A COMMERCIAL ACTIVATED CARBON POWDER AS A MEDIUM FOR ELECTROCHEMICAL HYDROGEN STORAGE: AN EXPERIMENTAL INVESTIGATION ON ELECTROCHEMICAL HYDROGEN STORAGE CAPACITY WITH POTENTIAL APPLICATION IN AUTOMOBILES

[1]AMANDEEP S. OBEROI, [2]BALJIT SINGH, [3]MUHAMMAD FAIRUZ REMELI

[1]Associate Professor, Chitkara University Research and Innovation Network (CURIN), Chitkara University, Chandigarh-Rajpura-Patiala National Highway (NH-64), Patiala, Punjab -140401, India.
[2,3]Faculty of Mechanical Engineering, Universiti Teknologi MARA, Shah Alam, Selangor, Malayasia.
Email – [1]amandeep_oberoi@hotmail.com, [2]bs_dhillon@hotmail.com, [3]fairuzremeli@gmail.com

Abstract— Emissions from automobiles running on conventional hydrocarbon-based fossil fuels have lead to increase in concentration of green-house gases (GHGs) that further have contributed in global warming to a great extent. For past few decades hydrogen has emerged as a potential alternative of conventional fossil fuels that could be stored on board and produced domestically and therefore, is globally considered as a future fuel. But, efficient and safe storage and few challenged to be addressed by the researchers. One solution to the problem is electrochemical storage of hydrogen in a porous medium and its utilisation in fuel cell to generate electricity to power the automobile. The presented paper therefore, focuses on determining the electrochemical hydrogen storage capacity of a commercial activated carbon (aC) electrode soaked in acid with potential application in hydrogen fuel cell. The method of fabrication of solid activated carbon electrode is explained in detail. The proton conductivity, double-layer capacitance and electrochemical hydrogen storage capacity of the sample electrode was measured at different levels of hydration. All the testing procedures are discussed and obtained results are used to reach conclusion and recommend future work. The proton conductivity of a fully hydrated commercial aC electrode soaked in 1 mol. sulphuric acid was found to be 0.0110 S/cm, double-layer capacitance as 41.0 F/g, and electrochemical hydrogen capacity as 1.08 wt%. The measured hydrogen capacity is comparable with commercially available metal-hydride based hydrogen storage canisters, lithium-ion and lithium-polymer batteries. The work demonstrates the flow of hydrogen to-and-fro activated carbon electrode soaked in acid that could be used in PEM fuel cell as an integrated hydrogen storage medium and has a potential application in automobiles.

Index Terms— Activated Carbon, Proton Conductivity, Double-Layer Capacitance, Electrochemical Hydrogen Storage.

I. INTRODUCTION

World has been observing a drastic change in climatic conditions due to global warming resulted from continuous increase in the concentration of green house gases (GHGs) from past many decades [1-3]. Pollution caused by emissions from thermal power plants, industries, automobiles, and human activities has lead to an exponential rise in the level of concentration of GHGs in earth's atmosphere [4-6].
Moreover, the extensive utilisation of fossil fuels for various purposes have pushed the oil reserves to its maximum limits and world is left with a very limited stock of crude oil to serve the entire mankind [7-9]. Therefore, what is required to mitigate these GHG concentrations in atmosphere and resolve the issue of limited reserves of fossil fuel is to shift from conventional to renewable energy economy [10-13].
Hydrogen has been identified by researchers as a potential candidate to be considered as future fuel due to its immense energy content, low atomic weight and zero emission [14]. It is possible to produce hydrogen domestically from renewable source and store it on-board of vehicle which makes it a promising alternate to currently used fossil fuels [15]. However, storing of hydrogen efficiently and in safe manner is still a challenge.

Hydrogen could be produced and stored in compressed gaseous form at high pressures or in liquid form at cryogenic temperatures by conventional ways. Both the forms require lot of energy expenditure and thus, have limitations to be used for automobile applications. One solution to problem is storage of hydrogen in solid form in a porous medium as a chemical compound [16], what is known as electrochemical hydrogen storage. A group of researchers at RMIT University Melbourne, Australia have been working under the leadership of Prof. John Andrews, on electrochemical hydrogen storage in porous materials like metal hydrides [17]. However, the result obtained in terms of gravimetric energy density was less than the expected figures. Moreover, metal hydrides being made of rare earth metals, are quite expensive [18]. Therefore, the research focus at RMIT shifted from metal hydride to porous activated carbon [19]. Activated carbon consists of range of pores (macropores, mesopores, micropores and ultramicropores) and thus, offers a wide range of pore volume, porosity and internal surface area.

One of the masters of engineering student at RMIT University reported on fabrication of composite activated carbon-nafion electrodes which he tested in a reversible proton exchange membrane (PEM) fuel cell as an integrated storage medium. Unfortunately, no detectable signs of hydrogen storage were obtained [19]. The reason reported was that nafion being a polymer did not penetrated inside the ultramicropores of aC samples which are considered as active sites for electrochemical hydrogen storage and hence, there was no medium for hydrogen proton conduction to the storage sites.

The present research project is thus, focused on testing a commercial activated carbon named as 'Nitro-50' soaked in a liquid sulphuric acid for its reversible electrochemical hydrogen storage capacity and hence, to check its feasibility for the hydrogen fuel cell applications. The liquid proton conductor medium used to assist the travelling for hydrogen atoms into storage sites of aC was liquid sulphuric acid (H_2SO_4) of different concentrations. The aC sample (Nitro-50) powder was used to fabricate three solid electrodes same physical and chemical configurations using commercial polytetrafluoroethylene (PTFE) as binder. The fabricated samples were then used for testing. The effects of using different concentration of electrolyte on proton conductivity, electron conductivity, double-layer capacitance and electrochemical hydrogen storage capacity are investigated.

II. EXPERIMENTAL

A. Selection of a sample

Activated carbon with wide range of pore sizes viz. macropores (diameter >50nm), mesopores (diameter from 2-50 nm), micropores (diameter from 0.7-2nm) and ultramicropores (diameter <0.7nm), is considered as a potential medium for electrochemical hydrogen storage [20]. Activated carbon with high internal surface area of particles is generally expected to have high electrochemical hydrogen storage capacity [21] In the present research work commercially available activated carbon powder named as 'Nitro-50' was selected based upon its easy availability and PTFE was used as the binder to hold the powdered aC sample.

B. Fabrication

A measured quantity of aC powder was mixed with a known amount of PTFE. The amount of PTFE added was 10% of that of aC powder to make sure that PTFE do not cover the internal pores of aC which are considered as storage sites for hydrogen atoms. The mixture was stirred well in a beaker for 2 hours and heated on a hot plate at 100 °C for 1 hour in order to evaporate solvent and moisture content and to obtain thick slurry. The obtained slurry was poured into the mould of desired shape and was heated in an electric oven for 2 hours at 110 °C to form the solid electrode. Total seven electrodes were fabricated with similar physical and chemical configurations to be tested in electrolyte of different concentrations ranging from 0.5 - 1.1 mol. The fabricated samples were given specific names: - aC0.5M, aC0.6M, aC0.7M, aC0.8M, aC0.9M, aC1.0M and aC1.1M.

C. Proton conductivity measurement

An ideal electrode employed in a PEM fuel cell as integrated hydrogen storage, need to be proton conductive. Thus, proton conductivity of any potential candidate for fuel cell application is an essential characteristic to be measured.

To measure the proton conductivity the fabricated sample aC electrodes were soaked in acid of different concentrations for 24 hours before testing. The acid soaked samples were sandwiched between nafion-117 (chemical name – perfuorosulfonic acid) membranes backed by gold plated electrodes. Electrochemical impedance spectroscopy (EIS) was used to measure the total series proton resistance across the setup as a function of frequency. The impedance with frequency range of 0.1 Hz to 10^6 Hz was applied across the gold plated electrodes and the nyquist plot between real and imaginary axes of the applied impedance was obtained. The intercept at high frequency end on the real impedance axis is considered as total series proton resistance of the system [22]. The measure resistance was then used to calculate proton conductivity of the sample with known thickness and area of sample using equation 1.

$$\sigma p = t / A \times R \qquad (1)$$

where

σp is the proton conductivity of the sample in S/cm

t is the thickness of the sample in cm.

A is the area of the sample in cm^2.

R is the proton resistance of the sample in ohm.

D. Double-layer capacitance measurement

The interface between the carbon particle's surface and that of sulphuric acid forms a double-layer capacitance that is considered to contribute to hydrogen storage capacity of the aC electrodes [20].

To measure the double-layer capacitance the fabricated sample aC electrodes were soaked in acid of different concentrations for 24 hours before testing. A split flat coin cell (shown in Fig. 1) was employed for measurement of double-layer capacitance using a well-known technique of cyclic voltammetry. The fabricated electrodes used in split flat coin cell were separated by a porous non-conducting filter paper. The electrolyte (dilute sulphuric acid) was poured and

electric potential was applied across the cell. The obtained result was in form of a cyclic-voltammogram. Peak current was recorded from the obtained voltammogram and used in equation 2 to determine the double-layer capacitance.

$$C = \frac{I_{peak}}{V_t \times M_c}$$

Eq. 2

where,

C → capacitance in F/g
Ipeak → peak current in mA
Vt → scan rate in mV/s
Mc → mass of carbon in grams



Figure 1: A split flat coin cell for battery R & D of 15 mm diameter. [Source: A. Oberoi, 2015]

E. Hydrogen storage capacity measurement

Galvanostatic charging and discharging is a well-known technique in electrochemistry to determine electrochemical hydrogen storage capacity [20]. A three-electrode electrolytic cell was used in the experimental setup (as shown in Figure 2) with Hg/HgO as reference electrode, platinum wire as counter electrode and fabricated aC electrode as working. The electrolyte used was dilute sulphuric acid of different concentrations viz. 0.6 mol, 0.7 mol, 0.8 mol, 0.9 mol, 1.0 mol and 1.1 mol.

The setup was connected with electrochemical workstation to supply the potential and record the result as shown in Figure 3. Two graduated cylinders were employed for collection of the generated oxygen and hydrogen gases separately (shown in Figure 4).

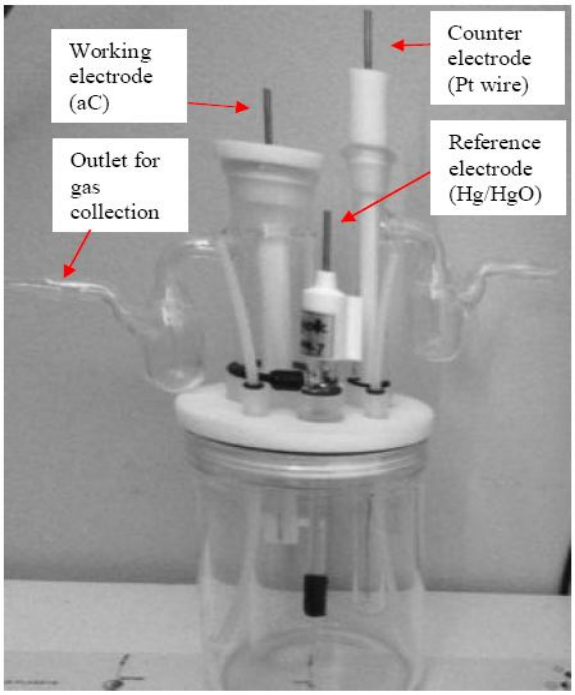


Figure 2. Three-electrode electrolytic cell. [Source: A. Oberoi, 2015]



Figure 3. Electrochemical workstation used in experiments



Figure 4. Graduated cylinder used for gas collection. [Source: A. Oberoi, 2015]

III. RESULTS AND DISCUSSIONS

The proton conductivity of all the fabricated samples was determined using the previously obtained proton resistance from nyquist plots from EIS and using the same in equation1. A typical nyquist plot obtained is shown in figure 5.

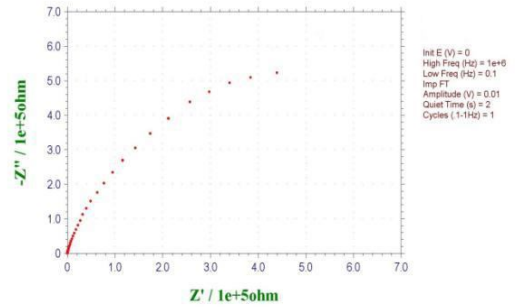


Figure 5. A typical nyquist plot obtained from EIS.
[Source: A. Oberoi, 2015]

The obtained proton conductivity of all the samples was compared and found to be in the range of 0.0050 – 0.00112 S/cm. The comparison of resulted figures is shown in graphical form in Figure 6. It was observed that proton conductivity of the aC sample increased with increase in concentration of the sulphuric acid used as electrolyte.

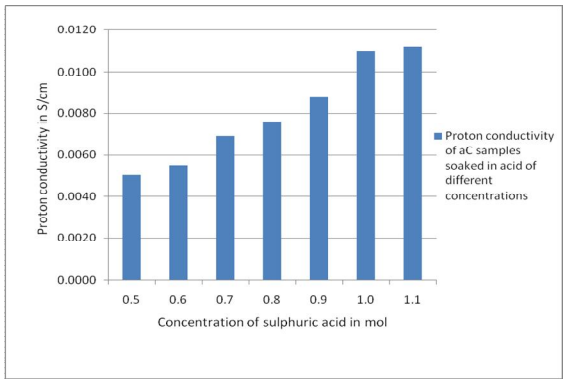


Figure 6. Comparison graph of proton conductivity of aC samples soaked in acid of different concentrations.

The double-layer capacitance of the fabricated aC samples were determined by a well known technique of cyclic voltammetry that gives result in form of cyclic voltammogram. The peak current read from cyclic voltammogram was employed in equation 2 to find out double-layer capacitance of the fabricated aC samples soaked in acid of different concentration. A typical voltammogram obtained from testing is shown in Figure 7.

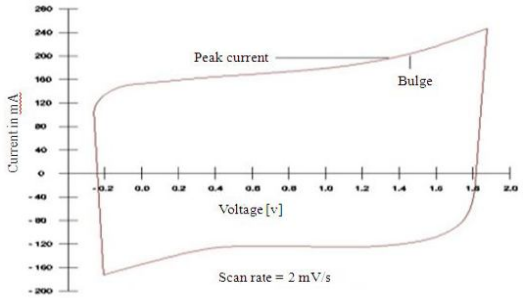


Figure 7. A typical voltammogram obtained from cyclic voltammetry of aC samples.
[Source: A. Oberoi, 2015]

The result obtained from calculations was recorded and compared. The comparison is shown in form of a graph in Figure 8. The measured double-layer capacitance was found to be in range of 19.5 – 41.0 F/g. It was observed that double-layer capacitance increased with increase in concentration of the electrolyte until 1.0 mol concentration and decreased at 1.1 mol concentration.

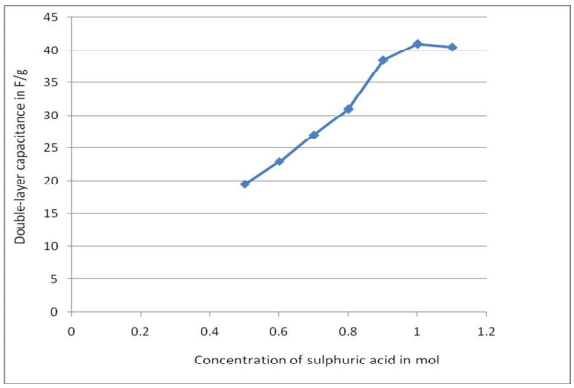


Figure 8. Graph representing the measured double-layer capacitance of aC samples soaked in acid of different concentrations.

Hydrogen storage capacity of the fabricated sample aC electrodes soaked in different concentration of acid electrolyte was determined by galvanostatic charging and discharging process. A set amount of charging current was supplied to the setup to initiate electrolysis of the contained water. Some the products of water electrolysis i.e. hydrogen and oxygen were generated and were either collected in graduated cylinders as gas or partially got stored in aC sample as electrochemical compund. The charging current was supplied until a sudden rise in gas production was observed which gave the impression that the storage was full. The charging operation was stopped thereafter.

The apparatus was allowed to rest for 1 hour before starting galvanostatic discharging operation. The aC sample was discharged at constant pressure of 30 mA until an open circuit was reached. No electric potential was applied in galvanostatic discharging operation and the whole operation was run solely by the hydrogen energy that was stored in aC sample during charging operation. The total time of discharging was noted and used later on calculations. The amount of hydrogen that came out of the storage was calculated by Faradays equation given in Eq 3.

$$M = \frac{I.t}{1000.F}$$

Eq. 3

where,

M → mass of hydrogen generated in kg.

I → discharge current in mA.

t → discharge time in sec.
F → Faraday's constant (96485 C mol^{-1})

The weight of collected hydrogen gas was calculated from ideal gas equation (given in Eq. 4) and was subtracted from the total equivalent amount of hydrogen produced to get the actual hydrogen stored in aC sample. A typical glavanostatic charging and discharging curve in shown in Figure 9. The result is compared in a graphical form and shown in Fig. 10.

$$PV = nRT \quad \text{Eq. 4}$$

where,
P → pressure of gas in pascals
V →volume of gas in m^3
n →number of moles
T → temperature in Kelvin
R → universal gas constant = 8.314 J K^{-1} mol^{-1}

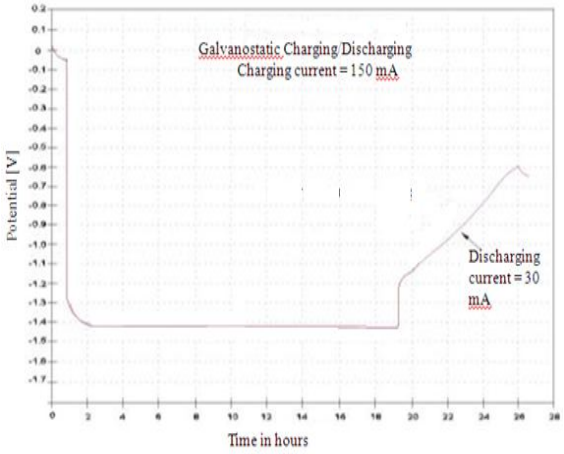


Figure 9. A typical galvanostatic charge-discharge curve for sample aC electrode in 1 mol sulphuric acid with charging current as 150 mA and discharging current as 30 mA.

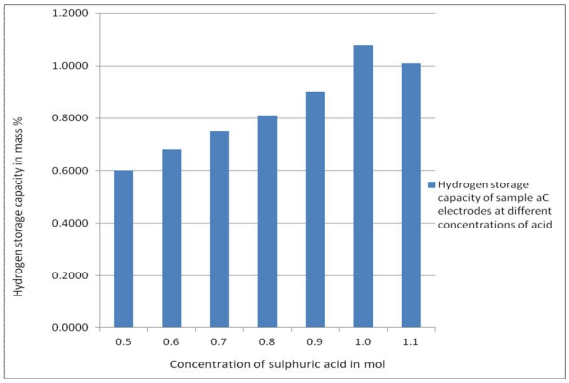


Figure 10. Comparison graph of hydrogen storage capacity of sample aC electrodes soaked in acid of different concentrations.

From analysis of the obtained result it was observed that hydrogen storage capacity of sample aC electrodes increased with rising concentration of the electrolyte. But, a sudden drop was observed when the concentration of acid used as electrolyte was increased from 1.0 mol to 1.1 mol. One of the possible reasons for this drop could be that after certain concentration level sulphate ions of acid assist hydrogen ions to form gas rather than getting stored as physisorption or chemisorptions.

CONCLUSION AND RECOMMENDATIONS

The present research showed that hydrogen could go in and out from the activated carbon electrode (made from a commercial activated carbon powder) soaked in dilute sulphuric acid during charging and subsequent discharging. The highest achieved gravimetric energy density is 1.08 mass% which is comparable with commercially available metal hydride-based compressed hydrogen canisters, lithium-ion and lithium-polymer batteries. Besides, activated carbon showed acceptable levels of proton conductivity and double-layer capacitance when soaked in dilute sulphuric acid.

The experiments that have been conducted in this research work showed the potential of a commercial activated carbon for hydrogen storage and to be considered in the field of fuel cell for automobiles.

Further investigation is now required to determine the relationship between characteristics of the aC material used to make hydrogen storage electrodes−such as porosity, pore sizes and structure and electrochemical hydrogen storage capacity.

CONFLICT OF INTEREST

The author declares no conflict of interest for the presented work.

ACKNOWLEDGEMENTS

The author thanks Prof. John Andrews from RMIT University, Australia and Brown Coal Innovation Australia for their technical and financial support.

REFERENCES

[1] Isaac M. Held and Brian J. Soden, "Robust responses of the hydrological cycle to global warming," Journal of Climate, vol. 19, pp. 5686-5699, March 2006.
[2] Jara Imbers, Ana Lopez, Chris Huntingford, and Myles Allen, "Sensitivity of Climate Change Detection and Attribution to the Characterization of Internal Climate Variability," Journal of Climate, vol. 27, pp. 3477-3491, 2014.
[3] Richard H. Moss, Jae A. Edmonds, Kathy A. Hibbard et al., "The next generation of scenarios for climate change research and assessment", Nature 463, pp. 747-756, February 2010.
[4] Christopher D. G. Harley, A. Randall Hughes, Kristin M. Hultgren et al., "The impacts of climate change in coastal marine systems", Ecology Letters (9), pp. 228-241, 2006.
[5] Robert Costanza, Lisa Graumlich, Will Steffen et al., "Sustainability or collapse: what can we learn from integrating the history of humans and the rest of nature?" A Journal of the Human Environment 36(7), pp. 522-527, 2007.

[6] Seung-ki Min, Xuebin Zhang, Francis W. Zwiers and Gabriele C. Hegerl, "Human contribution to more-intense precipitation extremes", Nature 470, pp.378-381, February 2011.
[7] Kilian Lutz, "Not all oil price shocks are alike: disentangling demand and supply shocks in the crude oil market", CEPR Discussion Paper No. 5994, December 2006.
[8] Noureddine Krichene, "World crude oil and natural gas: a demand and supply model", Journal of Energy Economics, vol. 24 (6), pp. 557-576, November 2002.
[9] Ibrahim Sami Nashawi, Adel Malallah and Mohammed Al-Bisharah, "Forecasting world crude oil production using multicycle Hubbert model", Energy Fuels, vol. 24 (3), pp. 1788-1800, 2010.
[10] Yuya Kajikawa, Junta Yoshiyuki Takeda and Katsumori Matsushima, "Tracking emerging technologies in energy research: towards a roadmap for sustainable energy", Journal of Technological Forecasting and Social Change, vol. 75 (6), pp. 771-782, July 2008.
[11] Ibrahim Dincer, "Renewable energy and sustainable development: a crucial review", Journal of Renewable and Sustainable Energy Reviews, vol. 4 (2), pp. 157-175, June 2000.
[12] M. K. Deshmukh and S. S. Deshmukh, "Modeling of hybrid renewable energy systems", Journal of Renewable and Sustainable Energy Reviews, vol. 12 (1), pp. 235-249, January 2008.
[13] Mikhail Granovskii, Ibrahim Dincer, and Marc A. Rosen, "Economic and environmental comparison of conventional, hybrid, electric and hydrogen fuel cell vehicles", Journal of Power Sources, vol. 159 (2), pp. 1186-1193, September 2006.
[14] John O 'M Bockris, "Hydrogen economy in the future", International Journal of Hydrogen Energy, vol. 24 (1), pp. 1-15, January 1999.
[15] John O 'M Bockris, "The origin of ideas on a hydrogen economy and its solution to the decay of the environment", International Journal of Hydrogen Energy, vol. 27 (7-8), pp. 731-740, July-August 2002.
[16] Vincent Bérubé, Gregg Radtke, Mildred Dresselhaus and Gang Chen, "Size effects of the hydrogen storage properties of nanostructured metal hydrides: a review", International Journal of Energy Research, vol. 31 (6-7), pp. 637-663, May 2007.
[17] Saeed Seif Mohammadi, "Investigation of a reversible PEM fuel cell with integrated metal-hydride hydrogen storage", Master of Engg. by Research thesis, RMIT University Australia, August 2012.
[18] John Andrews and Saeed Seif Mohammadi, "Towards a 'proton flow battery': investigation of a reversible PEM fuel cell with integrated metal-hydride hydrogen storage", International Journal of Hydrogen Energy, vol. 39, pp. 1740-1751, 2014.
[19] Mohammad Javad Jazaeri, "The feasibility of a unitized regenerative fuel cell with a reversible carbon-based hydrogen storage electrode", Master of Engg. by Research thesis, RMIT University Australia, August 2013.
[20] Amandeep Singh Oberoi, "Reversible electrochemical storage of hydrogen in activated carbons from Victorian brown coal and other precursors", PhD thesis, RMIT University Australia, November 2013.
[21] K. Jurewicz, E. Frackowiak and F. Beguin, "Electrochemical storage of hydrogen in activated carbons", Journal of Fuel Processing Technology, vol. 77-78, pp. 415-421, 2002.
[22] Amandeep Singh Oberoi, "Metal hydride-nafion composite electrode with dual proton and electron conductivity", International Journal of Smart Grid and Clean Energy, vol. 3 (3), pp. 270-274, July 2014.

★★★