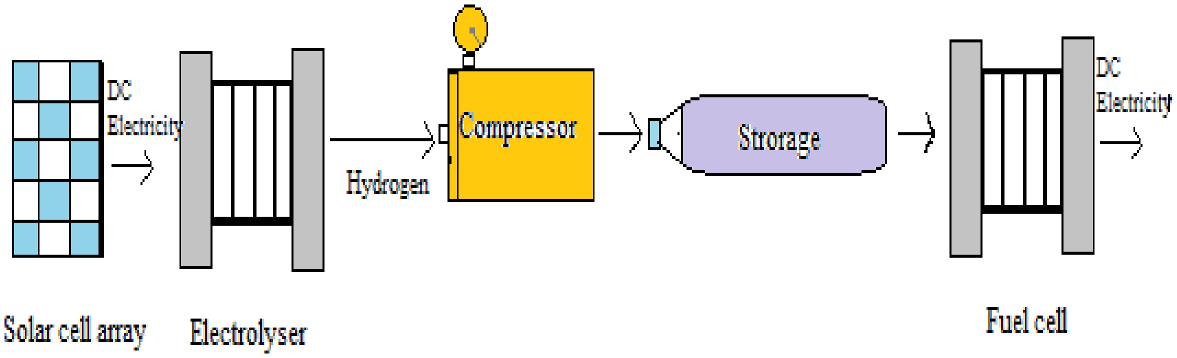


Fig 2.1: Schematic of a conventional hydrogen system

Production of hydrogen by splitting water is well know and is used commercially in industries [23]. The advantage of conventional hydrogen system includes silent operation, scalability and zero green-house gas emissions. Unlike other commercially available batteries energy in this case is stored in form of hydrogen which does not get self discharge over time. Therefore the energy stored in hydrogen is present till used whereas for normal batteries the energy storage is for short time.

Some of the disadvantages of conventional hydrogen storage include; as compared to batteries includes more number of devices in the system. The round trip efficiency i.e. from electricity in to electricity out is seventy to eighty per cent in case of batteries whereas in case of conventional hydrogen system it is forty to forty five percent [24]. The relative large size of system limits the mobile application.

2.2 A HYDROGEN SYSTEM EMPLOYING UNITIZED REGENERATIVE FUEL CELL AND STORAGE UNIT

A unitized regenerative fuel cell (URFC) is a single unit that can function as fuel cell as well as electrolyser. As in conventional hydrogen system both fuel cell and electrolyser does not work together proton battery can replace fuel cell and electrolyser in conventional hydrogen system. URFC while running in electrolyses mode **(**E-mode) splits water into oxygen and hydrogen using DC electricity produced from renewable sources. Fig 2.2 represents the hydrogen storage system using URFC.

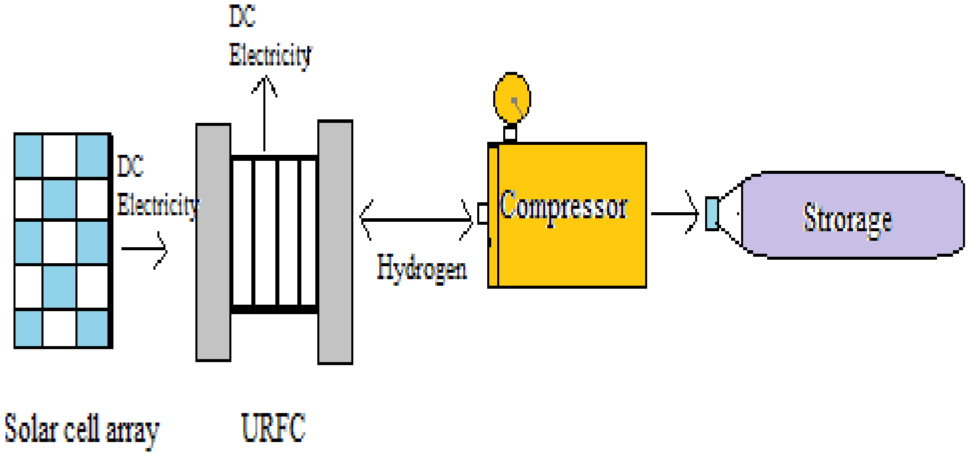
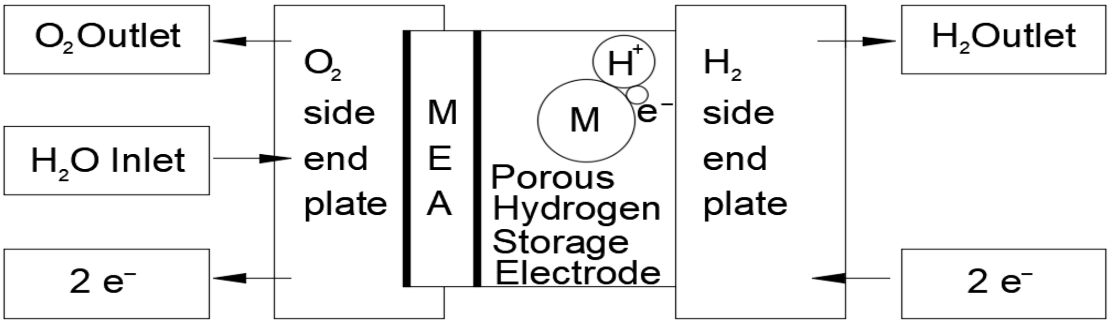


Fig 2.2: Schematic of a hydrogen storage system with URFC.

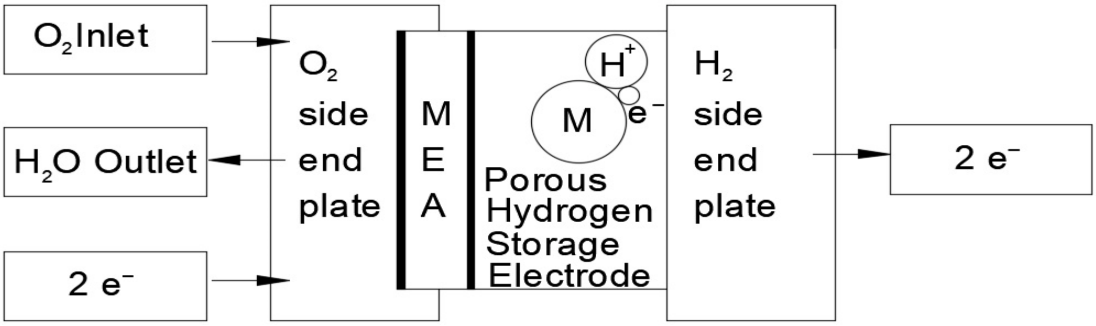
The hydrogen produced by water electrolysis is pressurized and stored separately. URFC, while running in (fuel cell mode) FC-mode combines' stored oxygen and hydrogen produced previously in E-mode. The UFRC gets its supply of hydrogen via storage unit [25]. The net volume and mass of this system is lower than conventionally hydrogen system because of fewer components. The URFC employed in system should be a dedicated fuel cell while running in FC-mode and an electrolyser while running in E-mode to achieve higher lifetime and efficiency. It is also financially advantageous as it saves the cost of separate fuel cell and electrolyser. There is an extensive research going on to increase the efficiency of fuel cell and electrolyser mode of URFC. Dedicated fuel cell and electrolyser performance can be achieved by URFC but it has limitations such as performance degradation after few 100 cycles and short lifetime [26]. URFC requires an external hydrogen supply which needs a separate unit for hydrogen storage.

2.3 INTEGRATED HYDROGEN STORAGE IN A PROTON BATTERY

The concept of proton battery includes solid hydrogen storage electrode integrated in a proton exchange membrane (PEM) fuel cell that would serve both as an electrolyser as well as fuel cell. Fig 2.3 represents hydrogen storage and retrieval in proton battery.



(a) Electrolyser mode of proton battery



(b) Fuel cell mode of proton battery.

Fig 2.3 (a) and (b): Schematic of integrated hydrogen storage in proton battery.

The unit comprised of a membrane-electrode-assembly (MEA) sandwiched between two bi-polar end plates and is loaded with catalysts. The membrane is made of a polymer named as 'Nafion-117' that serve as heart of the unit. The membrane is a proton conducting solid electrolyte that allows hydrogen to pass through but nit the electrons. In E- mode or while charging hydronium ions (H_3O^+) containing H^+ are produced by splitting water and these hydronium ions emerge from the membrane at cathode side where they get adsorbed in a porous storage electrode. The oxygen gas produced in this mode flows to oxygen side via flow channels and exits the cell. The protons form weak chemical bonds with solid storage electrode, ideally without production of H_2 gas. The external circuit helps electrons to pass through. As in E-mode, water is spilt into protons continuously, these proton flows to storage via system, this device is called 'a proton battery'. Electrolyser-mode operation reaction of the proton battery is mentioned in Equation 2.1 and 2.2.

$$\mathrm{H^+ + e^- + M \rightarrow M - H} \tag{2.1}$$

$$\mathrm{H_2O + electricity \rightarrow H^+ + \frac{1}{2}O_2 + 2e^-} \tag{2.2}$$

where, M is hydrogen storage material used as electrode.

In proton battery's first experiment, the solid electrode was made of metal with formation of a complex AB_5 metal hydride [26]. Other materials such as various forms of porous carbon may also be used. In FC-mode, the stored hydrogen from storage material comes out under the influence of electric potential. These hydrogen compounds split into H^+ and e- by a catalyst. Protons travels back to oxygen side through the membrane and the wires giving electricity on the oxygen side, oxygen is fed which reacts with H^+ and e- to reform water. The reactions associated with this mode are represented in Equation 2.3 and 2.4:

$$\mathrm{2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O + electricity} \tag{2.3}$$

$$\mathrm{M - H \rightarrow M + H^+ + e^-} \tag{2.4}$$

where. M is host material for hydrogen storage.

Various steps involved in the conventional hydrogen system have been eliminated by the use of proton battery. An observation can be done regarding proton battery that it does not require a separate electrolyser, storage and fuel cell. Thus the efficiency drop across various steps could be avoided thereby increasing the round trip efficiency of system [26]. Proton battery finds potential applications in mobile applications. Proton battery may be more convenient in comparison with proton battery hydrogen system and conventional hydrogen system, the reason is that its structure is compact with a single device serving as storage, electrolyser and fuel cell.

Thus it can be said that proton battery is convenient and simple form of battery. The proton battery saves expenditure of energy related to running of compressor and electrolyser. Hence by using proton battery it is possible to attain higher overall round-the-trip efficiency at lower cost as compared to conventional hydrogen system. In a proton battery protons (H^+) which is highly-reactive, diffuse directly into solid storage material forming weak chemical bonds with storage material.

This discovery has lead use of ample and light material such as graphite, carbon and aluminum to be used as electrochemical storage. The suggested material use provides higher volumetric and gravimetric energy densities and reduced cost of storage per unit mass of hydrogen in comparison with metal hydride based hydrogen cylinder that involves high cost and weight for commercial production of hydrogen gas.

2.4 WORK ON ELECTROCHEMICAL HYDROGEN STORAGE

Professor John Andrews, at the Royal Melbourne Institute of Technology (RMIT) University, Australia introduced the concept of proton battery. In 2010, one of Prof John Andrew's students worked on proton battery. The first paper on this concept was released in 2013. He had given some experimental results also in his paper. Royal Melbourne Institute of Technology, School of Aerospace, Mechanical and Manufacturing Engineering (RMIT SAMME) is involved in the extensive work onto the most suitable storage material of hydrogen that uses hydrated nafion as electrolyte.

A unitized regenerative fuel cell designed was given by the professor John Andrews and his student Saeed Seif Mohammadi. His design uses AB_5 complex metal hydride powder to store hydrogen. Use of PEM has given another concept to increase the efficiency as compared to conventional fuel cell where the hydrogen produced was stored and then used [27]**.** MEA allow the flow of proton through it that can be stored continuously in a proton battery. Water gets split with the help of electricity into hydrogen and oxygen. Hydrogen ion produced with the help of noble metal as catalyst and forms hydronium (H_3O^+) ion that passes through MEA and stored in storage material or metal hydride. In FC – mode stored protons due to opposite potential difference travel through membrane and react with the oxygen to produce water and electricity. It draws electrons from external circuit that produces electricity to flow in external device. So this experiment confirms the concept of proton battery technically. Substitute for metal hydride was searched as the electrode formed was heavy and favors generation of H_2 gas.

Considering carbon as potential candidate for hydrogen storage the research at RMIT was carried out at carbon instead of metal hydride. The reason for this shift was carbon being porous, cheaper than metal hydride and poor catalyst for (Hydrogen) H_2 gas generation. Other property of carbon includes high surface area and low densities making it suitable for storage of gas, filtering membrane, catalysis, and superconductor [28]. In another literature [29] containing work of Prof. Andrews and M.J. Jazarei, the feasibility of nafion and activated carbon in proton battery was carried out. This electrode could not store hydrogen reversibly. The explanation for this was, nafion being a polymer with larger molecular size than carbon electrode, it failed to penetrate in the carbon electrode and hence, there was no proton conducting medium within the electrode to conduct hydronium ions [29]. In another research work of Dr Amandeep Singh Oberoi under Prof Andrew, activated carbon electrode soaked in a liquid proton conductor (instead of nafion) was tested for hydrogen storage. The proton conductivity measurement was done by electrochemical impedance spectroscopy and by galvanostatic discharging and charging their H_2 storage capacity was measured. Reportedly, they were to store hydrogen electrochemically in the activated carbon electrode and hydrogen storage capacity was found to be as 1.29 wt %. It clearly showed the significance of a liquid conductor within the carbon –based electrode instead polymer nafion-based proton conductor [26].

Other forms of carbon such as graphene and carbon nano tubes have also been reported with high level of electrochemical hydrogen storage. Theoretical studies for validation of electrochemical hydrogen storage have been carried out in numerous research works. In literature [30] the author has found the electrochemical storage of $CoAl_2O_4$ pigment via thermal decomposition of green tea extract. The capacity of $CoAl_2O_4$ was found to be 1100mhg^{-1} for 20 cycles and 1mA current. Hydrogen storage capacity of Ni-CNT and purified CNT was compared. The discharge capacity of Ni-CNT was found more than CNT. Maximum discharge capacity was about 3520 mAhg^{-1} in Ni-CNT with current of 2mA for 15 charge and discharge cycles [31]. Electrochemical storage of hydrogen was employed to produce CNT/TiO_2 – Co nano composite. The maximum charging capacity was 305mAhg^{-1} for CNT/TiO_2 – Co which was twice amount stored in carbon nano tubes [32]. In another literature comparison between electrochemical hydrogen sorted in silver and carbon nano tube was performed. The silver electrode was hardly able to stored hydrogen during charging and discharging where as carbon nano tube was able to store 0.61wt% hydrogen. The cyclic charging and discharging was carried out for 10 cycles under regulated 10mA current. Hence the nano composite formed can be chosen as suitable candidate for electrochemical hydrogen storage [33].

As per literature [34] electrochemical hydrogen storage in carbon nano tube is possible because hydrogen gets diffused through the open tip then get adsorbed inside tubes. When TiO_2 (titanium oxide) nanoparticles are deposited on the surface of MWCNT, the hydrogen storage and discharge capacity was enhanced. The results of this experiment reported discharge capacity of 540mAh/g that is equivalent to 2.02wt % of hydrogen [35]. The characterization and hydrogen storage capacity of multi-walled carbon nanotubes (MWCNTs) have been studied in literature [36]. MWCNTs with bulk yield and high purity were achieved from a mixture of camphor on a nickel support by aerosol-assisted chemical vapor deposition. Hydrogen storage properties of produced MWCNTs were investigated via quartz crystal microbalance. Values between 1.2 and 2.0 wt % of adsorbed H_2 were reached depending on pressure applied [36]. Paladium doped MWCNT were prepared via supercritical carbon dioxide deposition method, enhancing the hydrogen uptake capacity of MWCNT at room temperature and pressure. Electron microscope was used to confirm that average palladium nanoparticle size distribution was around 10 nm. A drastic increment of hydrogen storage was recorded from 44 mmolg^{-1} sample for undoped material to 737 mmolg^{-1} sample for doped material [37]. The hydrogen storage capacities of the MWCNTs, Calcium-MWCNTs, Cobalt-MWCNTs, Iron- MWCNTs, Nickel-MWCNTs, and Palladium-MWCNTs under ambient conditions were determined to be 0.3, 1.05, 1.5, 0.75, 0.4, and 7 wt %, respectively [38]. The treated MWCNTs showed a maximum hydrogen uptake of 1.21 wt%, while the Palladium-MWCNTs and Vanadium-MWCNTs had a hydrogen uptake of 0.37 and 0.4 wt%, respectively. This is because the treated CNTs had the highest specific surface areas compared with those of the Pd-CNTs or V-CNTs. This indicates, physisorption was the mechanism responsible for the hydrogen uptake [39]. Hydrogen storage in Pd – functionalized MWCNT was tested by reducing size and facilitates uniform loading of MWCNT. Nanostructure modification enhanced the hydrogen adsorption capability by 2.3 times [40].

Hydrogen adsorption capacity of Pd-CNTs was found to be 0.125 wt% whereas V-CNT was found as 0.1 wt% during first cycle. In the second cycle the hydrogen wt% was found to be half of the first cycle. Electrochemical storage capacity of MWCNT was found to be 363mAhg^{-1} whereas Mg dopes MWCNT had capacity of 450mAhg^{-1}. When MWCT was decorated with Mg its surface area decreased [41]. $NiAl_2O_4$ /NiO nanocomposite are used with thermal decomposition method via green tea extract. In this research paper the effect of calcinations temperature on morphology, hydrogen storage capacity and band gap was determined. On increasing the calcinations temperature hydrogen storage capacity was 450 to 800mAh/g. The paper also suggests that $NiAl_2O_4$/NiO can become ideal material for electrochemical hydrogen storage [42].

The electrochemical hydrogen storage in the above mentioned literatures are analysised quantitatively by using X-ray powder diffraction or Brunauer–Emmett–Teller (BET) theory. These methods give rough estimate of hydrogen stored by considering parameters such as surface area of carbon. Hence there is need for evaluation of hydrogen stored and retrieved via practical experimentation. Using MWCNT in proton battery can determine experimental values of hydrogen stored and retrieved electrochemically.

Electrochemical hydrogen storage is useful in green hydrogen storage system and development efficient system for various applications. For performing experimentation on MWCNT electrode formation is required. Binder is used in formation of electrode which provides strength to electrode as well as variety of pores for storage of hydrogen. Till date nafion and polytetrafluoroethylene have been used as binder for electrode in proton battery [26]. Pores classification is based on size in nanometers [43]. Classification of pore is as per Table 2.1.

Table 2.1 Classification of pore according to size.

Type of Pore	Size
Macropores	50 nm
Mesopores	2 and 50 nm
Micropores	0.7 and 2 nm
Ultramicropores	< 0.7 nm

The pores are interconnected in nature and provide active sites for electrochemical hydrogen storage. Ultramicorpores play significant role in solid state hydrogen storage [44]. Egg white can be used as it is low cost, organic substitute for binder. Egg white or albumen consists of 90% water [45]. In this thesis albumen is used as binder binds MWCNT. Varying size pores are formed by evaporation of albumen's water content.

2.5 GAP OF RESEARCH

- The available literature does focus on theoretical study on electrochemical storage in multi walled carbon nano tube but, its experimental validation is yet to be done.
- Mutli walled carbon nano tubes have not been used as an electrode in proton battery for hydrogen storage.
- Cyclic testing of proton battery with an integrated mutli-walled carbon nano tube electrode is yet to be reported.
- Use of egg white as binder in electrode has yet to be explored by researchers.

CHAPTER 3

FUEL CELL

Fuel cell is electrochemical device which converts the chemical energy of fuel into electrical energy. As compared to conventional energy conversion in generators, direct conversion of fuel into electrical energy via fuel cell is promising that offers better efficiency and lower environmental impact. The intermediate step such as mechanical work and heat production are avoided therefore fuel cell output is not limited by Carnot efficiency. Fuel cells are different form batteries as batteries store charge where as fuel cell requires supply of oxygen and hydrogen to produce charge. One of the advantages of fuel cell over battery is that they provide output till the time supply of fuel is supplied. The commercial application of fuel cell was first done in space mission by NASA (National Aeronautics and Space Administration). Fuel cell finds application in various areas of power supply such as backup supply, residential and commercial supply. The basic constituents of fuel cell are cathode, anode and electrolyte. The function of electrolyte is to provide passage for ion flow from anode to cathode.

At cathode or oxygen side, reaction between oxygen ions, electron and hydornium ion (H_3O^+) takes place forming water and heat. At anode, the fuel gets oxidized in the presence of catalyst and form hydrogen ions and electrons. The produced electrons flow from anode to cathode satisfying the electrical circuit because they cannot pass through the membrane electrode assembly which only conducts proton.

Typical range of potential across fuel cell is 0.6 to 0.7V. In order to achieve the required amount of energy fuel cell are stacked in series and parallel combinations. The series combination increases the net voltage across the stack of fuel cell, whereas the parallel combination of fuel cell allows higher magnitude of current to flow though the system. Fuel cells are classified on the basis of electrolyte and fuel used [46]. The most popular fuel cells are listed below.

- Phosphoric acid fuel cell (PAFC)
- Molten carbonate fuel cell (MCFC)
- Solid oxide fuel cell (SOFC)
- Alkaline fuel cell (AFC)
- Proton exchange membrane fuel cell (PEMFC)
- Direct methanol fuel cell (DMFC)

3.1 ALKALINE FUEL CELL (AFC)

Alkaline fuel cell uses an alkaline electrolyte (most commonly used electrolyte is potassium hydroxoide) to generates electricity. A hydroxl ion present in the electrolyte allows circuit to be electrically operated and extract energy. Hydrogen redox reaction takes place at the anode where hydrogen gas molecules combine with each other in order to form hydroxyl ions.

The electrons get released on anode and reaches cathode via external circuit where they combine with water, generating OH^- ions. On cathode side, water and oxygen combines together forming electron and hydroxyl ions. The operating range of alkaline fuel cell is between 60 to 90° C. Nickel is the most common catalyst used in this fuel cell to increase reaction rate [47]. Anode and cathode side reaction are shown in the Equation 3.1 and 3.2

Anode : $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$ (3.1)

Cathode : $2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$ (3.2)

The first alkaline fuel cell was used by NASA to supply electricity and drinking water to its shuttle during a space mission. Recently, this fuel cell finds application in submarine, forklift, boats and niche transport application [48]. This fuel cell has advantage of simple structure and inexpensive catalyst. It consumes oxygen and hydrogen to give out electricity, heat and water. It does not give out any green house gas as an end product and work with seventy percent efficiency.

3.2 PHOSPHORIC ACID FUEL CELL

Phosphoric acid fuel cell or PAFC is made using liquid phosphoric acid and carbon paper as electrolyte. Phosphoric acid is a colourless liquid that finds application in detergents, fertilizer, pharmaceutical and food flavouring. Its operating temperature is high because phosphoric acid's ionic conductivity is low at low temperature. The range of working temperature of these fuel cell lie in the range of 150-220° C. Hydrogen acts as the charge carrier in this fuel cells and its ions pass from anode to cathode through electrolyte and expel electrons. Anode and cathode side reactions are mentioned in Equation 3.3 and 3.4. Equation 3.5 represents the overall reaction taking place inside fuel cell.

Anode : $2H_2 \rightarrow 4H^+ + 4e^-$ (3.3)

Cathode : $O_2 + 4H^+ + 4e^- \rightarrow H_2O$ (3.4)

Overall reaction: $2H_2 + O_2 \rightarrow 2H_2O$ (3.5)

The catalyst used in this fuel cell is platinum to enhance the reaction rate. This fuel cell does not require oxygen in pure form as carbon dioxide does not affect cell performance. So, air is used to run fuel cell. Phosphoric acid has long term stability and volatility.

PAFC has high initial cost and uses air as a reactant which is twenty one percent oxygen resulting in low current density. To enhance the current density of this fuel cell, the stack of bipolar plates are used which further increases the initial cost. These fuel cells are mainly expensive due to platinum coating on the electrode. Its typical efficiency is 40-50% and 85% in case of combined heat and power system (CHPS) [49].

3.3 SOLID OXIDE FUEL CELL

Solid oxide fuel cell or SOFC operates at high temperature and has electrolyte made form a metallic oxide solid ceramic. In this fuel cell oxygen is being reduced at cathode while oxidation is reported at anode. Reduction reaction takes place at a high temperature of 1000 C. SOFCs are adopted in power generation system that have capacity in MWs. Heat is a by-product produced by SOFC which is being used to generate electricity by turning turbines. The electrolyte used in this fuel cell is of high density which conducts oxygen ions.

The combined heat and power efficiency of a typical SOFC is 70-80%. These fuel cells are modular, reliable and fuel adaptable. The main issue that limits use of SOFC is its long cooling down and start-up time.

3.4 MOLTEN CARBONATE FUEL CELL

Molten carbonate fuel cells or MCFCs work at high temperature. The electrolyte used in these fuel cells is molten carbonate salt which is suspended in a chemically inert ceramic matrix. The hydrogen electrode serves as the site for reaction between carbonate ions and hydrogen fuel producing carbon dioxide along with electric charge and water. Methane is used as the gas at anode along with water. The reaction produces carbon dioxide, carbon monoxide and hydrogen. In reaction occurring at cathode carbonate ions are formed from the reaction between carbon dioxide and oxygen. Reaction taking place on anode and cathode side of fuel cell are mentioned in Equation 3.6 and 3.7.

Anode: $\mathrm{H_2 + CO_3^{2-} \rightarrow 3H_2 + CO_2 + 2e^-}$ - (3.6)

Cathode: $\frac{1}{2}\ \mathrm{O_2 + CO_2 +\ 2e^- \rightarrow CO_3^{2-}}$ (3.7)

MCFCs are used for coal based power plants and natural gas used in industrial, electrical utility and military application. The main disadvantage of this fuel cell is its high working temperature. Methanol is flammable and toxic hence its storage is also a matter of concern. The advantage of this fuel cell includes low requirement of infrastructure for installation.

3.5 DIRECT METHANOL FUEL CELL

Direct methanol fuel cells or DMFCs are developed version of a PEM fuel cell. It finds application in providing power to portable energy sources and works on low operating temperature. They do not require recharging and are considered as clean renewable source of energy. Methanol is considered as the energy source for a DMFC. The anode and cathode reaction are mentioned in equation 3.8 and 3.9.The overall reaction is mentioned in 3.10.

Anode: $\mathrm{CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2}$ (3.8)

Cathode: $\mathrm{\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O}$ (3.9)

Overall reaction: $\mathrm{CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2}$ (3.10)

The phenomenon of methanol diffusion takes place when methanol travels through the membrane electrode assembly without reacting. It is converted into carbon dioxide on anode side while on cathode side water is formed via oxygen available in air.

Classification of direct methanol fuel cell can be done as passive and active. An active DMFC is highly efficient and reliable comprising of a carbon dioxide separator, methanol feed pump, fuel cell stack, circulation pump, pump controller and drivers. An active direct methanol fuel cell finds application in control of quantities such as concentration, flow rate and temperature. In passive direct methanol fuel cell external process for blowing air and methanol pumping devices are eliminated. Methanol is defused in the anode with an integrated reservoir that works on the concentration gradient between reservoir and anode.

3.6 PROTON EXCHANGE MEMBRANE (PEM) FUEL CELL

PEM electroyser is a device that electrochemically splits water via DC electricity and produces oxygen and hydrogen. In 1800 William Nicholsm and Anthony Carlisle discovered a method by which water can be decomposed into its constituent elements [21]. In the experimental set up, Volta battery was connected with 2 conducting wires and immersed in salt water.

The result of experiment was formation of gas around the wire .The highlight of a PEM electrolyser is that it conducts proton, which are produced at positive electrodes by splitting water. On the positive electrode the liberation of oxygen along with proton produces hydronium ions. When this hydronium ion combine with two electrons on negative electrode hydrogen gas is formed. The most commonly used electrolyte in this fuel cell is based on a perfluorosulfonic acid (PESA) or nafion polymer.

Although nafion is costly but it copes-up with features such as higher energy efficiency and higher current density. PEM has ability of operating at current density up to 3 times as compared to alkaline electrolysers. As PEM electrolyser uses a thinner solid electrolyte it can be lighter and smaller than alkaline electrolysers of same capacity.

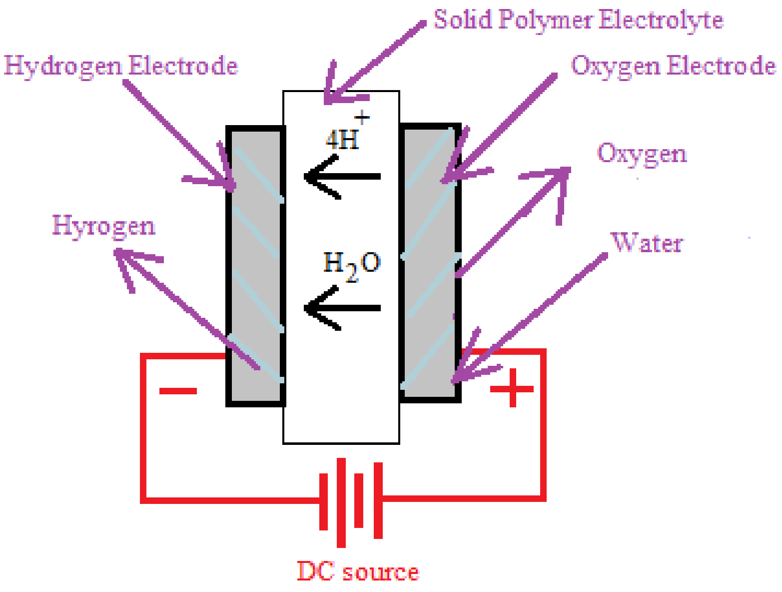


Fig 3.1: Schematic of a PEM electrolyser.

Some other advantages of PEM electroyser include potential to compress hydrogen when unit is under high pressure, it can cope up with transients in electrical power and provide higher safety [22].

It could be clearly seen in Fig 3.1 that water enters from anode and electrochemically splits into hydrogen protons, oxygen gas (or H+ and electrons) when DC electricity is supplied. This H^+ ion forms hydronium ion and travel through solid electrode and emerges at membrane. Electron moves to cathode via electric circuit, where electron and hydrogen ion combine to form hydrogen gas.

The overall reaction in PEM electrolyses is mentioned in Equation 3.11.

$$H_2O + \text{electricity} \rightarrow H_2 + \frac{1}{2}O_2 \tag{3.11}$$

The chemical reaction on hydrogen side is represented in Equation 3.12.

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{3.12}$$

PEM electrolyser overall reaction is mention in Equation 3.13.

$$2H_2O + \text{electricity} \rightarrow 4H^+ + O_2 + 4e^- \tag{3.13}$$

PEM fuel cell is one of the kinds of fuel cell that operates at efficiency of forty to sixty percent and working temperature of fifty to hundred degree Celsius [21]. In these types of fuel cell the cathode electrode is supplied with oxygen gas supplied where as anode is supplied with hydrogen gas. At anode hydrogen split in electron and proton (in Equation 3.14).

$$H_2 \rightarrow 2H^+ + 2e^- \tag{3.14}$$

Proton travels via membrane to oxygen electrode while electron passes by external load to cathode producing electricity. The overall reaction on cathode is represented by the Equation

3.15.

$$2H^{+} + 2e^{-} + O_2 \rightarrow H_2O \quad (3.15)$$

Advantages of this fuel cell include quick start up and low operating temperature. These advantages are used in car manufacturing. Some of the manufacturers are Toyota (FCHV-adv), General Motors (Chevrolet Equinox), Nissan (Xterra FCV), Honda (FCX Clarity) Hyundai-Kia (Kia Borrego SUV) and Volkswagen (Passat Lingyu) [23].

3.7 COMPARISON BETWEEN DIFFERENT FUEL CELL

Fuel cell finds application in according to its type. Fuel cells can produce power ranging from 1 to 10MW and hence can be used in any power application. They are use in devices of small power range such as laptops and phones, to medium power application such as domestic and military application. In case of large scale power applications fuel cell finds example in grid and power system. Proton exchange membrane fuel cells are most viable in portable power, backup power and vehicle transportation- as they can operate at room temperature. The efficiency of PEM fuel cell is 58 % and when used in combination with heat and power the efficiency is 70-90%. The other advantage includes low start-up time and high current density and presence of solid electrolyte reduces corrosion. Alkaline fuel cells have highest efficiency of 60%. The high operating temperature of 90-100°C makes them viable for space and military application. Solid oxide fuel cell and molten carbonate fuel cell work at very high temperature of 600°C and above. Application of such fuel cell is in auxiliary power and large distribution generation.

CHAPTER 4

DESIGN AND WORKING OF EXPERIMENTAL SETUP

Proton battery has the capability to work under E-mode and FC–mode. In E–mode water at anode is split into hydrogen and oxygen. The hydronium ions travel to cathode via membrane, where H^+ (proton) get stored in the form of weak chemical bonds. In FC-mode proton stored in storage material comes out under the influence of opposite potential. Protons travel back to anode side where it combines with electron and oxygen to re-form water under influence of oxygen side catalyst. The proton battery used in the current thesis has input water that continuously split into protons which pass the membrane into storage, hence device is termed as ‘proton battery’ (PB). The PB design and construction has been discussed below:

4.1 BI POLAR END PLATES OF PROTON BATTERY

The bi polar end plates of proton battery are made up of metals such as titanium, stainless steel, or metallic alloys. The bi-polar end plates should have desired properties such as high electrical conductivity, high thermal conductivity, low permeability to gas, high resistance to corrosion, low mass and high mechanical strength. Most widely used material of research activity is stainless steel as they have high thermal conductivity, low cost, high electrical conductivity, ease of manufacturing and good mechanical properties. Graphite is also generally used for end plates manufacturing as it has resistance to corrosion, possesses required thermal and mechanical properties, light weight [25]. Graphite is expensive and gets attacked by chemical in charging process.

Hence stainless steel (SS316) has been used for proton battery construction. The bi-polar end plates provide path for flow of gases (hydrogen and oxygen) via flow channels and header. The active area of electrode, membrane electrode assembly and gas diffusion layer is 25 mm x 25 mm. The end plates vary in thickness but have same dimension ie.72 x 84 mm^2. The oxygen side end plate has thickness of 7mm whereas hydrogen side is 9mm thick. The hydrogen side end plate holds electrode and gas diffusion layer inside it. Other specifications of end plates are mentioned in Table 4.1. The endplates are shown in Fig 4.1 represents front view of bi-polar end plates and flow channels. In order to accommodate the electrode inside proton battery, the hydrogen side end plate is 2 mm deeper than oxygen side. The carbon cloth and membrane electrode assembly are placed on both side of electrode. The flow channels allow flow of gases over the electrode and enable adsorption of gases.

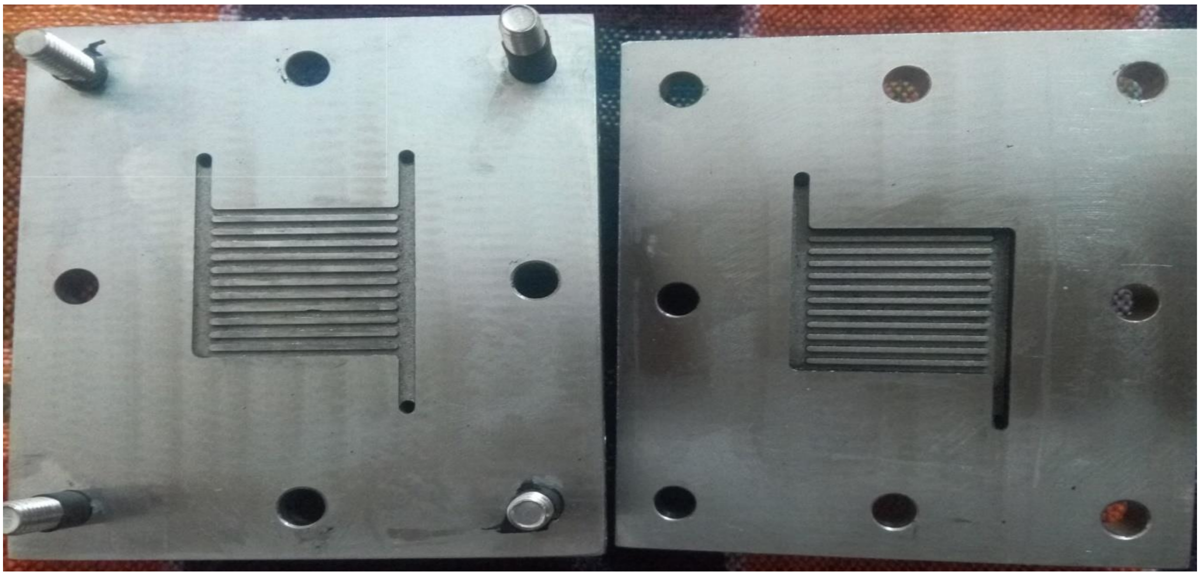


Fig 4.1: Oxygen and hydrogen side end plates.

Table 4.1: Bi polar end plates specifications.

Specification	Oxygen end-plate	Hydrogen end-plate
	Dimensions (mm)	Dimensions (mm)
Active area	25 ×25	25 ×25
Ribs width	1.0	1.0
Cell area	72 ×84	72 ×84
Thickness	7	9
Channel depth	1.0	1.0
No. of channels	11	11

4.2 FABRICATION OF ELECTRODE

As per literature carbon nano tubes are potential candidate for the storage of hydrogen. The carbon nano tubes can be single walled or multi walled. In this project 4-7 walled multi walled carbon nano tubes are used for the electrode formation. Multi walled carbon nano tubes (MWCNT) were purchased form Platonic Nanotech Private Limited. Fig 4.2 and 4.3 shows MWCNT pictorial description purchased from Plaonic Nano Private Limited. The specifications of MWCNT are in the Table 4.2:

Table 4.2: Specification of MWCNT used for electrode.

Specification	Unit	Standard
Diameter	nm	10 to 15 nm
Length	µm	2- 10 µm
Ash content	%	<2 %
Purity	%	>97 %

Specific surface Area	m^2/ g	250 to 270 m^2/ g
Bulk Density	g/ cm^3	0.06 to 0. g/ cm^3

Fig 4.2: Multi walled carbon nano tubes.

Fig 4.3: Multi walled carbon nano tubes from Platonic Nano Private Limited.

Weighed quantity (0.53g) of MWCNT and egg white (19.53%) used as binder to prepare electrode. Fig 4.4 and 4.5 shows the container and physical appearance of MWCNT. With the help of 3D printer the mould shown in Fig 4.4 for electrode has been prepared. The fabrication of mould was done in mechanical department of Thapar Institute of Engineering and Technology. The dimensions of slot in mould was 25x25 mm^2, same as that of elecrtode. The electrode formation was carried out by mixing weighed quantity of carbon nano tube and egg white. The electrode was sun dried for two days and filled from edges to smoothen the edges. One of the specimens used as electrode has been shown in Fig 4.5.

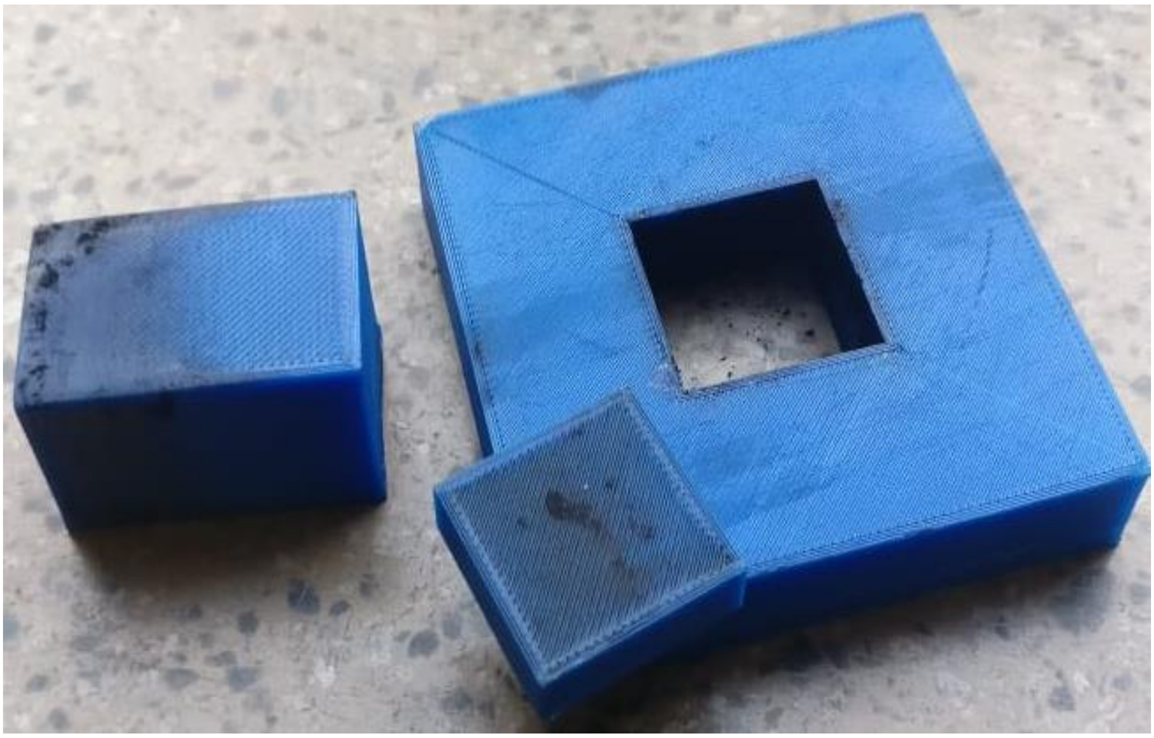


Fig 4.4: 3D mould for electrode prepared at MED, TIET Patiala.

Fig 4.5: Mutli walled carbon nano tube electrode.

4.3 MEMBRANE ELECTRODE ASSEMBLY

Membrane electrode assembly (MEA) consists of proton exchange membrane and catalyst for oxygen and hydrogen side**.** The main purpose of membrane in MEA is to help in the flow of proton form anode to cathode side vice versa. The presence of catalyst helps in initiating the breakdown of water at the anode side during E-mode and release of electron from electrode during FC-mode. In this project the MEA is reversible type that is it can work in E-mode as well as FC-mode.

The catalyst loading on oxygen side is iridium and ruthenium oxide (Ir and RuOx) and platinum black (Pt_{bl}) whereas for hydrogen side the loading is of platinum black. The activated area of MEA is 2.5 x 2.5 mm^2 which is equal to size of electrode. The loading on both the side is 2mg/cm^2 while nafion concentration is 25%. Fig 4.6 shows snapshot of MEA facing Anode side.

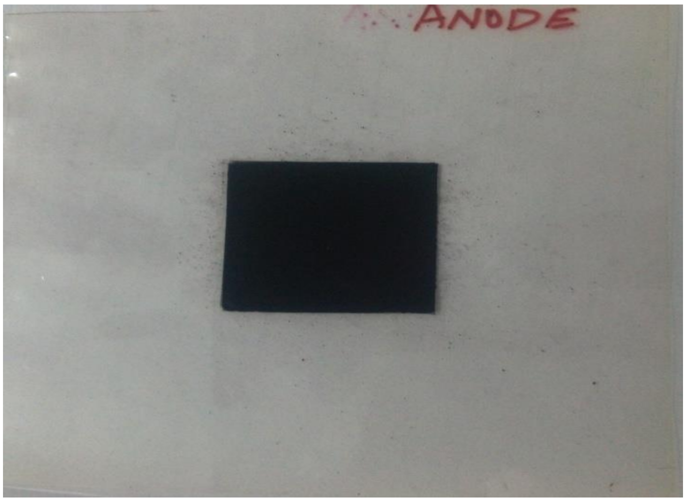


Fig 4.6: Membrane electrode assembly used in proton battery.

4.4 GAS DIFFUSION LAYER

Gas diffusion layer (GDL) is a important part of proton battery that is used on either side of MEA. The GDL is generally consists of porous material containing carbon fiber bunch woven together. The some of the function of GDL includes: providing MEA mechanical support, allowing diffusion of gas into and out of active area and protecting catalyst from erosion and corrosion. The main purpose of GDL is to provide conducting path between catalyst and end plates of proton battery. In this thesis carbon cloth is used as gas diffusion layer on anode and cathode side. The active area of carbon cloth is 2.5 x 2.5 cm^2 same as that of electrode and MEA. Fig 4.7 shows the carbon cloth / GDL used on oxygen and hydrogen side.

Fig 4.7: Gas diffusion layer or carbon cloth.

4.5 GAS COLLECTION CYLINDERS

To measure the volume of gases collected two gas cylinders are used for hydrogen and oxygen side. The gas cylinders are made leak proof by sealing them with plaster of Paris and silicone gel. In E-mode hydrogen and oxygen gas enter these gas collection cylinder by upward displacement of water. The gases under pressure cause water displacement and get collected in sealed chamber. Water and oxygen are present in the same chamber at same pressure, having two different cylinder will make measurement of oxygen and water getting collected in both cylinder difficult. Therefore one cylinder with two outlets is used: one for oxygen storage and other for water inlet/ outlet to the proton battery as shown in Fig 4.8. The hydrogen cylinder has been used one outlet which is used to collect gas under via water displacement. Stop cock are used with the pipes of cylinder in order to safely remove the cylinders from the assembly and store gases.

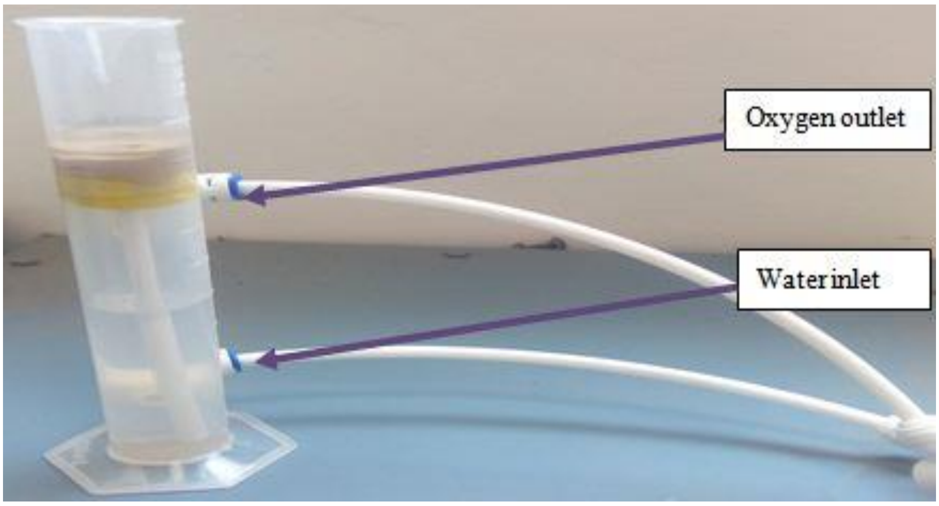


Fig 4.8: Gas collection cylinder for oxygen side.

4.6 PROTON BATTERY ASSEMBLY

Proton battery is assembled in by placing gas diffusion layer over the by polar end plate of oxygen side as shown in Fig 4.11. The gas diffusion layer used in this thesis is carbon cloth for both hydrogen and oxygen side. Above gas diffusion layer rubber gasket is placed which prevents gas and water leakage. Membrane electrode assembly with catalyst loading of platinum black and iridium is placed facing towards oxygen side end plate whereas the other end with catalyst loading of platinum black is placed facing towards hydrogen side end plate.

The porous MWCNT electrode is placed over the membrane electrode assembly aligned with the slot in hydrogen side end plate. The rubber gasket for hydrogen side end plate is placed to cover the area external to flow channels. Gas diffusion layer of hydrogen side is placed inside the 2mm slot of hydrogen end plate. The whole assembly is tighten with nut and bolt assembly and silicone gel applied between endplates and rubber gaskets to avoid any voids.

If the placement of catalyst layer in membrane electrode assembly is not according to the oxygen and hydrogen side, evolution of gas is not as desired. On reverse application of membrane electrode assembly the cut-in voltage levels is very high, in order of 20-30V. Other issues such as irregular ratio of collected gases, damage to membrane electrode assembly occur. So it is highly recommended to crosscheck the positioning of membrane electrode assembly with respect to hydrogen and oxygen end plates. Fig 4.9 shows schematic diagram of proton battery assembly.

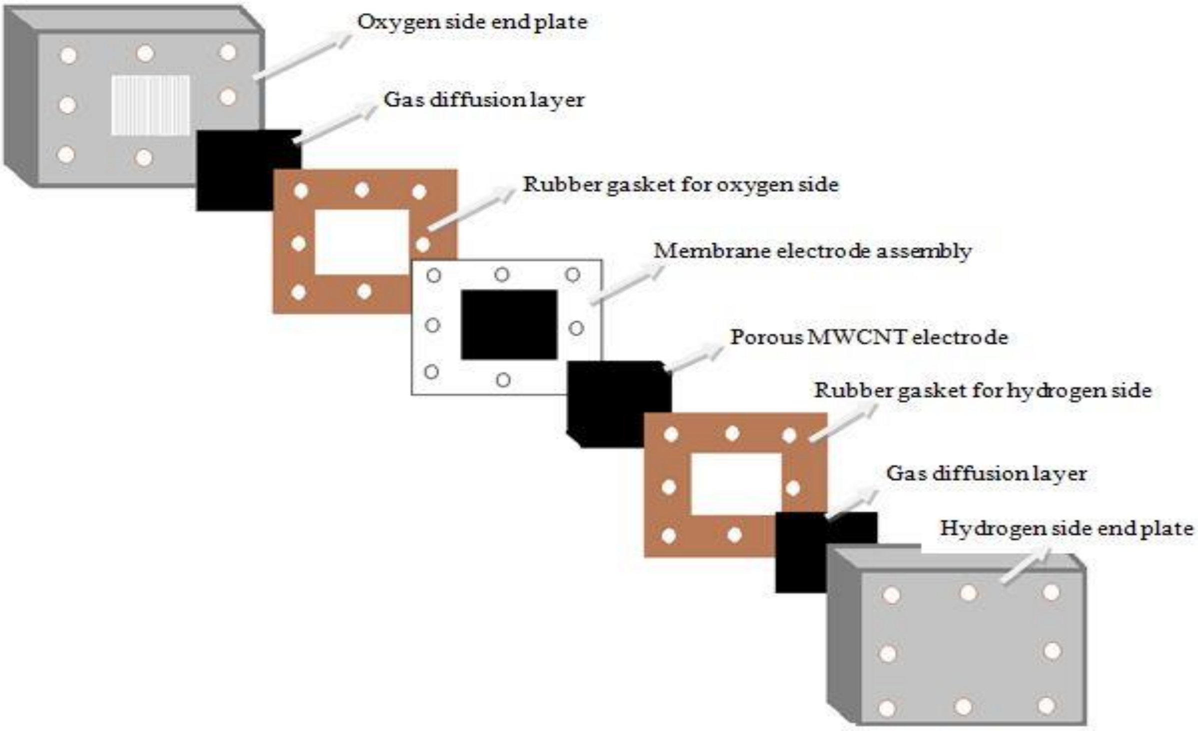


Fig 4.9: Schematic diagram of proton battery assembly

4.7 EXPERIMENTAL SETUP WORKING

Experiment being carried out on the proton battery in two stages: charging and discharging. The proton battery has been tested for number of charging and discharging cycle in order to find its capacity to store and retrieve charge. The experimental setup of proton battery has been shown in Fig 4.10. The variable DC source is used to supply variable voltage with constant variation of 0.2V. Gas collection cylinders are used to collect oxygen and hydrogen from anode and cathode side. Mutlimeters provides the function of voltage and current measurement during charging and discharging process.

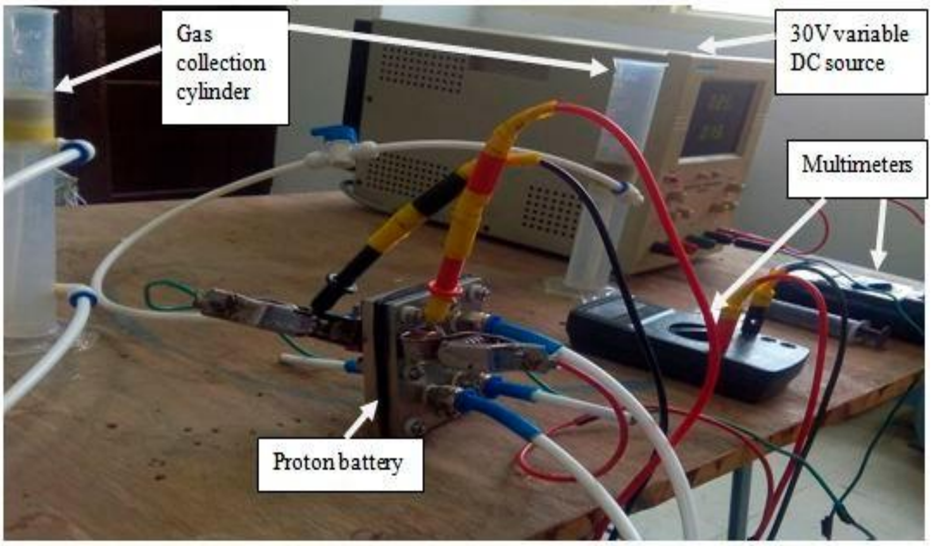


Fig 4.10 Experimental setup of proton battery

4.7.1 Process of Charging or E-Mode

For E-mode, the proton battery is connected to a variable voltage source of 30V which is able to supply current up to 3A. The voltage of proton battery is increased to the level of cut-in voltage i.e. the voltage at which hydrogen gas is produced. The cut-in voltage is set as benchmark for dissociation of water in proton battery. The dissociation of water leads to formation of proton and oxygen gas. The proton passes through membrane electrode assembly towards the hydrogen side. On hydrogen side proton gets adsorbed in porous MWCNT in the form of chemisorption (weak chemical bond) or physisiortion (weak Van der Waals forces).

The charging process is continued by raising DC supply potential for 0.1V for every half cycle till rapid evolution of hydrogen gas is observed. The rapid evolution of hydrogen gas indicates that the storage area inside the electrode has been filled and no more hydrogen ion can absorbed via physisorption or chemisorption. The charging mode or E-mode has been shown in Fig 4.11. During this mode oxygen gas is being collected and water is used from the collection cylinder.

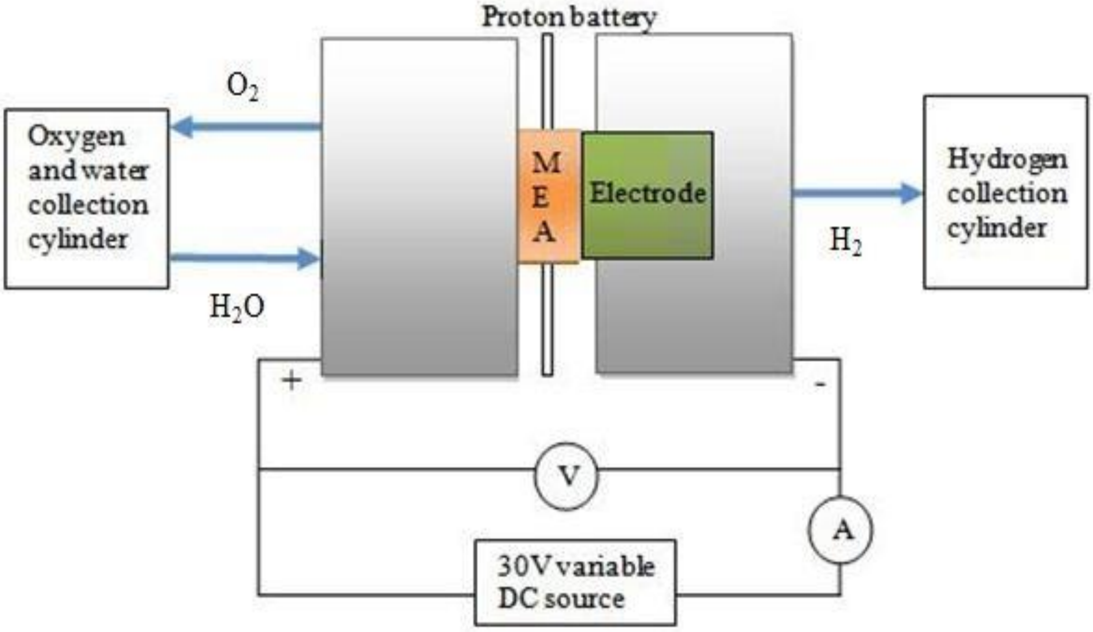


Fig 4.11 Schematic diagram of charging or E-mode of proton battery.

4.7.2 Process of Discharging or FC-Mode

During discharging or FC-mode, the proton battery is connected across resistive load to draw electric current. During discharging the hydrogen reduction reaction take place, in which the platinum black catalyst breaks the weak chemical bond forming hydrogen ion and electron. Hydrogen ion passes through the membrane electrode assembly to the oxygen side, while electron passes through the electrical wire. Oxygen and hydrogen ion interact in the presence of catalyst platinum and iridium to form water. The schematic diagram of the circuit has been shown in Fig 4.12.

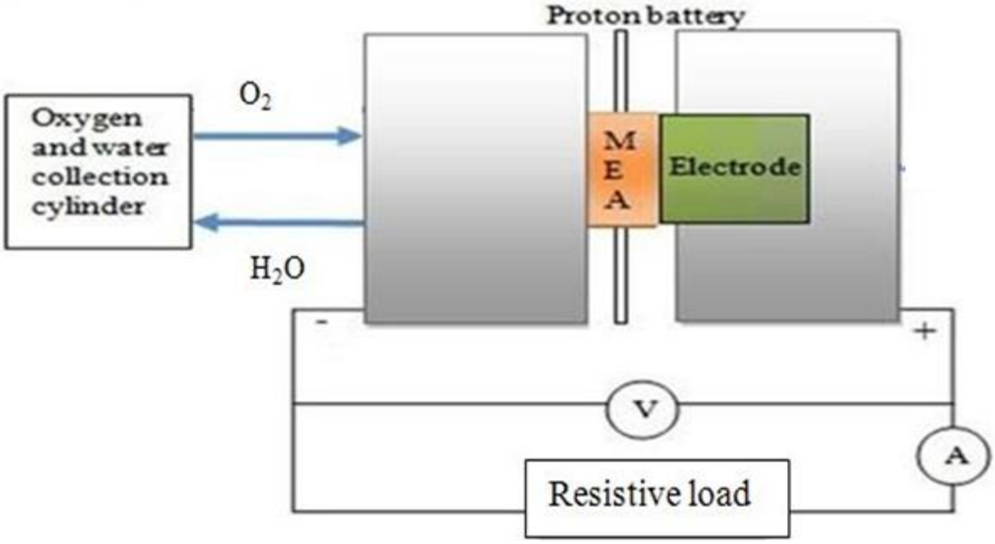


Fig 4.12 Schematic diagram of discharging mode of proton battery.

During cyclic testing of battery to test the life cycle, multiple charging and discharging cycles were conducted. The charging and discharging process for all the cycles remains same as described earlier for single cycle. The cyclic testing is determines the charge that can be stored and retrieved during different cycles.

CHAPTER 5

RESULTS AND DISCUSSION

Various components of the fabricate proton battery were subjected to microscopic examination using Scanning Electron Microscopy (SEM) before assembling the setup. Both sides of the membrane electrode assembly, carbon cloth and porous MWCNT electrode were examined and images were captured. The mention SEM and EDS tests were performed at the sophisticated analytical instruments laboratory (SAI Lab) located in Thapar Institute of Engineering and Technology campus in Patiala, Punjab, India.

5.1 TEST RESULTS OF EDS AND SEM

Energy-dispersive X-ray spectroscopy (EDS) is a method used for chemical characterization or analytical analysis of the sample under consideration. During EDS there is an interaction of sample with X-ray and each atomic structure gives unique electromagnetic emission spectrum. In order to get X ray emission high energy beam of electrons or proton is focused on the sample. EDS help in determining chemical composition of a specimen. The EDS spectrum obtained for nafion membrane in the used membrane electrode assembly (MEA) is Table 5.1.

Table 5.1: Components of nafion membrane in the used membrane electrode assembly.

Element	Weight%	Atomic%
C K	13.07	19.69
O K	23.05	26.07
F K	44.72	42.59
Al K	4.01	2.69
Si K	10.39	6.69
S K	0.63	0.36
K K	4.12	1.91

Nafion is perflurosuphonic acid which is a polymer with main constituents such as carbon and oxygen. The spectrum (shown in Fig 5.1) of EDS shows maximum presence of florine with 44.72% followed by oxygen with a percentage of 23.05%. SEM test was performed on nafion in order to determine the presence of long chain perflurosuponic acid polymer presence. Nafion act as proton exchange membrane and has coating on both the sides. The coating on anode is of platinum black with iridium whereas in the cathode side the coating is of platinum black.

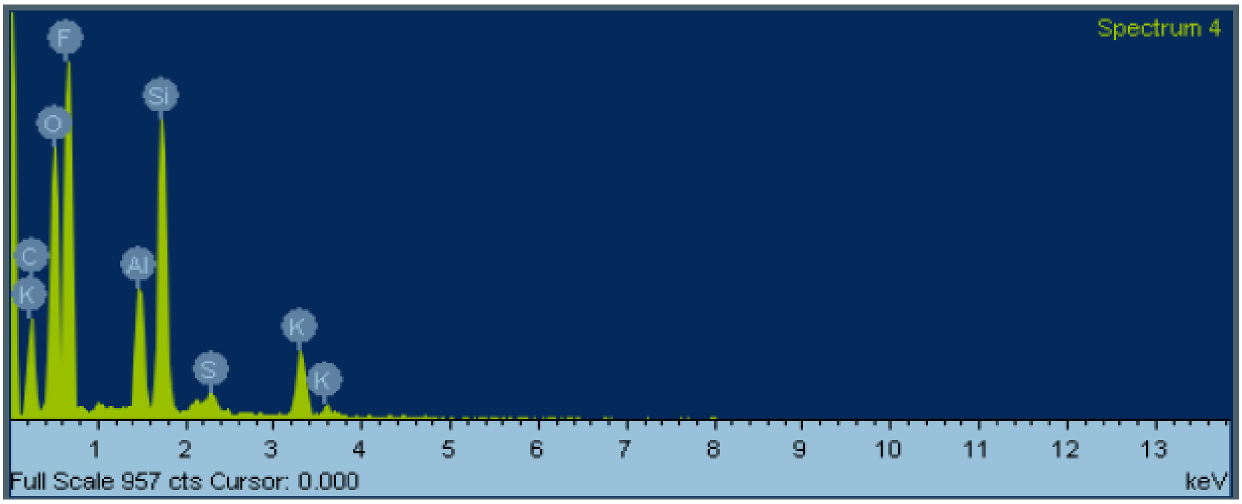


Fig 5.1: EDS spectrum of nafion.

Long chain of perfluorosulfonic acid can be seen in the SEM image of nafion. The test was conducted to ensure the presence of long chain acid in the structure of solid electrolyte that favors proton conduction.

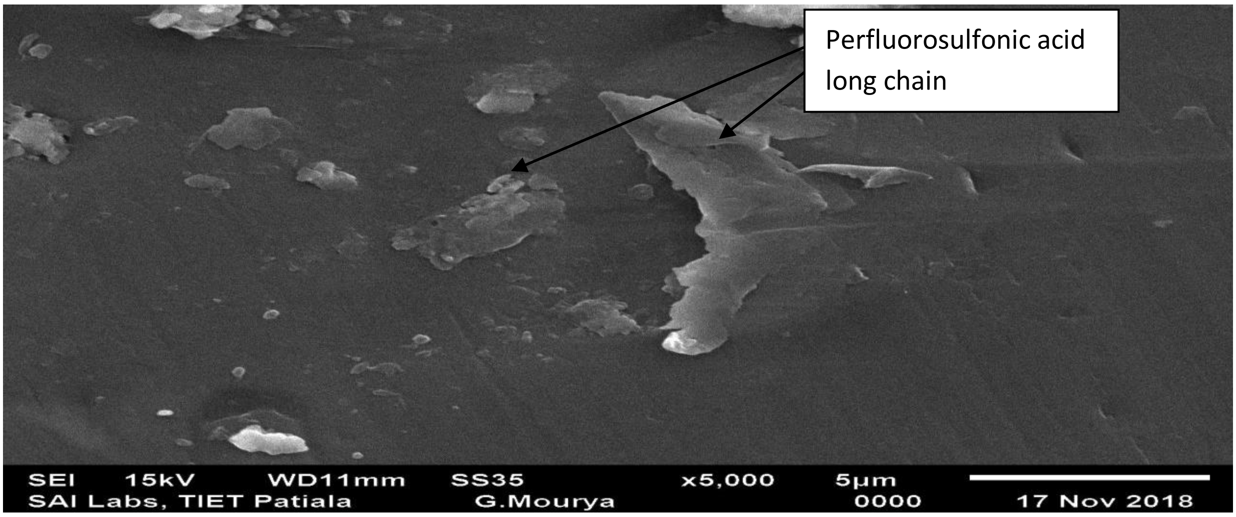


Fig 5.2: SEM image for nafion membrane.

The composition of a porous mutli-walled carbon nanotube (MWCNT) electrode was also checked via EDS. The electrode was fabricated using a commercial MWCNT powder and 19.53 wt% of egg white as binder. The EDS result reported has maximum amount of carbon 84.15% (reported in Table 5.2 and Fig 5.3), which is more than MWCNT carbon percentage due to addiction of carbon content of egg white.

Table 5.2: Components of MWCNT electrode.

Element	Weight%	Atomic%
C K	84.16	88.54
O K	13.28	10.49

Na K	0.41	0.23
Mg K	0.30	0.16
Al K	0.71	0.08
Si K	0.05	0.02
S K	0.43	0.17
Cl K	0.38	0.14
Fe K	0.82	0.19

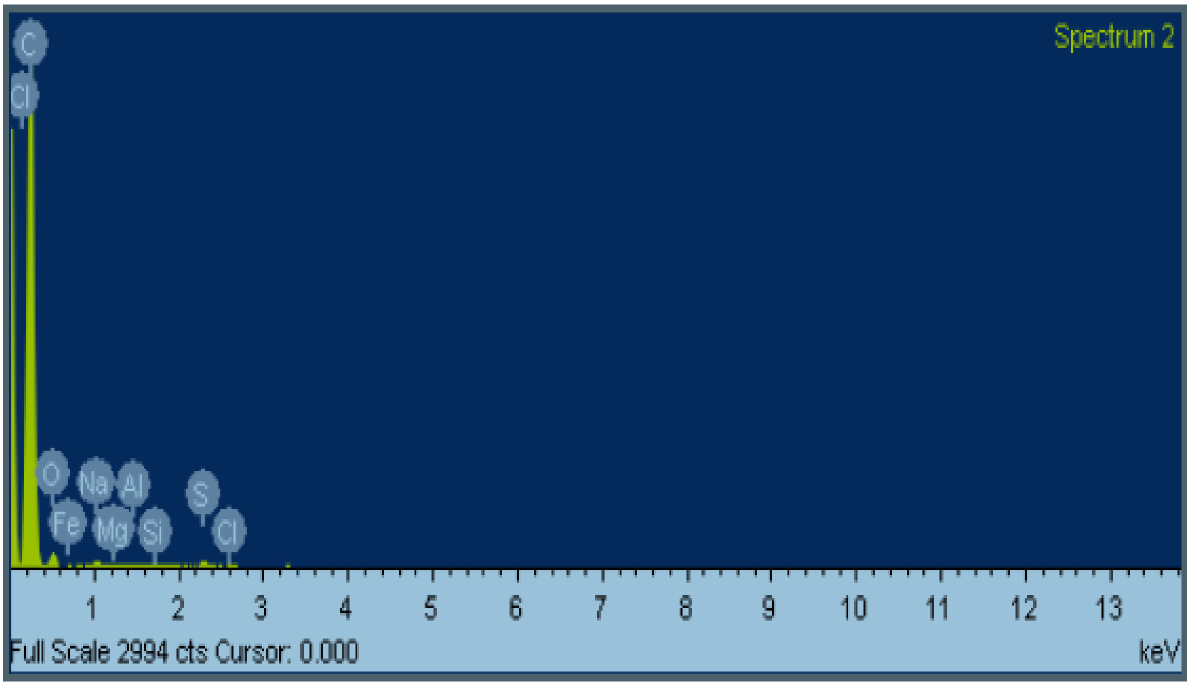


Fig 5.3: EDS spectrum of MWCNT electrode.

To understand the structural morphology of the fabricate MWCNT sample electrode Scanning electron microscope (SEM) was used. SEM produces sample images by focusing the beam of electron on the sample surface. The specimen was observed under the microscope in high vacuum, low vacuum and wet conditions. The presence of pores can be seen in Fig 5.4. These pores are considered as active sites for chemical and physical adsorption of hydrogen ions in the MWCNT electrode.

The major advantage of using MWCNT with egg binder is that the pore size distribution is even as all the pores via macropores, mesopores, micropores and ultramicropores plays significant role in hydrogen ion transport. Egg contains ninety percent of water that gets evaporated in fabrication of electrode leaving pores of various sizes. The SEM test ascertains various size of pores presence in the electrode. The black patches present in the Fig 5.4 represent the pores whereas the grey globules represent MWCNT along with egg white.

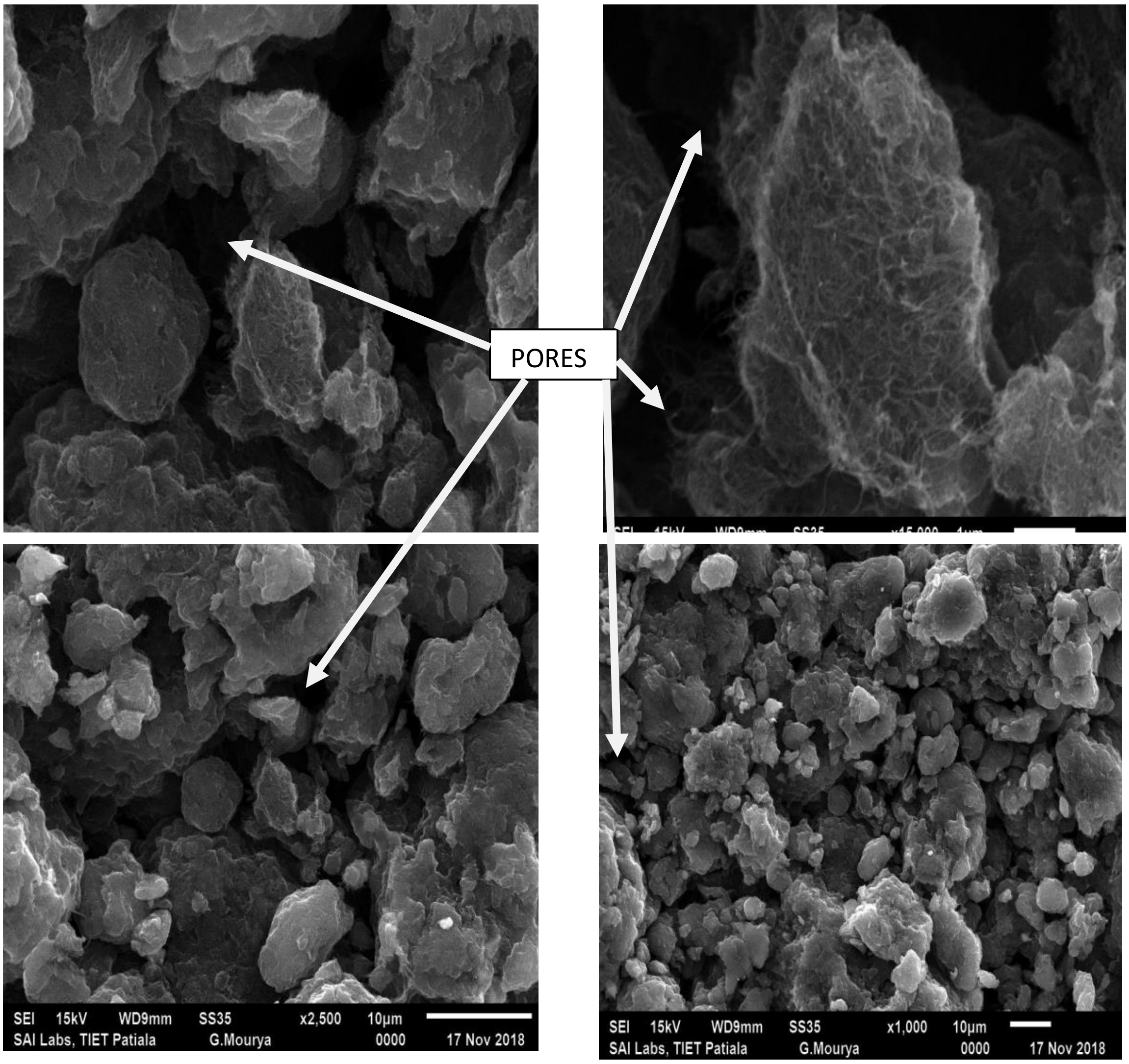


Fig 5.4: SEM test images for MWCNT electrode.

5.2 MWCNT POROUS ELECTRODE TESTING FOR HYDROGEN STORAGE AND CYCLIC TESTING.

In the first phase of testing the hydrogen storage capacity of MWCNT electrode was tested in charging mode. This testing was done to check electrochemical hydrogen storage in charging process. In the second phase of experimentation, the life cycle of electrode was determined by cyclic charging and discharging of proton battery.

5.2.1 Testing of MWCNT Electrode for Hydrogen Storage Capacity

The proton battery (PB) with an integrated MWCNT electrode was setup for testing by connecting the gas collection cylinder both to oxygen (anode) and hydrogen (cathode) side. The inlet of the PB was connected to a water reservoir though an air-tight connector. The testing was set-up to run PB first in electrolyer mode (E-mode) or charging and later in fuel cell mode (FC-mode) or discharging. In E-mode a portable DC power supply was used to apply potential across the cell. The charging was done by increasing 0.1V in an interval of half hour. The current passing through the battery was recorded and has been mention in Fig 5.5. The maximum rise in current was observed to be 230mA at 2.5V resulting in rapid evolution of hydrogen gas indicating that the storage is full and any further charging would liberate hydrogen gas only which was not desired. The charging process was stopped thereafter at 2.6V. The completion of charging process indicates that the storage was full and hydronium ion do not enter the porous electrode. Initially sharp dip in the Fig 5.5 was observed as electrical potential was mainly utilized to disassociate water. The rise in current took place when electrical potential was sufficient to break the molecular bonds of water.

During the process of E-mode water breaks down in the presence of electrical potential forming ions and electron as represented in Equation 5.1. The hydrogen ions pass from oxygen side to hydrogen side through membrane electrode assembly. On reaching cathode, hydrogen ions and electron combine with electrode material forming weak chemical bond and acting as stable atom. Equation 5.2 represents the chemisorptions process taking place on cathode.

$$H_2O + \text{electricity} \rightarrow H^+ + \frac{1}{2}O_2 + 2e^- \qquad (5.1)$$

$$H^+ + e^- + M \rightarrow M - H \qquad (5.2)$$

where M is host material.

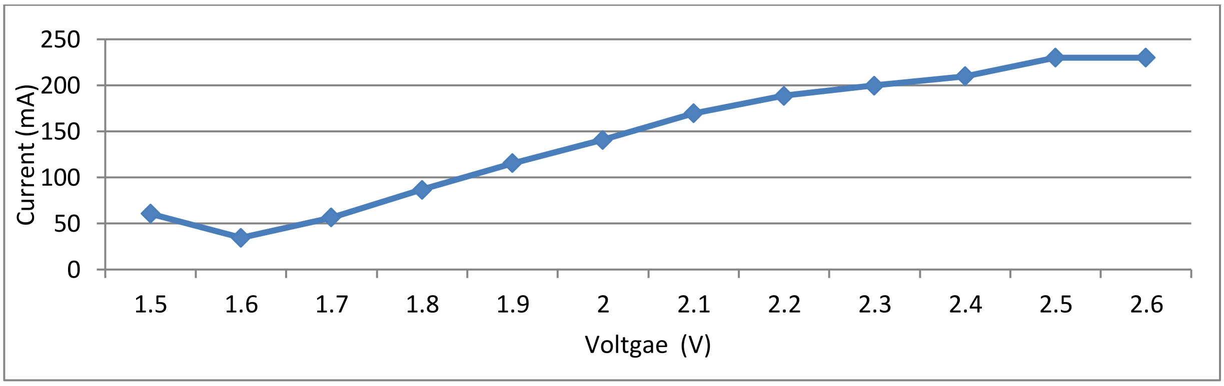


Fig 5.5. Graph representing current and voltage relation while charging or electrolyser mode of proton battery.

The potential was increased after specified time interval that lead to increment in current as well as hydrogen ions. There was no hydrogen gas generation observed in the gas collection cylinder for the first 1.5hrs. Oxygen production started at the cut- in voltage i.e. 1.5V. It can be stated that hydrogen produced in 1.5hrs got adsorbed in the porous MWCNT electrode giving no visible sign of hydrogen generation. Hydrogen generation during discharging is shown in Fig 5.6. From the figure it can be observed that the hydrogen gas generation increase with increase in time.

Oxygen production was noticed at cut-in voltage i.e. 1.5V as shown in Fig.5.7. The oxygen produced during charging was collected in a gas collection cylinder and later used in discharging. The production of oxygen increases with the rise in applied voltage. As per

Faraday's law (Equation 5.3) it can be stated that the production of oxygen gas increases with increase in the current.

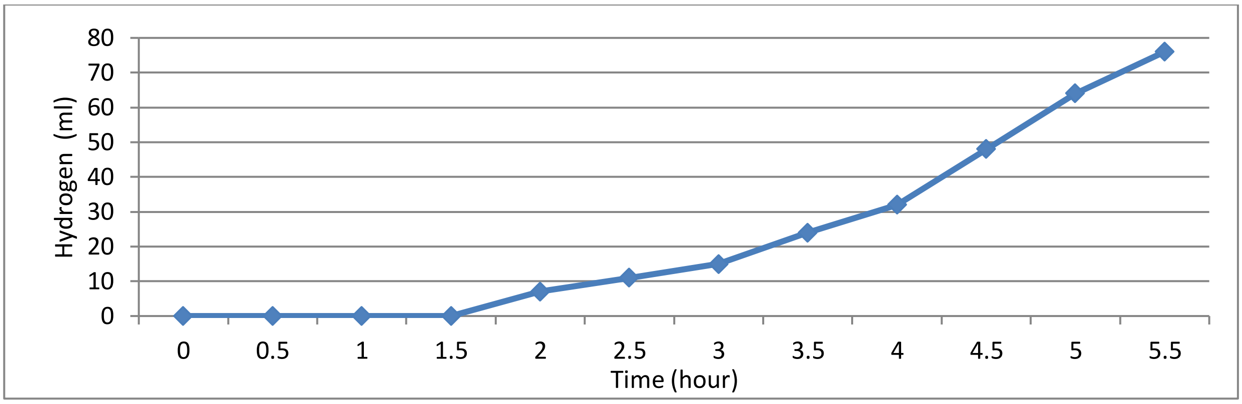


Fig 5.6. Graph representing relation between hydrogen gas produced and time during charging of proton battery.

The oxygen ions produced in the charging mode combines together in the presence of catalyst forming oxygen gas and releasing electron.

$$M_o = \frac{I * t}{4F * 1000} * \frac{R.T}{P} \tag{5.3}$$

where ,

M_O → mass of oxygen generated in Kg.

R → gas constant = 8.314 J/mol.K.

t → time in seconds.

T → ambient temperature in Kelvin.

I → current in amperes.

F → faraday's constant = 96485 J per volt gram equivalent.

P → atmospheric pressure in kilo Pascals.

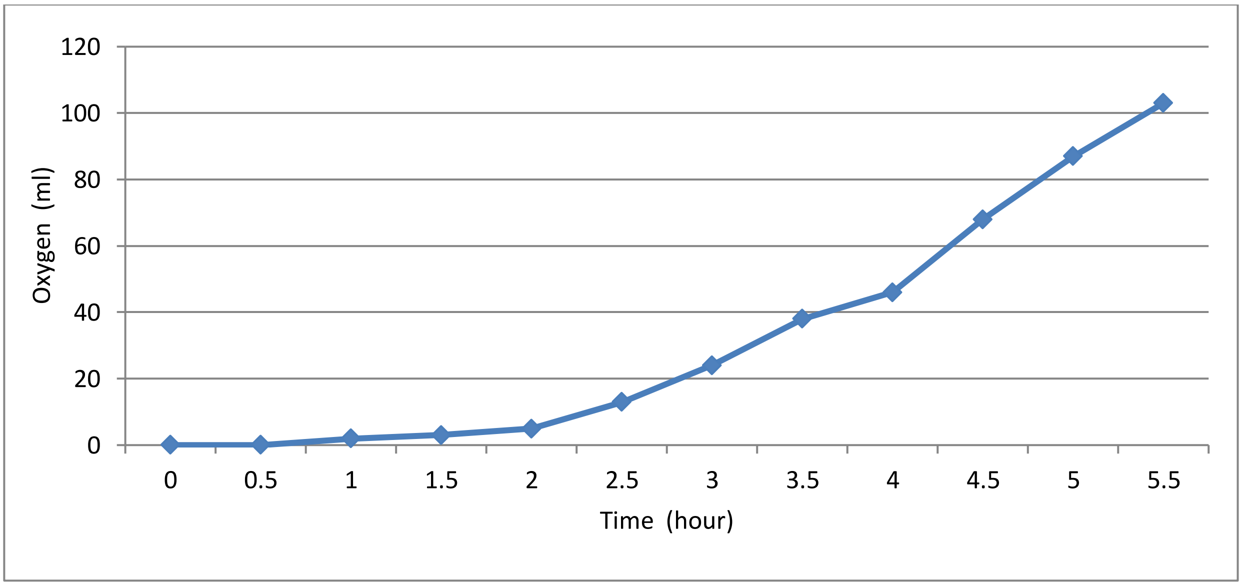


Fig. 5.7. Graph between oxygen gas produced with respect to time for charging process in proton battery.

The amount of hydrogen produced during the process of charging can be calculated with the help of Faraday's law given in Equation 5.4.

$$M = \frac{I * t}{F * 1000} \qquad (5.4)$$

where,

M → theoretical mass of hydrogen generated in kg.

t → discharge time in sec.

F → Faraday's constant (96485 C mol^{-1}).

I → discharge current in mA.

For calculating the mass of hydrogen stored in porous MWCNT equation 5.5 was used. The mass of hydrogen produced theoretically using equation 5.4 was subtracted from practically produced hydrogen to determine the amount of hydrogen stored in electrode. The calculated mass of hydrogen was divided by sum of hydrogen stored in electrode and mass of carbon as per Equation 5.5.

$$H_c\% = \frac{H}{H + C} \qquad (5.5)$$

where,

H → mass of hydrogen stored in MWCNT.

H_C → weight percent of hydrogen stored in MWCNT.

C → mass of MWCNT used in electrode.

Fig 5.8 represents the variation of mass percent of hydrogen with respect to voltage during charging of proton battery.

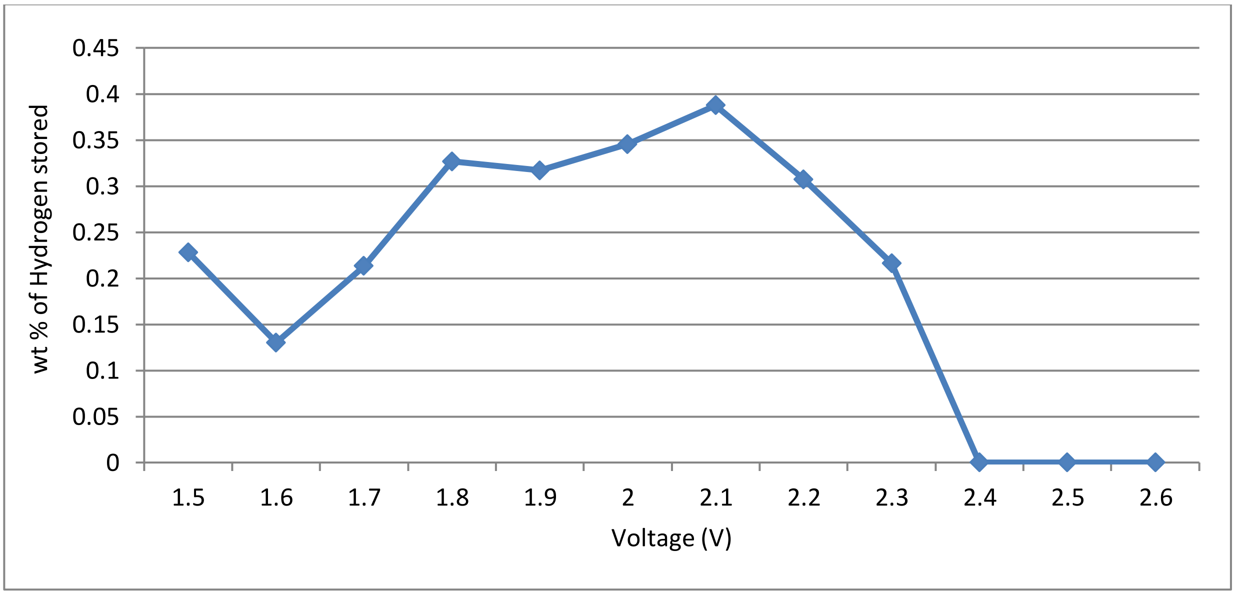


Fig. 5.8. Graph representing relation of hydrogen wt% and voltage during electrolysis or charging mode of proton battery.

The electrochemical storage of hydrogen in MWCNT was performed at low current to discourage hydrogen gas generation. Fig 5.9 represents the relation between current and hydrogen stored during charging process.

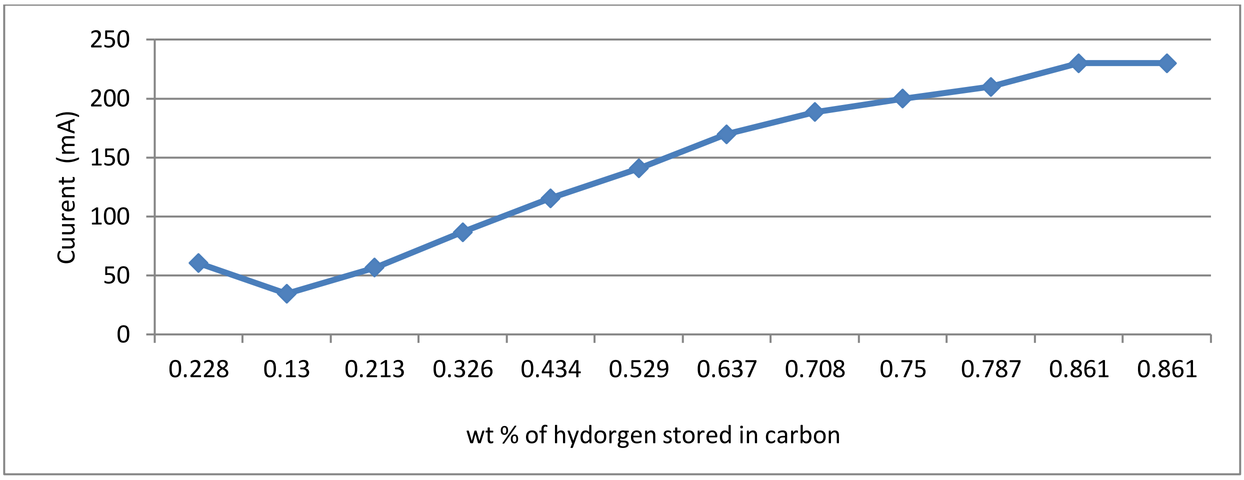


Fig. 5.9. Graph showing relation between current and wt% of hydrogen stored in carbon during charging of proton battery.

The relation between hydrogen wt% stored in MWCNT for intervals of half hour is shown in Fig 5.10. During charging it was observed that a maximum of 0.387wt% was stored after three hours of electrolysis. The storage was reduced after three hours due to filled storage in MWCNT.

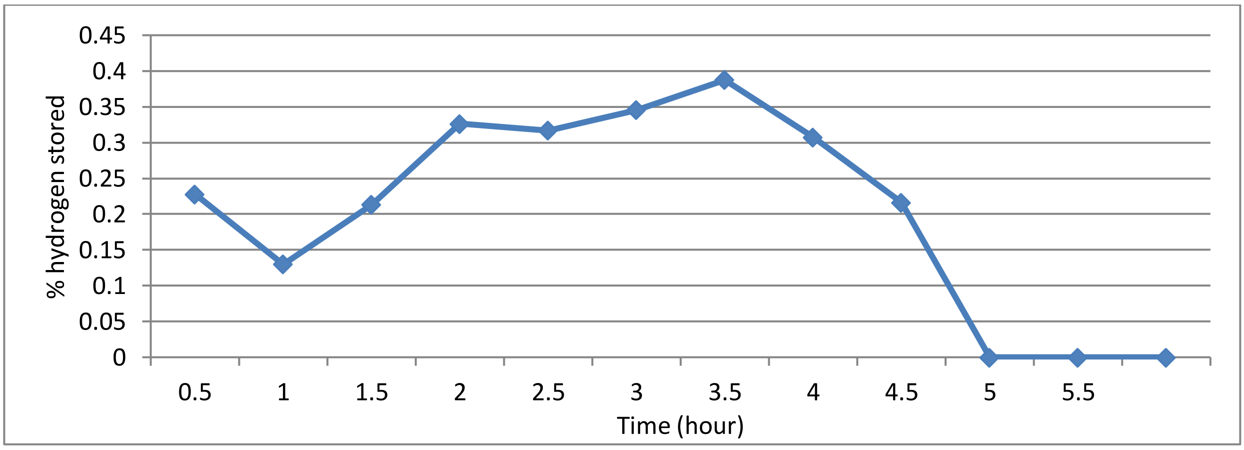
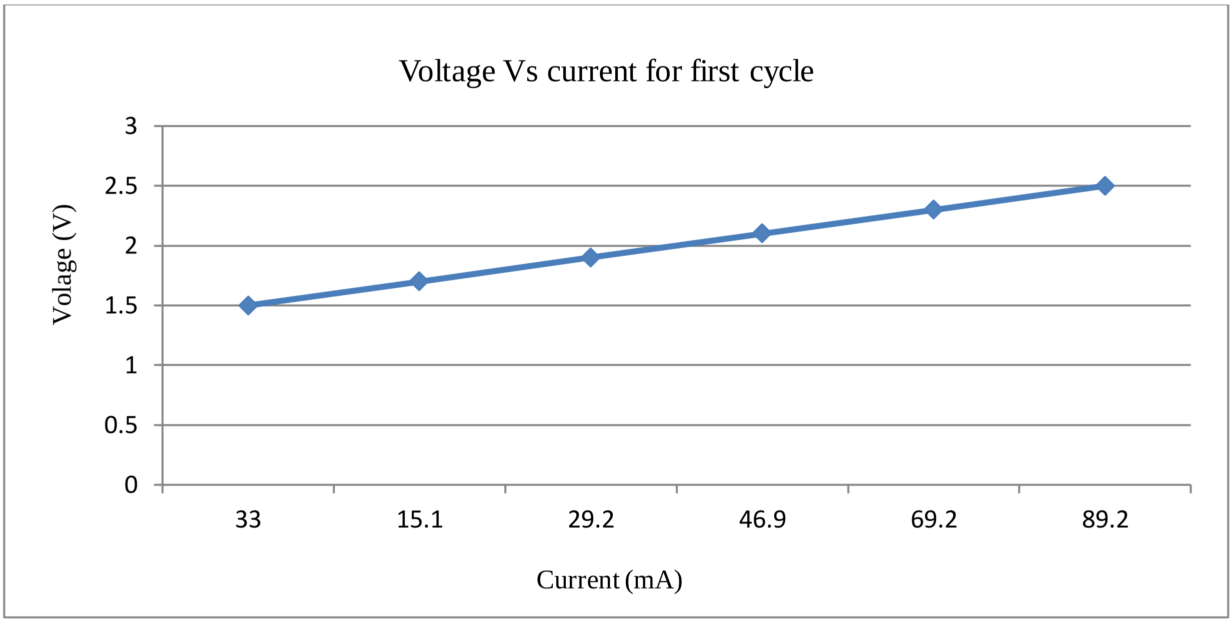


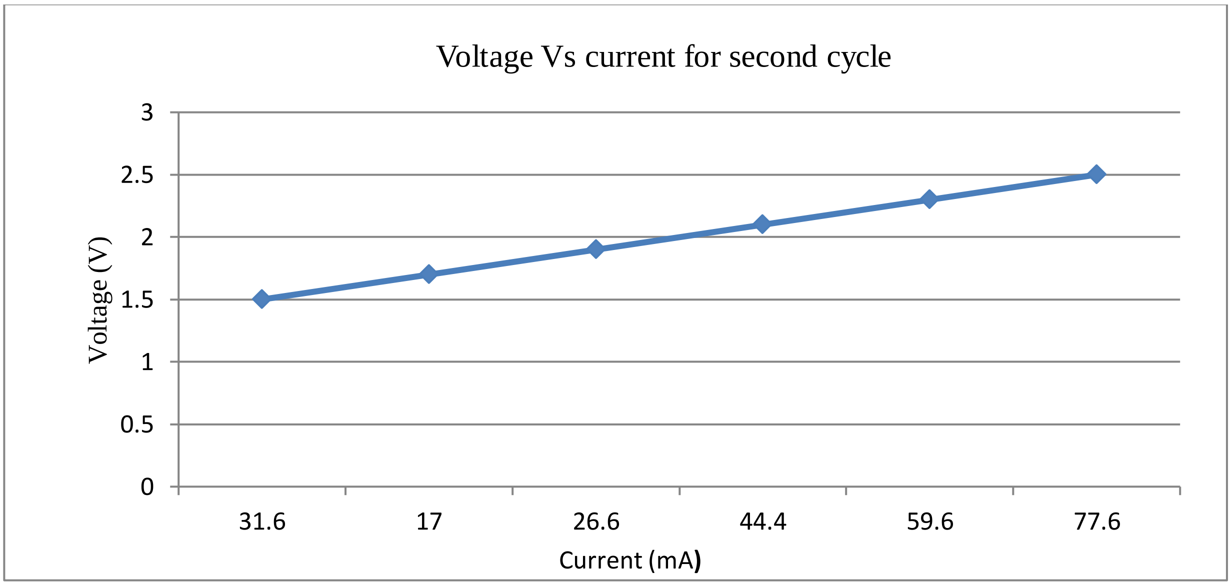
Fig. 5.10. Graph representing relation of wt% of hydrogen stored with time in MWCNT during process of proton battery charging.

5.2.2 Cyclic Testing of Proton Battery

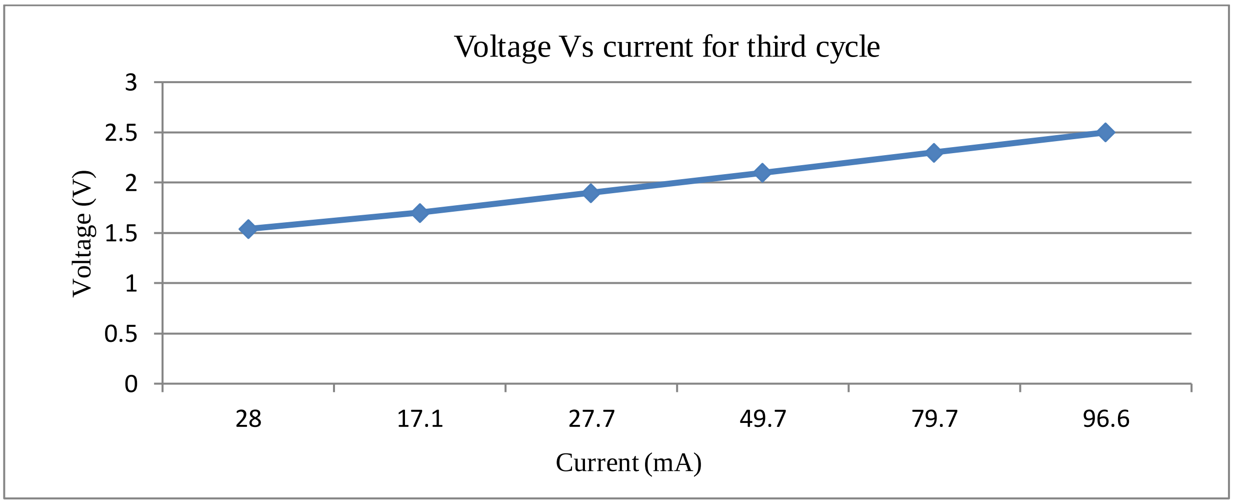
The life cycle of proton battery is ascertained by cyclic charging and discharging. Four charging and discharging cycle were carried out. The cut in voltage was observed in the range of 1.7 to 1.9V**.** During charging or electrolysis process voltage was increased by 0.1V within an interval of half hour. The process of charging was complete when rapid hydrogen gas evolution takes place. The electrolysis process was stopped at 2.5V. Fig 5.11 show relation between current and voltage during charging.



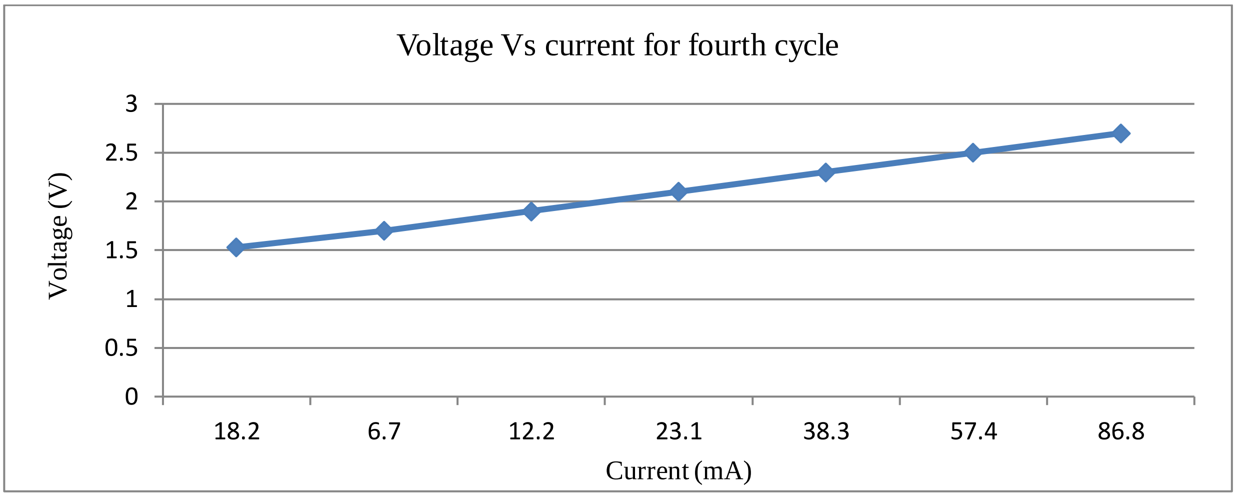
(a)



(b)



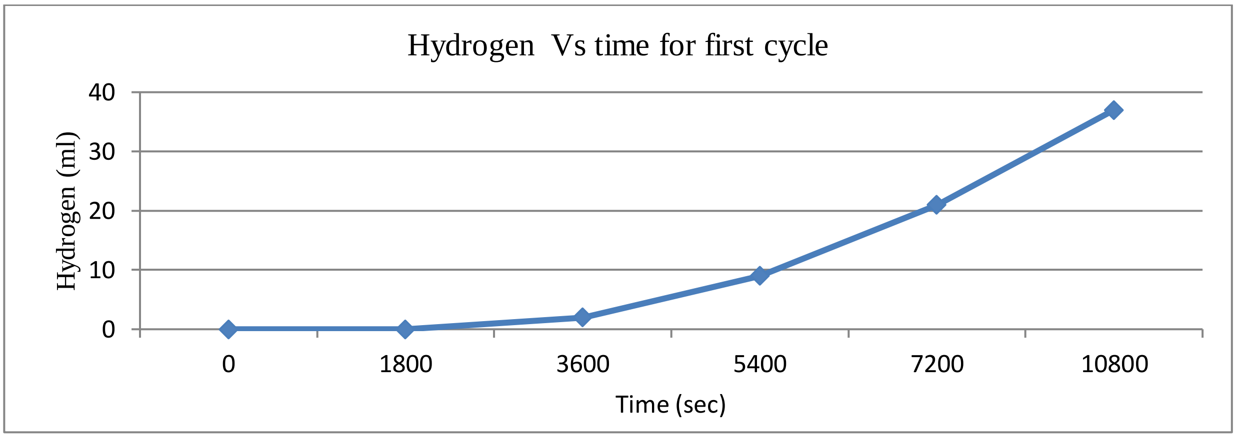
(c)



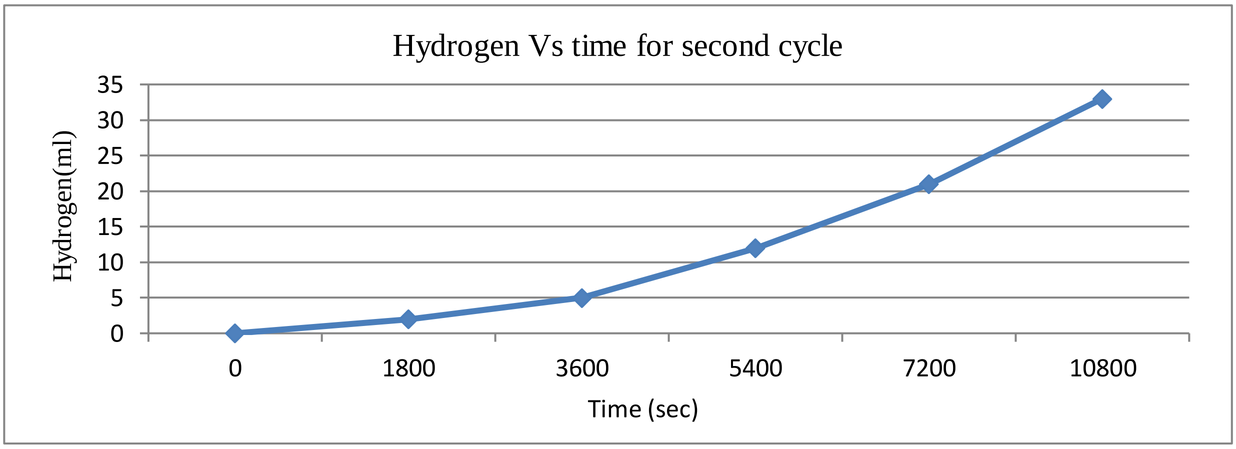
(d)

Fig 5.11 . Graph representing relation of current and voltage for electrolyser mode of proton battery in four cycles.

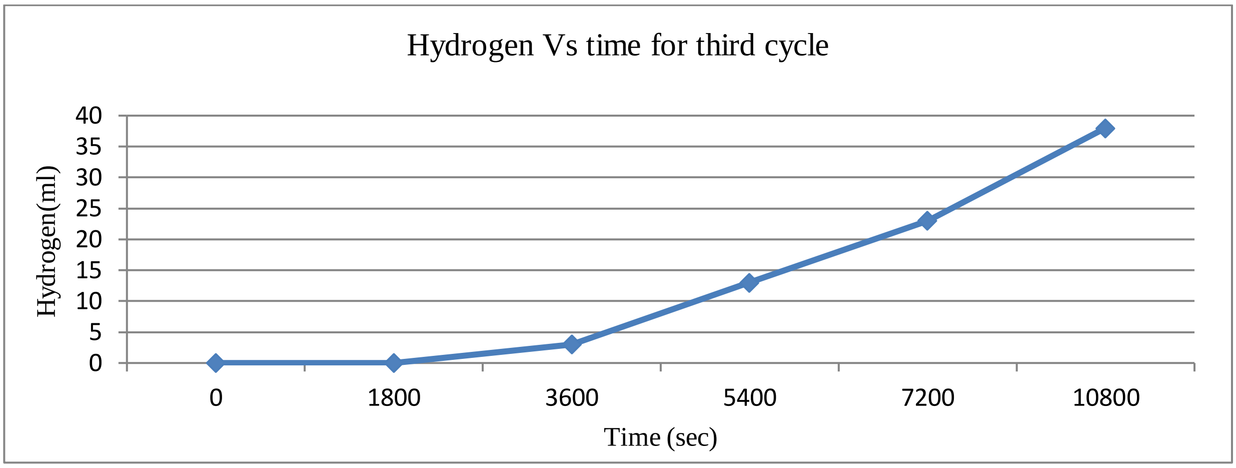
During charging hydrogen ions passed through membrane electrode assembly and get stored in the porous electrode. When the vacant pores inside electrode gets filled, any further charging results in hydrogen gas evolution. The production of hydrogen gas was noticed from half hour up to completion of charging as shown in Fig 5.12. The gas production during charging varies from 30 to 38ml.



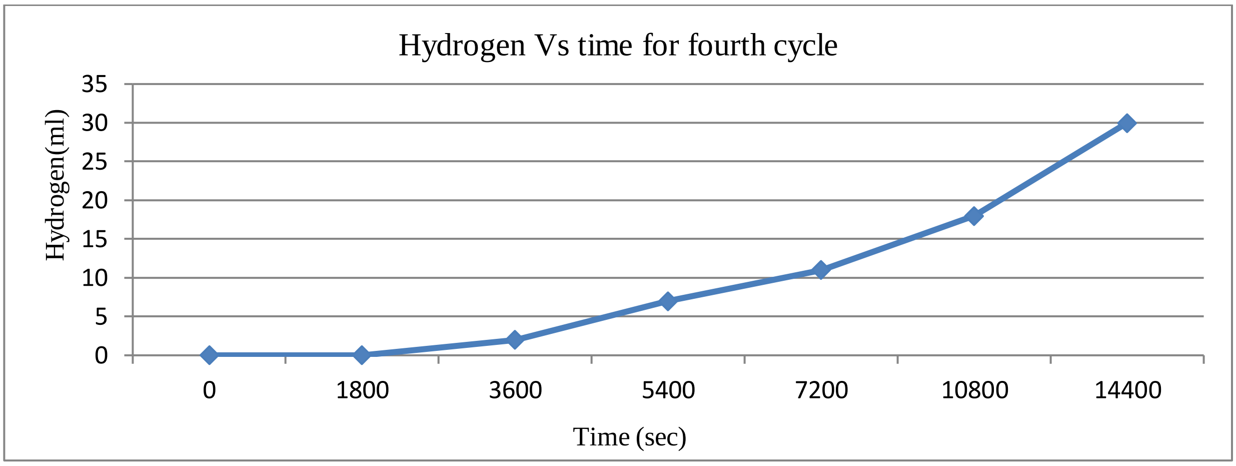
(a)



(b)



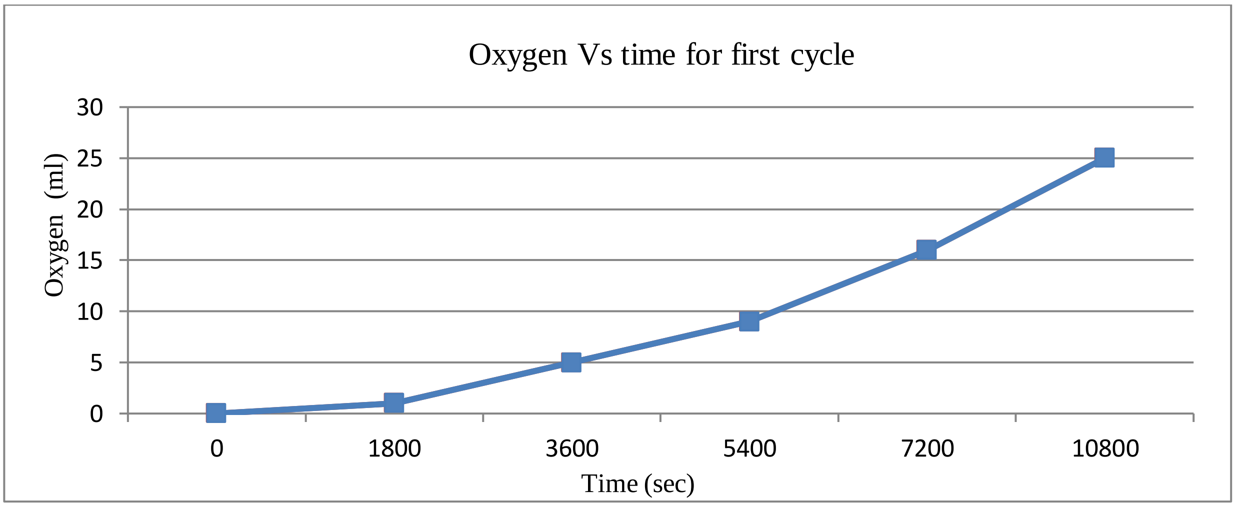
(c)



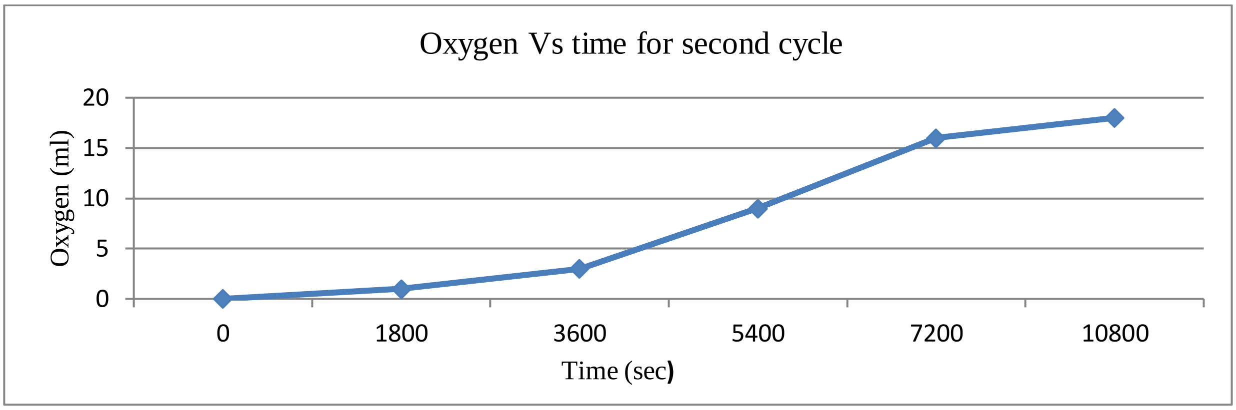
(d)

Fig 5.12. Graph showing relation between time and hydrogen produced in charging of proton battery.

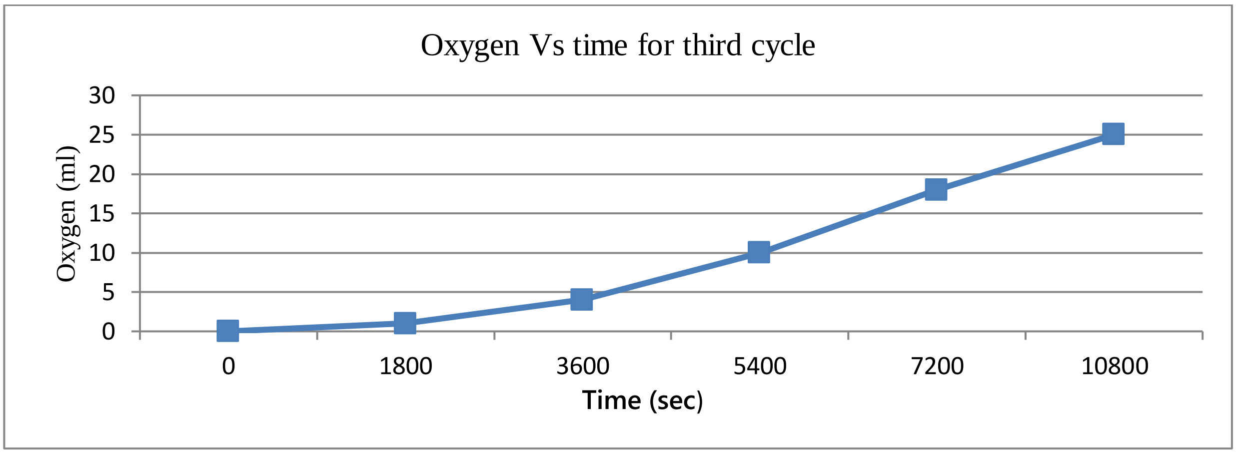
During charging process, oxygen production starts as soon water dissociation takes place. The dissociation of water starts at the cut-in voltage i.e. 1.7V. The oxygen gas production increases with rise in voltage. Form Faraday's law (Equation 5.2) it can be stated that charge flow is increased with oxygen ion produced. Oxygen gas combine together to form gas. Fig 5.13 represents the graph for oxygen released during charging cycles.



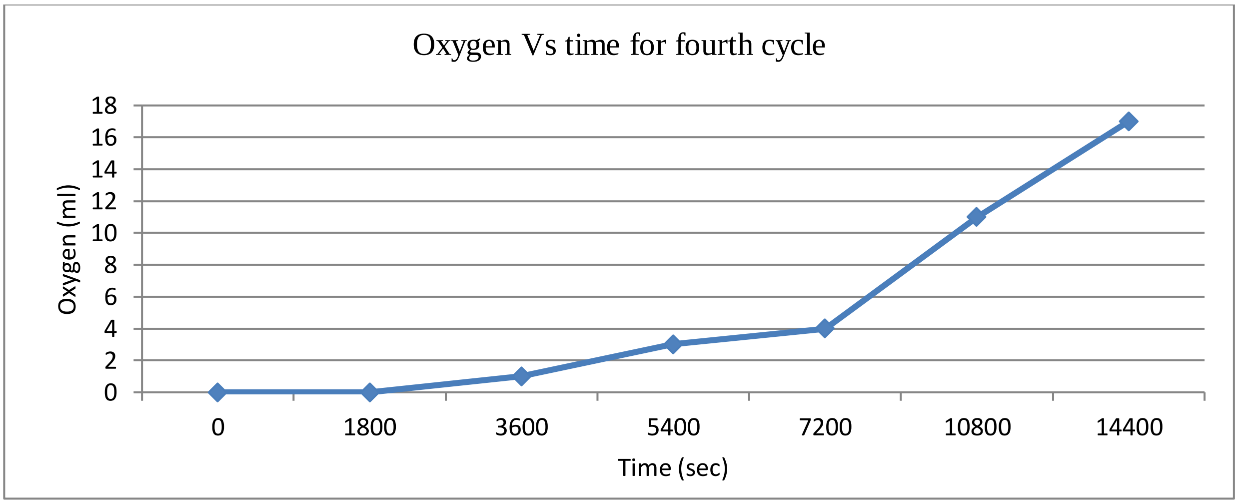
(a)



(b)



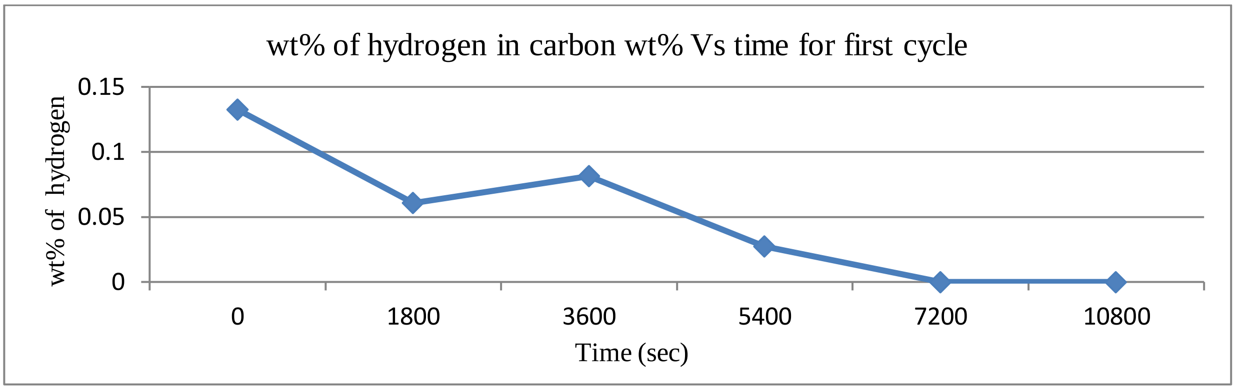
(c)



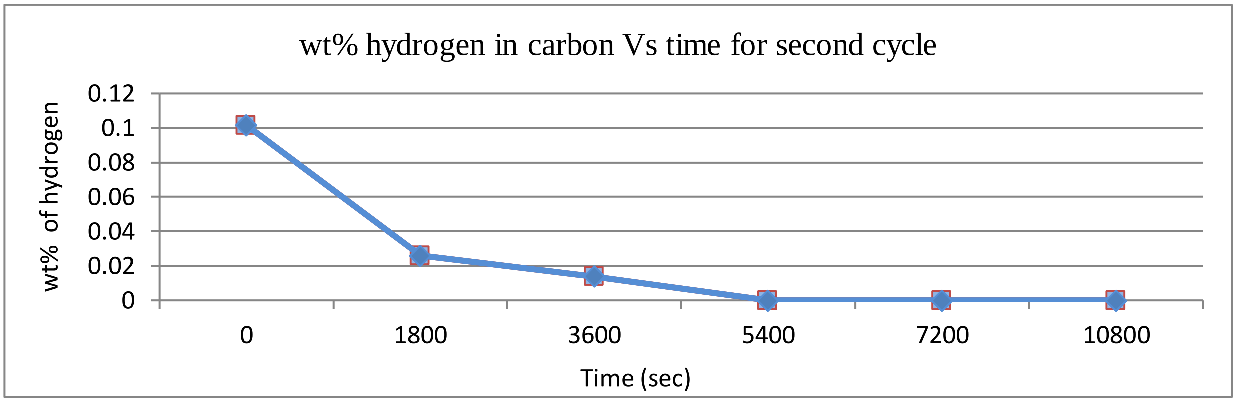
(d)

Fig 5.13 Graph represents relation between time and oxygen gas for electrolyser mode of proton battery during four cycles.

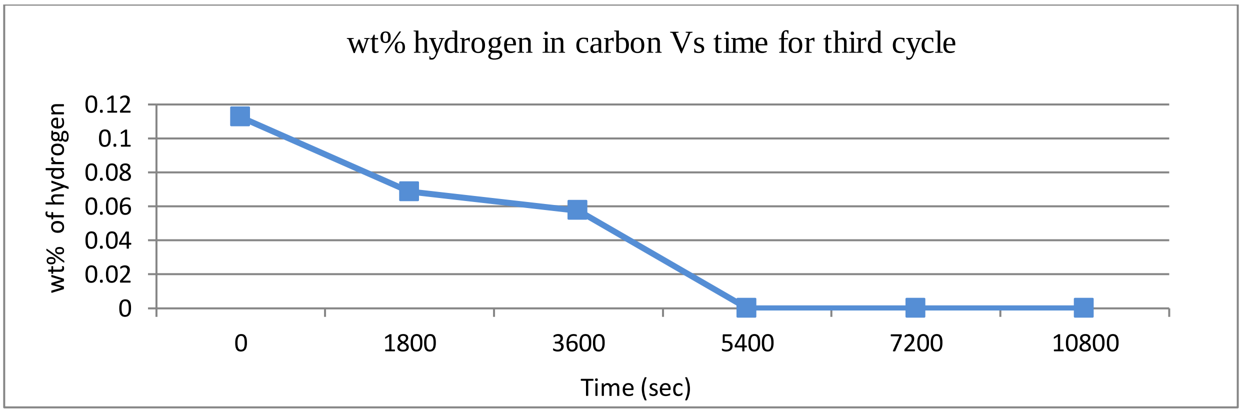
For theoretical calculation of weight percent of hydrogen Faraday's law (mention in equation 5.4) is used. The amount of hydrogen gas adsorbed in electrode is calculated by subtracting theoretical mass of hydrogen and hydrogen gas produced during charging process. The weight percentage of hydrogen stored in MWCNT for all cycle is calculated using Equation 5.5.



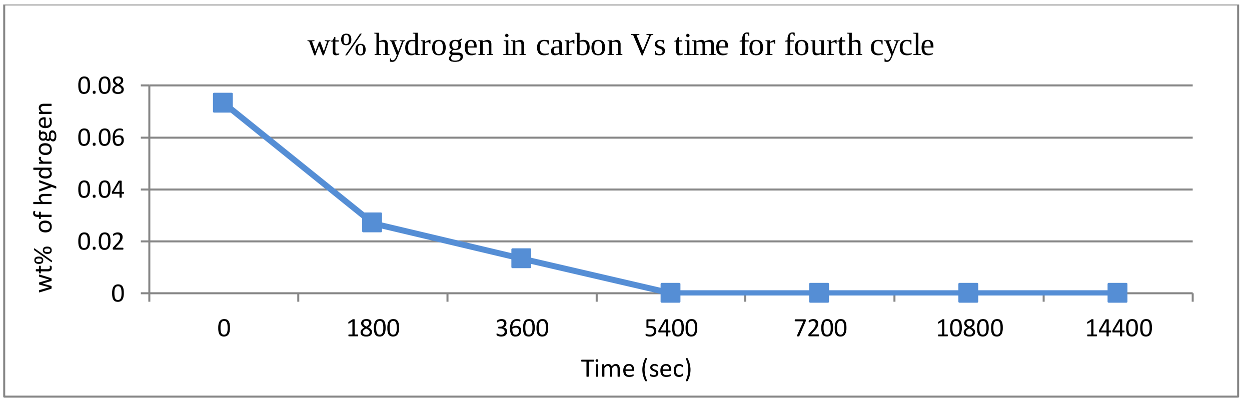
(a)



(b)



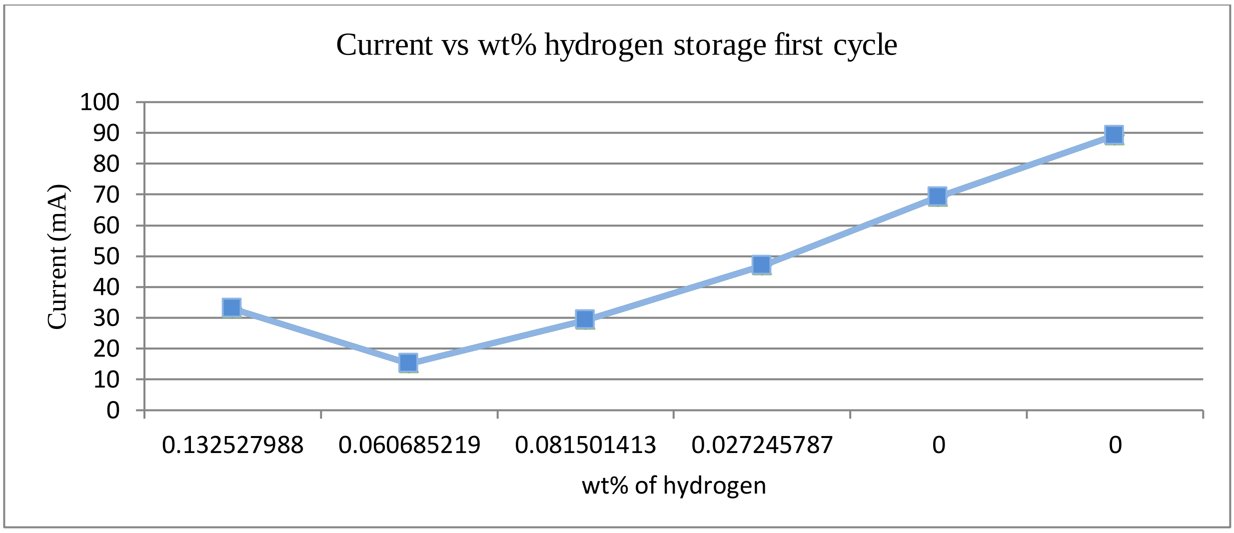
(c)



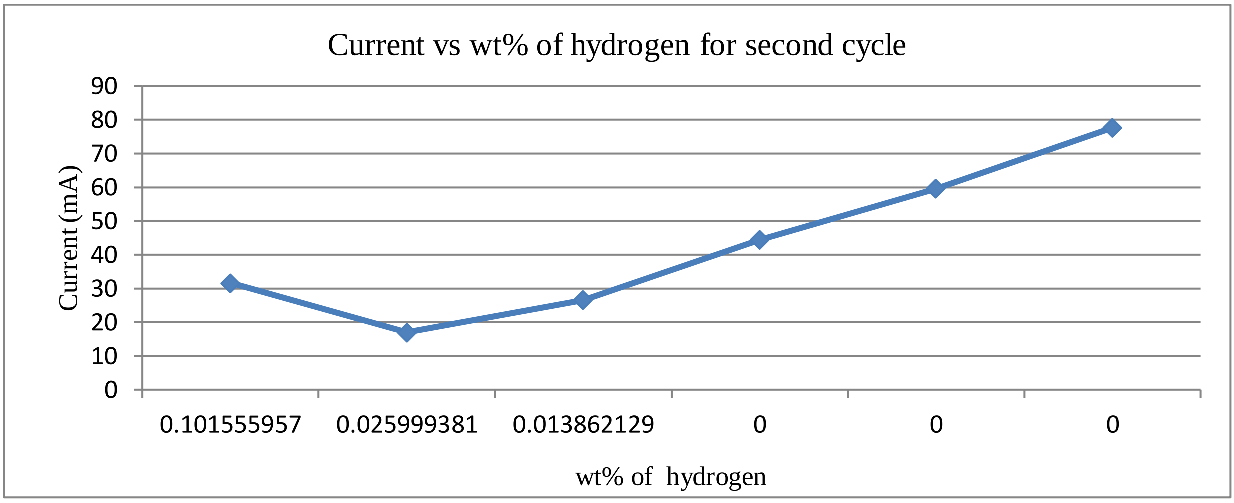
(d)

Fig 5.14. Graph showing relation between voltage and wt% of hydrogen stored in carbon during charging mode of proton battery.

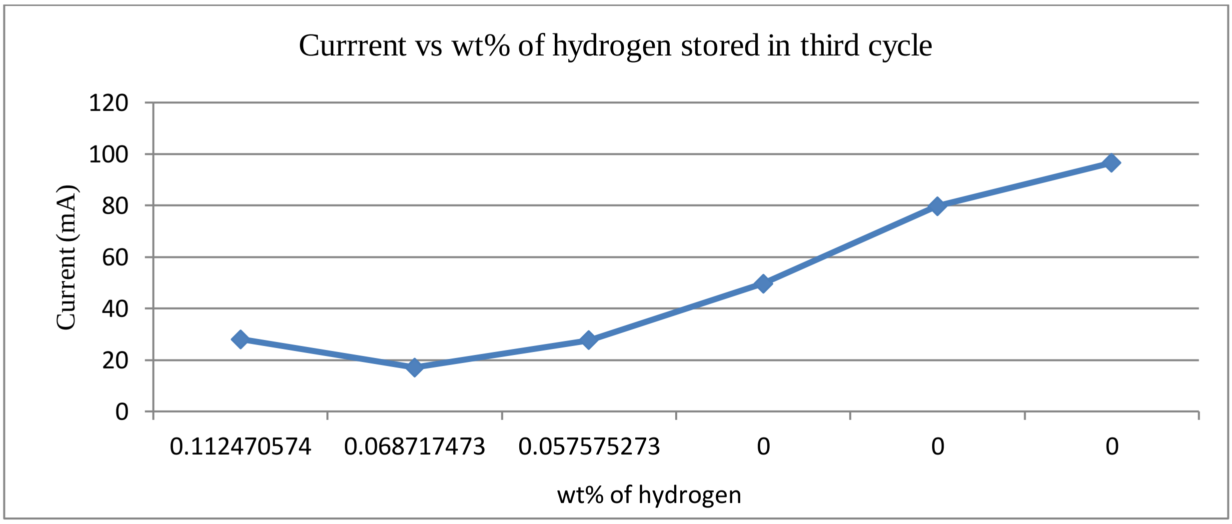
Fig 5.15 shows relation of current with weight percent of hydrogen during charging of proton battery. From cyclic charging it is inferred that with rise in current electrochemical hydrogen storage decreases in porous electrode. The wt% of hydrogen has been calculated using Faraday's law. The storage of hydrogen inside MWCNT increases with increase in current.



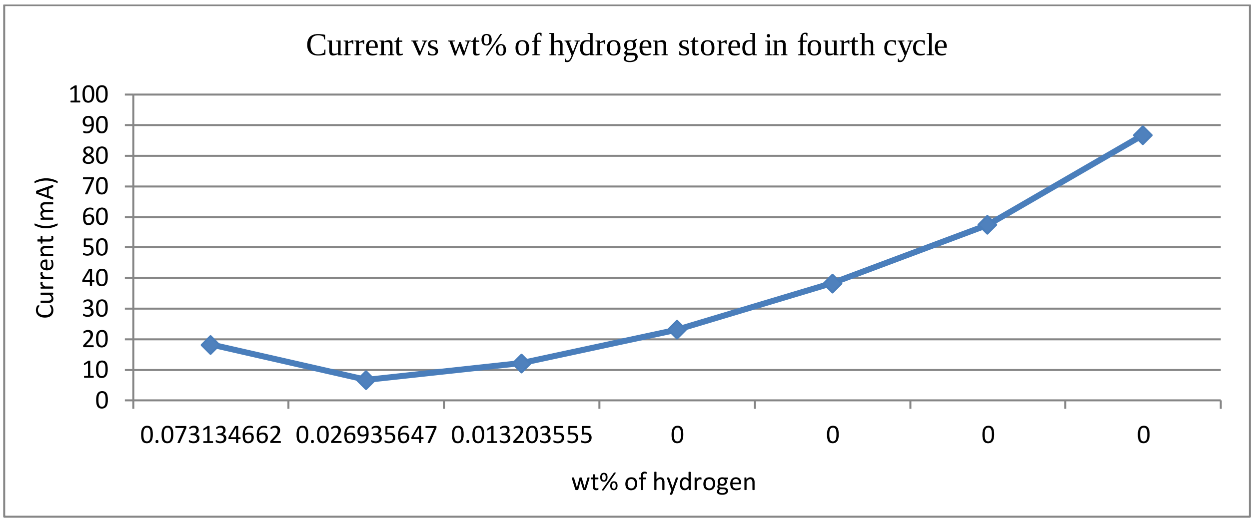
(a)



(b)



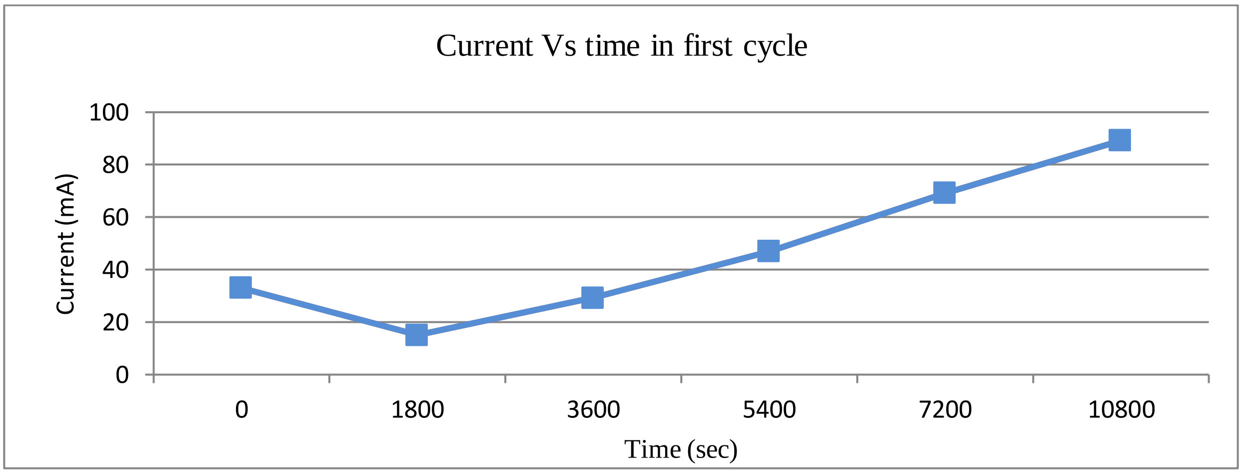
(c)



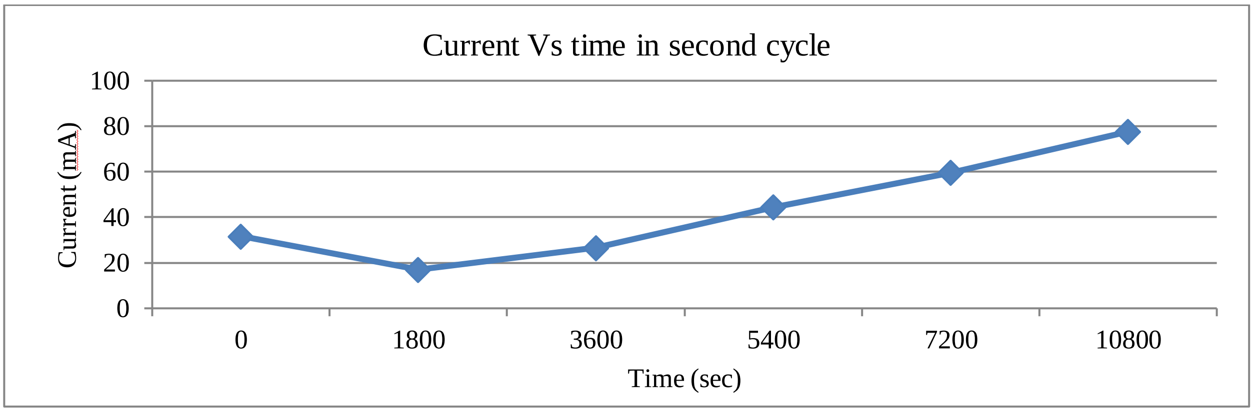
(d)

Fig 5.15. Graph showing relation between weight percent of hydrogen and current during charging of proton battery for four cycles.

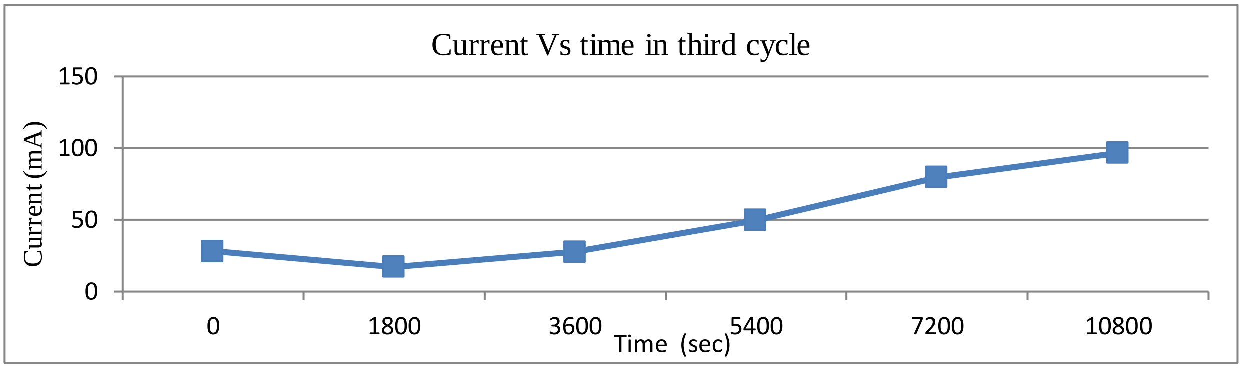
Graph between current and time during electrolysis has been shown in Fig 5.16. The value of current increased form 33mA to 89.2mA during first cycle whereas in second cycle current range from 31.6mA to 77.6mA. In the third cycle current varies from 28 to 96.6mA and in last cycle it changes from 18.2 to 86.8mA.



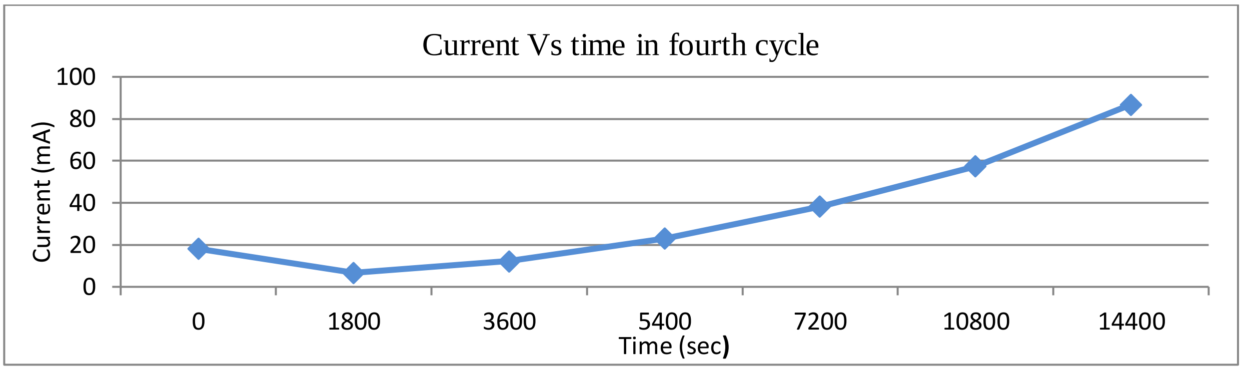
(a)



(b)



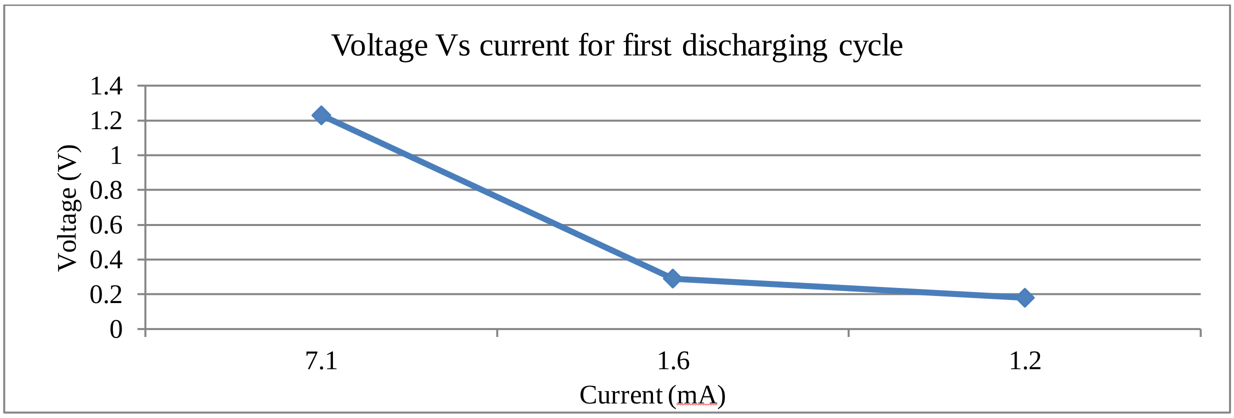
(c)



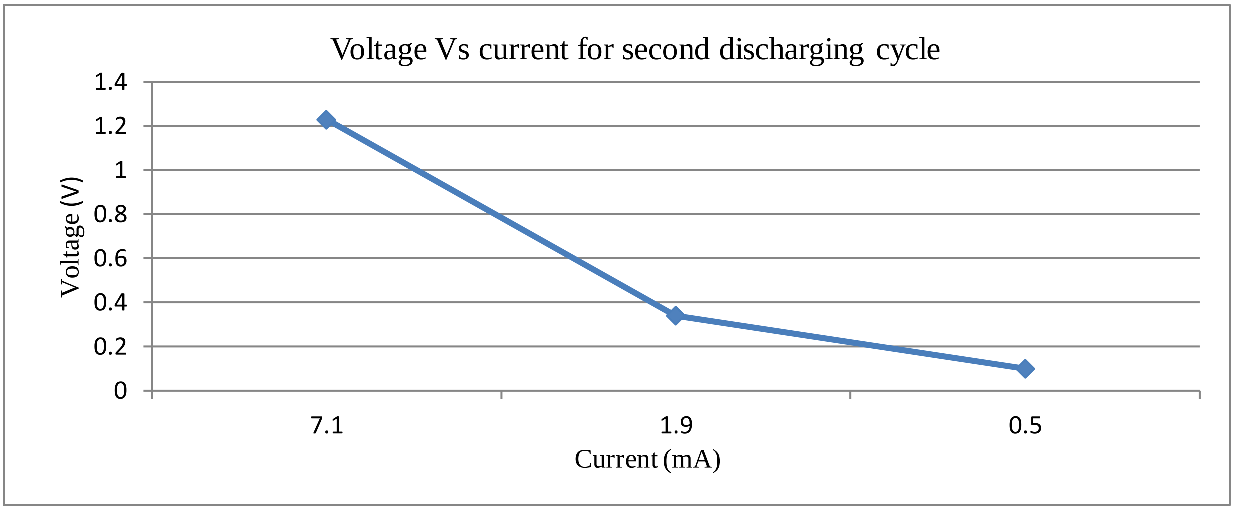
(d)

Fig 5.16 Graphs showing relation of time with current for four cycles of proton battery charging.

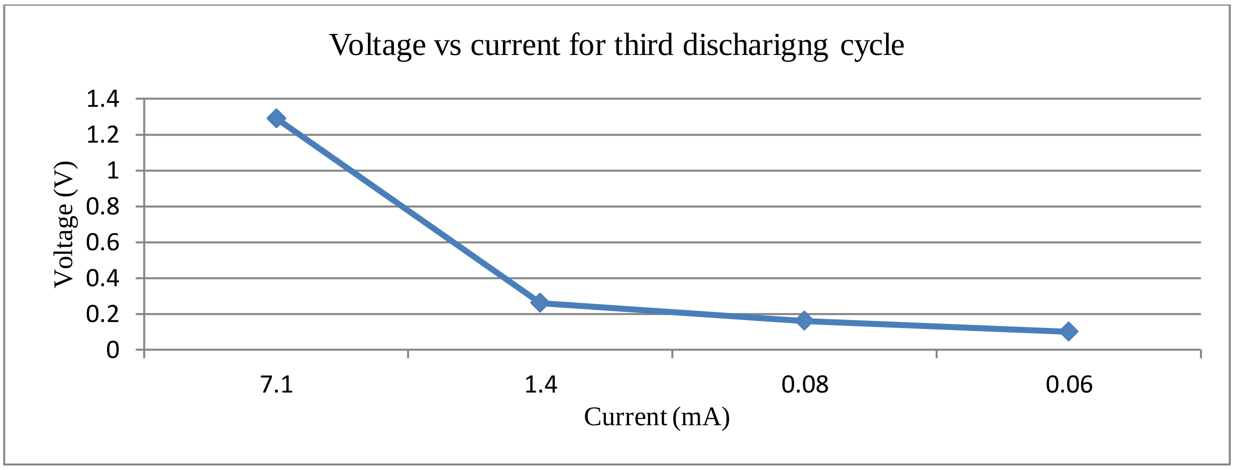
In the process of discharging or fuel cell mode, proton battery is subjected to an electrical load. The hydrogen atoms stored in MWCNT electrode emerge out and reacts with platinum black catalysts that breaks it to H^+ and e^-. The produced H^+ ions travel through membrane electrode assembly towards oxygen side whereas. e^- travels through the electric circuit satisfying the electronic load. On the oxygen side, the oxygen gas produced during charging is supplied back that reacts with iridium and ruthenium catalyst that breaks it into ions. The travelled hydrogen ions combine with oxygen ions reform water here. The discharge curve is shown in Fig 5.17. Discharging process is carried out after half hour of charging process. The maximum voltage reported was 1.29V for which was discharged in half hour.



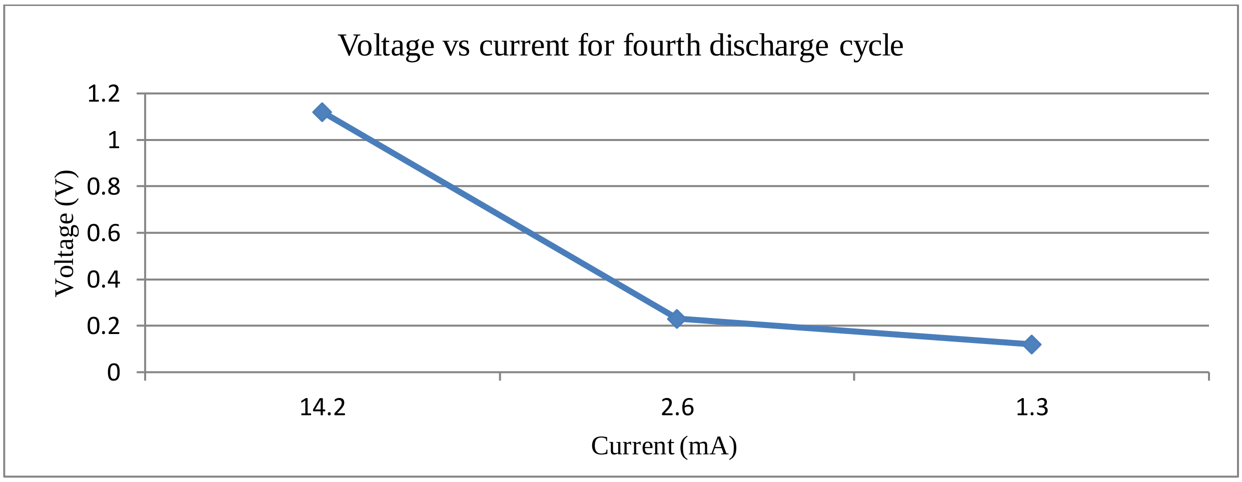
(a)



(b)



(c)



(d)

Fig 5.17. Graph showing relation between voltage and current during fuel cell mode or discharging mode of proton battery for four cycles.

The hydrogen released during discharging is calculated by using Faraday's law. For wt% calculation of hydrogen the hydrogen released is divided by the weight of MWCNT present in electrode.

During electrolyser and fuel cell mode of operation in proton battery for 4 cycles of fuel cell and electrolyser mode have been summarised in Table 5.3 and 5.4. The oxygen stored in electrolyser mode was used as supply to the cell in fuel cell mode. It is evident from the Table 5.3 and 5.4 that not all the stored hydrogen moved out of the storage during discharging.

Few hydrogen atoms might have formed strong chemical bonds at the surface of pores that did not break during the applied potential difference during discharging. Hence, it limits the storage capacity for the next successive charging cycle. Therefore, a minute decrease in the electrochemical hydrogen storage capacity of the fabricated MWCNT electrode was observed in every successive charging/ discharging cycle.

Table 5.3. Capacity of stored hydrogen for electrolyser mode of proton battery.

Cycle	Hydrogen released (kg)	Wt % of hydrogen stored in electrode	Wt % of hydrogen stored in carbon
1	0.005272	0.2416	0.30196
2	0.00479	0.1064	0.1414
3	0.00557	0.1932	0.2387
4	0.00452	0.0945	0.1132

Table 5.4. Capacity of stored hydrogen for fuel cell mode of proton battery.

Cycle	Wt % of hydrogen released from carbon
1	0.0050
2	0.00388
3	0.0023
4	0.0150

DISCUSSION

The energy demand is rising day by day and there is need for alternate resources to take over this challenge. Batteries play curtail role in storing energy and removing intermittent nature of renewable energy sources. Proton battery with integrated MWCNT is a step towards green and sustainable growth.

During the electrolyser or E-mode, water breakdown to release two hydrogen and oxygen ion. Ideally the amount of hydrogen retrieved should be twice the amount of oxygen produced, but it was observed that the amount of hydrogen produced was less. Presuming no leakage it can be stated that hydrogen got stored electrochemically in porous MWCNT electrode. The electrochemical hydrogen storage is in form of physisorption and chemisorption. In the process of physisorption weak Van der Waals forces formed between hydrogen and MWCNT whereas in chemisorptions, weak chemical bonds are form between hydrogen, MWCNT and electron.

In the first stage of thesis the proton battery with integrated MWCNT was tested for hydrogen storage. The result ascertains that MWCNT has the capability to store hydrogen in electrochemical storage. Further, cycle testing was performed to check performance and life of proton battery.

On performing charging and discharging for various cycles on the electrode, it can be stated that MWCNT have the capability to store hydrogen in solid state. In cyclic testing it was found that maximum of 0.301 wt% can be stored in MWCNT which is equivalent to 81.793mAhg^{-1} while maximum discharging wt% was 0.005wt% equivalent to 1.358mAhg^{-1} [50]. From results it can be observed that at low current the gas formation is less and storage of hydrogen is more. Therefore current controlled dissociation is needed to surpass gas formation and improve solid state hydrogen storage.

CHAPTER 6

CONCLUSION AND FUTURE WORK

CONCLUSION

Power demand can be fulfilled by renewable energy resources along with storage system. The storage system should not cause environmental pollution. Proton battery is a step towards green and wholesome growth of humankind. It has been demonstrated experimentally that hydrogen can be stored electrochemically in MWCNT integrated in a proton battery.

An experimental proton battery is fabricated that works on the principle of a reversible polymer electrolyte membrane fuel cell. The feasibility of the fabricated proton battery with an integrated porous MWCNT electrode for electrochemical hydrogen storage is demonstrated successfully.

From the results it is evident that hydronium ion travelled through membrane electrode assembly from oxygen to hydrogen side via polymer electrolyte and got adsorbed. The fabricated porous MWCNT electrode of 2.5cm x 2.5cm is able absorb above 1wt% of hydrogen electrochemically through chemisorptions and phyisorption. By performing cyclic testing ON proton battery integrated with MWCNT electrode, it was found that hydrogen can be stored in electrochemical form in MWCNT. The electrochemical hydrogen storage capacity of the fabricated MWCNT electrode was found to be above 1wt% which is comparable with the commercially available metal hydride based hydrogen storage canisters and lithium-based batteries.

Though the energy retrieved in $mAhg^{-1}$ was less than the energy stored the possible reason can be strong bond formation between host, hydrogen and electron. These strong bonds were not broken in the presence of electrical load as sufficient potential was not present. The by product in this battery are water and heat, which makes it qualified to be used as replacement of conventional batteries such as lithium based battery. It is worth noting that proton battery does not emit any fumes like commercially available lead- acid and lithium based batteries. Proton battery with an integrated MWCNT proves to play key role in sustainable development of mankind in terms of continuous power supply applications.

FUTURE WORK

1. It is evident that different pore sizes present in the porous hydrogen storage electrode played their individual roles in transportation of hydronium ions and adsorption of hydrogen in the host materials. However, it is yet to found that how surface morphology of the material effects its electrochemical hydrogen storage capacity.

2. It is worth checking that how much each type of pores does contribute in mass transfer of ions within the host material. In other works, it is worth checking, that how much is the optimum number of macropores, mesopores, mucropores or ultamicropores are required to enhance hydrogen capacity of the employed porous material.
3. Material with better discharging capacity is needed to be searched and implemented as electrode for storage and retrieval of hydrogen.
4. Cell design can be improved by using different form of channels to improve the circulation of hydrogen on the surface of electrode.
5. The catalyst loading needs to be varied on anode and cathode side to observe the change in solid state storage of hydrogen.
6. Alternate catalyst other than platinum can be used for proton battery performance enhancement.
7. Protic ionic liquids can be used in place of sulfuric acid as proton conducting medium.

LIST OF PUBLICATIONS

1. D. Kapoor, A.S. Oberoi and P. Nijhawan, "Hydrogen Production and Subsequent Adsorption/Desorption Process within a Modified Unitized Regenerative Fuel Cell,"*Processes*, vol.7, pp. 238 -257, 2019.
2. D. Kapoor, A.S. Oberoi and P. Nijhawan, "A Multi-walled Carbon Nanotube Electrode for Renewable Energy Storage An Experimental Investigation on Cyclic Charging and Discharging," *International Journal of Advanced Trends in Computer Science and Engineering*, vol. 8, pp. 513-518, 2019.

REFERENCES

[1] Ecology global network, “Environmental Unity,” Available: http://www.ecology.com/2011/09/03/the-history-of-energy-use/. Accessed: 06 February 2019.

[2] N. Zhang, L. Noam and J. Hongguang, "The energy situation and its sustainable development strategy in China," *Energy*, vol. 36, no. 6, pp. 3639-3649, 2011.

[3] P. K. Bose and M. Dines, "An experimental investigation on engine performance and emissions of a single cylinder diesel engine using hydrogen as inducted fuel and diesel as injected fuel with exhaust gas recirculation," *International journal of hydrogen energy*, vol. 34, no. 11, pp. 4847-4854, 2009.

[4] Live science, “Effect of Global Warming,” Available: https://www.livescience.com/37057-global-warming-effects.html. Accessed: 07 March 2019.

[5] World health organization, “Air Pollution,” Available: https://www.who.int/airpollution/en/. Accessed: 11 March 2019.

[6] K. A. Kavadias, D. Apostolou and J. K. Kaldellis, "Modelling and optimisation of a hydrogen-based energy storage system in an autonomous electrical network," *Applied energy*, vol. 227, pp. 574-586, 2018.

[7] X. Luo, J. Wang, M. Dooner and J. Clarke, "Overview of current development in electrical energy storage technologies and the application potential in power system operation," *Applied energy*, vol. 137, pp. 511-536, 2015.

[8] P. P. Edwards, L. Vladimir, W. I. Kuznetsov and N. P. Brandon, "Hydrogen and fuel cells: towards a sustainable energy future," *Energy policy*, vol. 36, no. 12, pp. 4356-4362, 2008.

[9] M. Ali, J. Ekström, and M. Lehtonen, "Sizing hydrogen energy storage in consideration of demand response in highly renewable generation power systems," *Energies*, vol. 11, no. 5, pp. 1113-1125, 2018.

[10] K. Riahi, S. Rao, V. Krey, C. Cho, V. Chirkov, G. Fischer, G. Kindermann, N. Nakicenovic, and P. Rafaj. " A scenario of comparatively high greenhouse gas emissions." *Climatic Change*, vol. 109, no. 1-2, pp. 109-116, 2011.

[11] J. Dufour, D. P. Serrano, J. L. Galvez, J. Moreno, and C. Garcia, "Life cycle assessment of processes for hydrogen production. Environmental feasibility and reduction of greenhouse gases emissions," *International journal of hydrogen energy*, vol. 34, no. 3, pp. 1370-1376, 2009.

[12] F. Zhang and P. Cooke, "Hydrogen and fuel cell development in China: a review," *European*

Planning Studies, vol. 18, no. 7, pp. 1153-1168, 2010.

[13] S. Mekhilef, R. Saidur, and A. Safari, "Comparative study of different fuel cell technologies," *Renewable and Sustainable Energy Reviews,* vol. 16, no. 1, pp. 981-989, 2012.

[14] L, Gracia, P. Casero, C. Bourasseau, and A. Chabert. "Use of Hydrogen in Off-Grid Locations, a Techno-Economic Assessment," *Energies,* no. 11, pp. 3141-3152, 2018.

[15] V. R. García, N. Espinosa, and A. Urbina, "Simple PEM water electrolyser model and experimental validation," *international journal of hydrogen energy,* vol. 37, no. 2, pp. 1927-1938, 2012.

[16] J. M. Andújar and F. Segura, "Fuel cells: History and updating. A walk along two centuries," *Renewable and sustainable energy reviews,* vol. 13, no. 9, pp. 2309-2322, 2009.

[17] A Züttel, "Materials for hydrogen storage,"*Materials today,* vol. 6, pp.24-33, 2003.

[18] A. Züttel, A. Borgschulte, L. Schlapbach, Hydrogen as a future energy carrier, 2nd ed. Weinheim, Wiley, 2011.

[19] S. A. Sherif, N. Zeytinoglu, T. N. Veziroğlu, "Liquid hydrogen: potential, problems, and a proposed research program," *International journal of hydrogen energy,* vol. 22, pp. 683-688, 1997.

[20] S. Brennan, V. Molkov, "Safety assessment of unignited hydrogen discharge from on board storage in garages with low levels of natural ventilation," *International Journal of Hydrogen Energy,*vol. 38, pp. 8159-8166, 2013.

[21] M. Hosseini, I. Dincer, G. F. Naterer, M. A. Rosen, "Thermodynamic analysis of filling compressed gaseous hydrogen storage tank," *International journal of hydrogen energy,* vol. 37, pp. 5063-5071, 2012.

[22] F. Zhang and P. Cooke. "Hydrogen and fuel cell development in China: a review," *European Planning Studies,* vol. 18, no. 7, pp.1153-1168, 2010.

[23] O. Blanchard, "The economic future of Europe," *Journal of Economic Perspectives,* vol. 18, no. 4, pp. 3-26, 2010.

[24] W. R. Grove, "XXIV. On voltaic series and the combination of gases by platinum," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science,* vol. 14, no. 86-87 , pp. 127-130, 1839.

[25] A. Doddathimmaiah, "Unitised regenerative fuel cells in solar-hydrogen systems for remote area power supply," Ph.D., RMIT, 2008.

[26] A. S. Oberoi, J. Andrews, A. L. Chaffee and L. Ciddor, "Hydrogen storage capacity of

selected activated carbon electrodes made from brown coal," *International Journal of Hydrogen Energy*, vol. 41, pp. 2309-2318, 2016.

[27] S. S. Mohammadi, "Investigation of a reversible PEM fuel cell with integrated metal- hydride hydrogen storage," M.E., RMIT, 2013.

[28] J. A. Alons, I. Cabria, M. J. López, "Simulation of hydrogen storage in porous carbons. Journal of Materials Research," vol. 28, pp. 589-604, 2013.

[29] M. J. Jazaer, "The feasibility of a unitized regenerative fuel cell with a reversible carbon-based hydrogen storage electrode," M. E., RMIT, 2013.

[30] T. Gholami, M. Salavati-Niasari, and S. Varshoy. "Investigation of the electrochemical hydrogen storage and photocatalytic properties of $CoAl_2O_4$ pigment: Green synthesis and characterization," *International Journal of Hydrogen Energy*, vol. 41, no. 22, pp. 9418-9426, 2016.

[31] M. Mohammadi, B. Khoshnevisan, "Electrochemical hydrogen storage in EPD made porous Ni-CNT electrode," *International Journal of Hydrogen Energy*, vol. 41, pp. 10311-10315, 2016.

[32] M. Bordbar, T. Alimohammadi, B. Khoshnevisan, B. Khodadadi, A. Yeganeh-Faal, " Preparation of MWCNT/TiO_2–Co nanocomposite electrode by electrophoretic deposition and electrochemical study of hydrogen storage," *International journal of hydrogen energy*, vol. 40, no. 31, pp. 9613-9620, 2015.

[33] Y. Yürüm, A. Taralp, T. N. Veziroglu, "Storage of hydrogen in nanostructured carbon materials," *International journal of hydrogen energy*, vol. 34, pp. 3784- 3798, 2018.

[34] E.T. Thostenson, Z. Ren, T. W. Chou, "Advances in the science and technology of carbon nanotubes and their composites: a review," *Composites science and technology*, vol. 61, no. 21, pp. 1899-1912, 2018.

[35] E. Liu, J. Wang, J. Li, C. Shi, C. He, X. Du, N. Zhao, "Enhanced electrochemical hydrogen storage capacity of multi-walled carbon nanotubes by TiO2 decoration," *International journal of hydrogen energy*, vol. 36, no. 15, pp. 6739-6743, 2011.

[36] E. Mosquera, D. E. Diaz-Droguett, C. N. Carvajal, M. Roble, M. Morel, R. Espinoza, " Characterization and hydrogen storage in multi-walled carbon nanotubes grown by aerosol-assisted CVD method," *Diamond and Related Materials*, vol. 43, no. 7, pp. 66-71, 2014.

[37] E. Erünal, F. Ulusal, M. Y. Aslan, B. Güzel, D. Üner, "Enhancement of hydrogen storage capacity of multi-walled carbon nanotubes with palladium doping prepared through supercritical CO2 deposition method," *International Journal of Hydrogen Energy*, vol. 43, no. 16, pp. 1075-1076, 2018.

[38] A. Reyhani, S. Z. Mortazavi, S. Mirershadi, A. Z. Moshfegh, P. Parvin, A. N. Golikand," Hydrogen storage in decorated multiwalled carbon nanotubes by Ca, Co, Fe, Ni, and Pd nanoparticles under ambient conditions,"*The Journal of Physical Chemistry C,* vol. 115, no, 11, pp. 6994-7001, 2011.

[39] Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan, M. Williams, P. Ndungu, M. V. Lototskyy, A. Nechaev, V. Linkov, S. Kulprathipanja, "Investigation of hydrogen storage capacity of multi-walled carbon nanotubes deposited with Pd or V," *International journal of hydrogen energy,* vol. 34, no. 13, pp. 6669-6675, 2018.

[40] P. Singh, M. V. Kulkarni , S. P. Gokhale, S. H. Chikkali, C. V. Kulkarni, "Enhancing the hydrogen storage capacity of Pd-functionalized multi-walled carbon nanotubes," *Applied Surface Science,* vol. 258, no. 4, pp. 3405-3409, 2012.

[41] A. Reyhani, S. Z. Mortazavi, S. Mirershadi, A. N. Golikand, A. Z. Moshfegh, " H_2 adsorption mechanism in Mg modified multi-walled carbon nanotubes for hydrogen storage," *International journal of hydrogen energy*, vol. 37, no. 2, pp. 1919-1926, 2012.

[42] T. Gholami , M. Salavati-Niasari, S. Varshoy, "Electrochemical hydrogen storage capacity and optical properties of NiAl2O4/NiO nanocomposite synthesized by green method," *International Journal of Hydrogen Energy*, vol. 42, no. 14, pp. 5235-5245, 2017.

[43] O. W. Achaw, "A study of the porosity of activated carbons using the scanning electron microscope,"*Scanning Electron Microsc,* vol. 8, no. 12, pp. 125-152, 2012.

[44] F. Béguin, K. Kierzek, M. Friebe, A. Jankowska, J. Machnikowski, K. Jurewicz, E. Frackowiak, "Effect of various porous nanotextures on the reversible electrochemical sorption of hydrogen in activated carbons," *Electrochim. Acta,* vol. 51, pp. 2161–2167, 2006.

[45] A. Nangsuay, Y. Ruangpanit, R. Meijerhof , S. Attamangkune, " Yolk absorption and embryo development of small and large eggs originating from young and old breeder hens," Poultary *Science*, vol. 90, no. 30, pp. 2648–265, 2011.

[46] Spiegel C: Designing and building fuel cells, 2nd ed. New York: McGraw-Hill, 2007.

[47] Fuel cell today. Available: http://www.fuelcelltoday.com. Accessed: 07 April 2019.

[48] K. Kordesch, V. Hacker, J. Gsellmann, M. Cifrain, G. Faleschini, P. Enzinger, R. Fankhauser, M. Ortner, M. Muhr, R. R. Aronson, "Alkaline fuel cells applications," *Journal of Power Sources,* vol. 86, no. 11, pp. 162-165, 2000.

[49] The U.S. Department of Defense (DoD), "Fuel Cell Test and Evaluation Centre (FCTec)," Available:http://www.fctec.com/fctec about.asp. Accessed: 21 May 2019.

[50] K. Babel, D. Janasiak, K. Jurewicz, " Eectrochemical hydrogen storage in activated carbons with

different pore structures derived from certain lignocellulose materials," *Carbon*, vol. 50, no. 31, pp. 5017–5026, 2012.

Diksha Thesis

Parag

ORIGINALITY REPORT

16%	9%	10%	7%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Kapoor, Oberoi, Nijhawan. "Hydrogen Production and Subsequent Adsorption/Desorption Process within a Modified Unitized Regenerative Fuel Cell", Processes, 2019 Publication	3%
2	researchbank.rmit.edu.au Internet Source	3%
3	www.mdpi.com Internet Source	1%
4	S. Mekhilef, R. Saidur, A. Safari. "Comparative study of different fuel cell technologies", Renewable and Sustainable Energy Reviews, 2012 Publication	1%
5	Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan, M. Williams, P. Ndungu, M.V. Lototskyy, A. Nechaev, V. Linkov, S. Kulprathipanja. "Investigation of hydrogen storage capacity of multi-walled carbon nanotubes deposited with	<1%