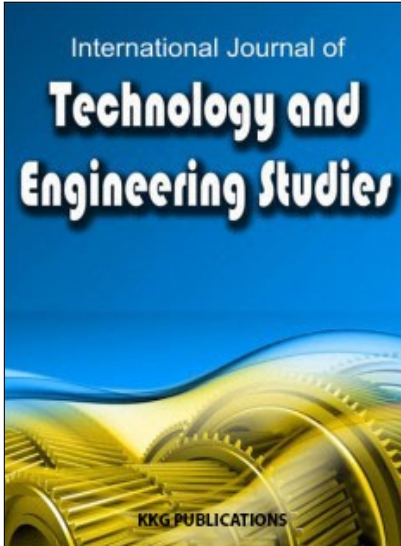


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IMPROVEMENT OF FUEL CELL PERFORMANCE BY APPLICATION OF CARBON NANOTUBES

SNATIKA SARKAR ¹, VIJAYA ILANGO ^{2*}^{1,2} Birla Institute of Technology & Science, Bits Pilani, Dubai**Keywords:**Carbon Nanotubes
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Abstract. Energy conservation is an important issue in a world that is still largely dependent on non-renewable energy resources. Despite the growing awareness about the advantages of renewable resources, fossil fuels in the form of coal and petroleum dominate the energy consumption scenario. The primary reason for this situation is the greater commercial viability of fossil fuels. Fuel cells are an important, environment friendly means of utilizing the energy stored in hydrogen. Proton Exchange Membrane Fuel Cells (PEMFCs) are the most advantageous fuel cells for automobiles as they are compact, more efficient and can operate at lower temperatures. However, the traditional PEMFCs require performance improvement. The paper discusses a possible material that may find potential application in the fuel cell as an alternative to the carbon nanotubes existing so far. The material allows the storage and application of solar energy in addition to hydrogen energy (which was utilized in traditional PEMFCs).

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INTRODUCTION

Carbon nanotubes have played an important role in ensuring the economic feasibility of fuel cells due to their application as a catalyst support. However, research on further improving upon these nanostructures still continues. This paper explores the possibility of using azo-benzene-based carbon nanotubes as a catalyst support in Proton Exchange Membrane Fuel Cells. These special type of functionalized carbon nanotubes were originally developed as a means to convert and store solar energy to chemical energy. The objective of this review is to put forward the idea of combining this particular nanostructure's applications to harness two forms of renewable energy-solar energy and hydrogen energy.

Carbon nanotubes were first observed by Japanese researcher Sumio Ijima, in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps that was intended to produce fullerenes. A Carbon Nanotube is essentially an allotrope of Carbon, comprised of graphite sheets rolled up into hollow cylinders. These structures can be classified as separate molecules due to their dimensions. Their diameters range in the order of nanometers, and their length in approximately micrometers. The folding of graphite sheets can occur in numerous ways, resulting in different diameters and microscopic structure. The resulting geometric structures can be used to explain various properties of the nanotubes. The synthesis processes adapted to manufacture CNTs (Single walled, or Multi-walled) depend on the applications [1]. Carbon nanotubes are commonly produced

by the following techniques: [1]

- Arc Discharge
- Laser Ablation
- Chemical Vapor Deposition

Carbon nanotubes have an average tensile strength of approximately 35 GPa, nearly 7 times that of HS Steel and Kevlar 49. They also have thermal conductivity of 5000W/mK, which is 5 times that of Carbon Fiber. Carbon nanotubes have much higher electrical conductivity compared to any other form of carbon. This makes them useful in the field of energy as effective electrodes (when grown on graphene sheets) and catalyst supports in fuel cells, due to their large surface area. [2] carried out BET calculations to determine the surface area of carbon nanotubes. It was found to be $1315m^2/g$ for SWNT and $50m^2/g$ for MWNT with a diameter of 35nm and 40 walls. Carbon nanotubes are of primary importance as a catalyst support in Proton Exchange Membrane Fuel cells.

Though copper has a much higher electrical conductivity than carbon nanotubes, it does not have as high a surface area, which is also an important criteria for a catalyst support in such fuel cells. A fuel cell is a device that generates electricity from electrochemical reactions as long as it is supplied with an external source of chemical energy [3]. This source of chemical energy is Hydrogen. Hydrogen can be directly supplied from hydrogen storage devices or indirectly. Indirect hydrogen supply is provided in the form of hydrocarbon fuels like Methane, coal-based gases etc.

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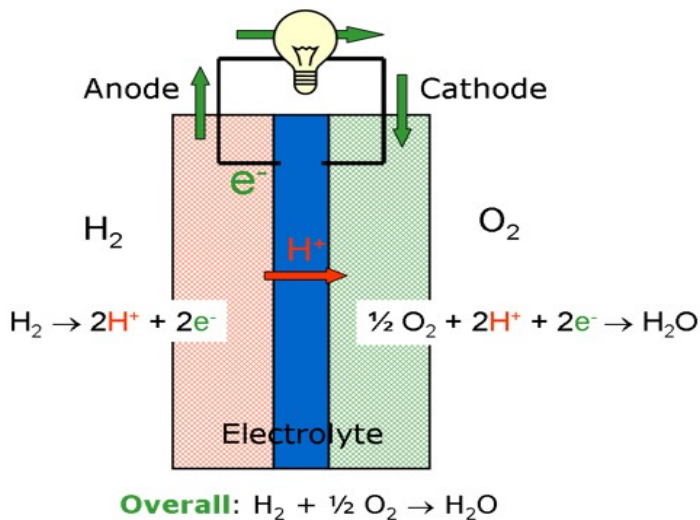


Fig. 1. A typical fuel cell

The basic working of a typical fuel cell can be summarized as follows:

- Hydrogen enters the cells at the anode to get oxidized to H⁺ ions. Electrons generated pass through external circuit.
- Protons pass through the electrolyte towards the cathode.
- Oxygen enters the cathode and combines with the electrons and protons to release Water as the final by-product.

PROTON EXCHANGE MEMBRANE FUEL CELLS

These are low temperature fuel cells operating at temperature ranges between 80 – 100°C (Low temperature

PEMFC) and 100 – 200°C (High Temperature PEMFC). High temperature PEMFC have a higher Platinum loading and resistance to impurities, but a lower power density than low temperature PEMFCs. The average current density in these fuel cells should ideally be 3321A/m² for commercial viability [3].

These cells comprise of a solid electrolyte in the form of a water-based, acidic, thin membrane sheet, usually made from polymers. E.g., Nafion. The electrolyte consists of Platinum catalyst on either side. Thus we have Platinum-based electrodes in this cell. Platinum speeds up the reactions at both the electrodes.

Platinum is present as small particles on larger carbon particles that act as catalyst support.

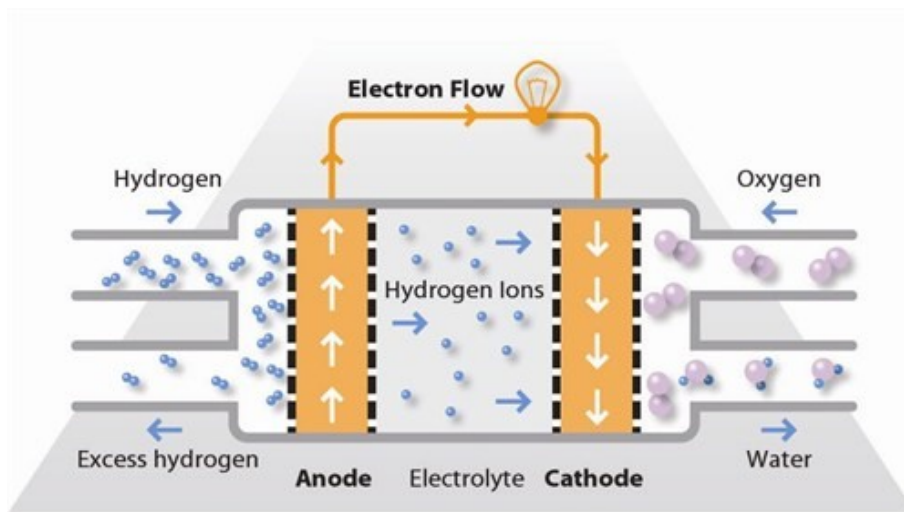


Fig. 2. Proton exchange membrane fuel cell

Hydrogen gets oxidized at the anode to produce hydrogen ions which migrate across the nafion polymer membrane (electrolyte) towards the cathode where they combine with oxygen and electrons to form water as the final product. The catalyst is coated onto the electrolyte by rolling, spraying or hot pressing.

These fuel cells are compact, have quick start up (due to low operating temperature) and light weight. There is also little hazard of corrosive fluid storage. These fuel cells are more efficient compared to others (40% efficiency).

APPLICATION OF CARBON NANOTUBES IN FUEL CELLS

Despite their advantages, these fuel cells originally had certain limitations that have been more or less successfully combated by the use of carbon nanotubes.

Improvement of Platinum Loading at the Electrodes, Especially the Cathode

Originally, Platinum black was used as the catalyst for PEMFC. Platinum Black as a catalyst involved coating black platinum powders as a thin film on a platinum surface. But due to the presence of less active sites and higher Platinum loading ($\sim 25 - 50 \text{ mg/cm}^2$), it was replaced by carbon supported Platinum catalysts which have a higher surface area [4]. With the introduction of more active sites, a smaller Platinum loading is feasible as it is distributed over a larger area. Platinum loading reduced to $0.4-0.5 \text{ mg/cm}^2$, thus making the fuel cell an economically more viable option. Alternative catalyst support combinations can also be considered to improve Platinum utilization. E.g., Pt/X (X is Co, Ni or Fe). Carbon nanotubes have also gained popularity for the role of catalyst support because of their high surface area thereby leading to greater number of active sites and smaller catalyst particles. Vertically aligned CNTs can be a promising catalyst support compared to other CNTs due to their highly ordered structure. This ensures larger surface area, good electrical conductivity and more active sites for Pt utilization.

Complex Oxygen Reduction Reaction at the Cathode

Unlike the oxidation reaction at the anode, Oxygen reduction reaction at the cathode has a slow and complex mechanism. Thus it requires more Platinum loading to speed up the reaction. Increased Pt loading requires more number of active sites, and hence a greater surface area catalyst support. The Catalyst support can be modified with additional functional groups that can act as sites for Pt. CNTs with their higher surface area can ensure availability of more active sites and higher Pt loading. However, it is important not to exceed a

certain limit for Pt loading in the catalyst support. Too many Pt particles usually include larger particles which effectively reduce the availability of active surface areas. Thus, even with Carbon Nanotubes as a catalyst support, the cell performance is adversely affected [5].

Loss of Stability of the Catalyst

Sintering of Pt particles reduces the number of active sites. The Pt particles dissolve in the acidic environment and precipitate into larger particles which further reduce the availability of active sites. The main aim in this case would be to strengthen the bond between the metal catalyst and support so as to decrease the mobility of Pt particles. Corrosion of the carbon catalyst support is another major disadvantage. This process occurs by oxidation of the carbon followed by hydrolysis and gasification to carbon dioxide [6], [7]. A thin Pt film can be coated on the electrode surface using techniques like sputter deposition. The resulting film completely covers the CNT, reducing carbon corrosion. The use of carbon nanotubes implies increased graphitization, thereby reducing the number of oxidation sites for carbon corrosion to take place in. Also, the strong connection between the Pt surface and the CNT wall hinders detachment of Pt molecules, ensuring stability of the catalyst.

RESULTS AND DISCUSSION

It has been found from current literature that multi-walled, vertically aligned and preferentially functionalized carbon nanotubes have greater potential for use in fuel cells [8], [9], [10], [11]. However, it would be an interesting challenge to counter the limitations of single walled nanotubes, and one such technique is their functionalization. Single walled carbon nanotubes can be functionalized covalently as well as non-covalently.

Common functional groups attached to CNTs used in Proton Exchange Membrane Fuel Cells include carboxyl groups. However, based on our findings regarding carbon nanotube functionalization, we would like to suggest a type of functionalized CNT that has recently gained attention for solar energy storage. These are Azo-based carbon nanotube systems [12].

Azobenzene (2 phenyl rings linked by N-N double bond) or their derivatives can be chemisorbed to the CNT substrates with the help of amide linkers. The nanotubes help create a close-packed and ordered crystalline structure. However, these structures require the use of a solvent where the Azo/CNT structure can remain dissolved for greater stability. The azobenzene structures, on exposure to sunlight get excited from trans to cis state.

The resulting difference in energies between the ground state and excited state gets stored as chemical energy in the bonds.

The advantages of the suggested CNT-based catalyst support are as follows:

- Azo/CNT systems have an energy density of 690 Wh/L (Each CNT can support 4-8 azobenzene molecules around its circumference)
- Additional energy is stored in the form solar energy, and can be released on applying heat or using a cata-

lyst [8]. Since one CNT can support 4-8 azobenzene molecules, total heat application for the cis to trans reaction would be between 100 – 200°C. Since proton exchange membrane fuel cells can operate at temperatures up to 200°C, the resulting heat (producing a temperature of 347°C [12]) can be used by the compound to return to the ground state, releasing the stored solar energy which can be utilized for various purposes. Moreover, the excitation of the compound results in the release of electrons that contribute to the circuit flow outside.

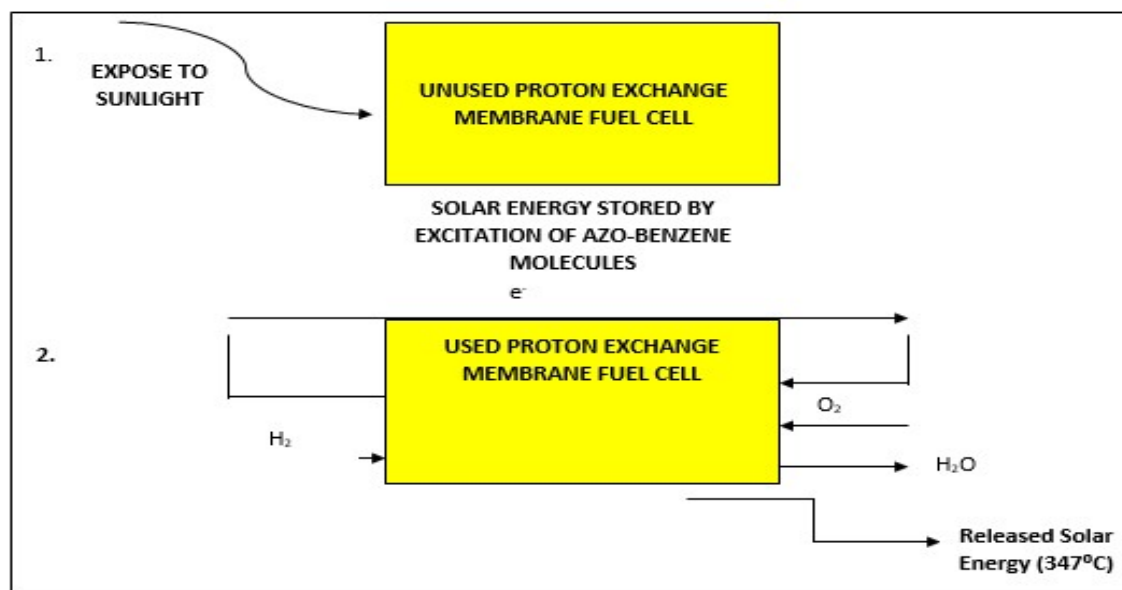


Fig. 3. Proposed mechanism of modified PEMFC

- An ordered structure also leads to ease of manipulation of inter and intra molecular interactions, which in turn increases energy storage. Manipulations of molecular interactions include addition of polar functional groups to those portions of the molecules exposed to the solvent. This may have negligible effect on the H and Ea value, but it increases the solubility of the nanostructures, ensuring greater stability of the crystalline structure [12]. E.g., to increase the fuel efficiency, it is desirable to have both H and Ea reasonably high. Substitution of hydroxyl groups for one or more hydrogen in the phenyl rings can ensure this due to the addition of more hydrogen bonds. The more the number of hydrogen bonds, the greater is the stability of the molecule.

The disadvantages of these AZO-based systems are [2], [12]: Requirement of a suitable solvent to maintain the CNT/Azo structures in. Proton Exchange membrane fuel cells require the use of solid polymeric Nafion electrolyte. However,

in place of Nafion, a liquid electrolyte can be used. Liquid electrolytes are not completely unheard of in these fuel cells. Many such liquids are used as electrolytes in place of Nafion for Accelerated Durability Tests of these fuel cells. Less severe and corrosive liquids could be utilized. A solvent, may be better but not entirely compulsory. If however, it is used, the requirement of Platinum as catalyst can be eliminated. Doping these structures with nitrogen may serve as a better option as a catalyst support system.

CONCLUSION

Presently, Azo-Benzene-based carbon nanotubes are considered as an economically viable means for storing chemical energy, but they can also find application as an alternative catalyst support to other types of carbon nanotubes used for this purpose. The resulting fuel cell can utilize two green energy sources, namely Hydrogen and Solar energy. Solar Energy which gets stored as chemical energy on excitation of

Azo-Benzene-based carbon nanotubes gets released during the working of the fuel cell and can be simultaneously utilized for other practical applications such as heating applications, running electrical appliances etc. Application of Azo-Benzene-based carbon nanotubes in Proton Exchange Membrane Fuel Cells may result in changes to their functioning or even their

basic structure, but the advantageous properties of these carbon nanotubes allow it to store and convert solar energy to chemical energy thereby qualifying it to be a strong candidate as a multi-tasking catalyst support in PEMFCs. Azo-benzene-based carbon nanotubes display immense possibilities of increasing the impact of Fuel Cells in the energy market.

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