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Miniaturized 3D Printed Carbon Cloth-Based Hydrogen Fuel Cell

Vanmathi S[1], Jayapiriya U S[2] and Sanket Goel[3]

[1]MEMS, Microfluidics and Nanoelectronics (MMNE) Lab, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India

[2]MEMS, Microfluidics and Nanoelectronics (MMNE) Lab, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India

[3]Department of Electrical and Electronics Engineering, Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, Hyderabad 500078, India

Abstract

Hydrogen is the most fascinating renewable energy source. Hydrogen fuel cells have facilitated the capture of hydrogen and converted power into useful energy. In this work, carbon cloth-based electrodes were used to develop miniaturized hydrogen fuel cells (HFC) using 3D-printed sealing parts. Cobalt (II) Oxide (Co_3O_4), synthesized from Cobalt (II) chloride hexahydrate and reduced Graphene Oxide (rGO) based nanoparticles, was used to advance the catalytic activity at the anode, and Platinum-Carbon (Pt/C) coated carbon cloth serves as the cathode. A 4.5 mg of aluminum foil embedded inside the carbon cloth was utilized for hydrogen generation. The cell discharge analysis was observed to be stable up to 4h 60 minutes, as during this time aluminum foil produced hydrogen. This compact 3D-printed HFC device was capable of producing an open circuit potential of 480 mV and a peak power density of 25.6 µW cm^2 when the Sodium Hydroxide (NaOH) alkaline electrolyte was introduced into the HFC. Furthermore, the series and parallel combination of devices produced higher voltage and power output. This cell design can be used as the power source for devices with small power applications.

Keywords: Fuel cell, Carbon cloth, 3D printer, Aluminum, Catalyst, Renewable energy.

NOMENCLATURE

Abbreviations	
HFC-Hydrogen fuel cell	
CC – Carbon Cloth	
GDE – Gas Diffusion Electrode	
OCV – Open Circuit Voltage	
PLA – Polylactic acid	
CNT-Carbon Nano Tube	

1.Introduction

Hydrogen is a sustainable and clean energy carrier that can be produced through chemical reactions or electrochemical approaches[1]. Hydrogen–based fuel cells (HFCs) have an edge in terms of efficiency and overall performance to be a true fuel of the future[2]. Hydrogen is a chemical energy carrier that can produce electricity[3]. The dynamic hybrid hydrogen fuel cell is an alternate tuning parameter method for to improvement of component loss in vehicles [4]. The fuel cell provides full energy even to electric vehicles and permits the utilization of electric energy. This electrochemical process is necessary to produce efficiency during the transition period of the recent power systems and batteries for cars, which can be replaced by fuel cells. It is a safe and efficient generation, storage, and usage of the hydrogen-based fuel cell power system[5].

3D printing techniques are generally used in external manufacturing technologies and produce maximum energy sources[6]. The maximum work of hydrogen fuel is based on the entropy accuracy of the fuel cell converts chemical energy- to electrical energy and provides possibly the most efficient and flexible power output with a 3D printed device[7]. Fuel cells offer better fuel efficiency and near-zero-emission[8]. Further, with the increased use of HFCs, it will be more efficient for future generations. It can be used in transportation, and portable electronic and small power applications[9].

Typically, a fuel cell consists of an anode for oxidation reaction, a cathode for reduction reaction, and an electrolyte that allows ions. Hydrogen is oxidized on the anode side to give free electrons and protons to the cathode side. Such electrons flow through the cathode side, while protons go through the electrolyte. Then, the proton combines with the oxygen at the cathode side and produces water as a by-product[10]. The electricity produced by this method is clean and it does not have any negative impact fact on the environment[11]. Yifei Wang et al., proposed a paper-based hydrogen fuel cell, with platinum/carbon(Pt/C) as an anode, and manganese dioxide/carbon nanotube(MgO_2/CNT) was used on the cathode, which delivered a maximum power density of 4 mW cm^{-2}[12]. J.P. Esquivel et al., developed a portable paper-based fuel cell with magnesium-iron (MgFe) alloy that generate hydrogen and obtained a power density of 25 mW cm^{-2}[13].

In this work, a carbon cloth-based hydrogen fuel cell has been developed and its performance optimization has been discussed. Here, aluminum foil embedded inside the paper substrate was utilized as the hydrogen source. The catalyst was deposited on the anode side and Pt-coated carbon cloth acted as the cathode. Sodium hydroxide (NaOH) acted as an alkaline electrolyte solution which was supplied through capillary action. The aluminum foil reacted with the electrolyte to produce H_2 gas at the anode side and the cathode O_2 from the ambient air was utilized to generate power. The electrolyte and catalyst concentration were optimized and polarization performance was studied. In this manner, a low-cost, concise, lightweight fuel cell system was developed.

2. Experimental methods

2.1. Chemicals

Commercially available hydrophobic carbon cloth (CC) and Platinum (Pt/C)-0.2mg/cm^2- 20%) coated gas diffusion electrode (GDE) (Fuel Cell Store, USA) was used. Catalysts, such as Cobalt (II) chloride hexahydrate, were purchased from Tokyo Chemical Industries (TCI), Japan, and the reduced Graphene Oxide (rGO) Synthesized material was used. Sodium hydroxide Pellets (NaOH) were purchased from Sisco Research Laboratories (SRL), India. A Fused Deposition Modeling (FDM) based 3D Printer was purchased from Flashforge. The double-distilled 18.2 MΩ.cm Milli-Q (Wasserlabs) water was utilized to prepare all the experimental solutions. Grade 1 filter paper was used for the substrate, and Aluminum Foil-Food grade 11-micron thickness was used as a hydrogen source.

2.2. Synthesis and deposition of Co_3O_4 – rGO nanoparticles.

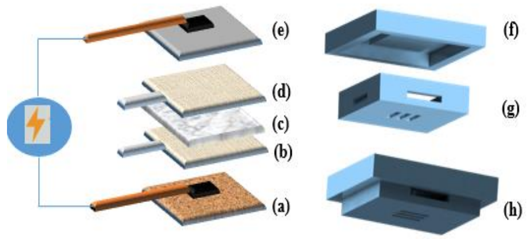
To obtain the Co_3O_4 nanostructures, the $CoCl_2$-$6H_2O$ were mixed in 60 ml deionized water and stirred for 30 min to convert uniform solution[14]. Then Grade 1 filter paper dip-coating into the solution for 1 hr coated paper dry to use hot air oven 70°C at 3h, then take out the paper and Lash it out the coated Co_3O_4-rGO and grind it for small nanoparticles.

2.3. Preparation of carbon cloth electrode

The hydrophobic carbon cloth (0.25 cm^2) was plasma treated for 1 minute [15] to induce hydrophilic groups on the electrode surface, which will aid in the absorption of the cobalt oxide (II)-reduced Graphene oxide (Co_3O_4 - rGO) composite. The anode ink was prepared by dispersing 3 mg of Co_3O_4 - rGO composite in 2 ml of acetone, followed by 30 minutes of sonication to achieve uniform distribution of catalyst ink. After sonication, 100 µl of catalyst ink was drop cast on the anode CC electrode surface and dried in a hot air oven at 60°C for 5 minutes. Commercially available Platinum-coated carbon cloth GDE (Pt/C)-0.2mg/cm^2- 20% was used as the cathode. The platinum catalyst reaction was attributed to improving the performance of hydrogen production[16]. Grade 1 filter paper was used as a separator between the electrodes. The wax barrier makes them organize separate fuel streaming and improves a proper hydrophobic region. Wax was patterned on filter paper using a manual dipping process.

3. Fuel cell device design and integration:

Once the electrodes were prepared, integrated with anode cobalt oxide-Rgo coated cloth and cathode platinum cloth was used. Fig (a, e). An Aluminum foil enclosed with grade 1 wax-coated filter paper was placed in between the electrodes (Fig. 1d, b) and then integrated into a miniaturized 3D printed device (Fig. 1h). The miniaturized device was designed by



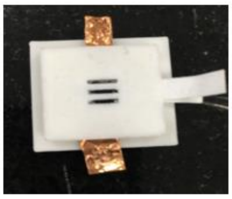


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Figure 1: Exploded view of the hydrogen fuel cell a) Cobalt oxide coated anode carbon cloth, b) and d) Grade 1 filter paper, c) Al foil, e) Pt coated cathode carbon cloth, f) 3D printed top, g) 3D printed bottom and h) complete device after sealing, I) real image of 3D printed hydrogen fuel cell device.

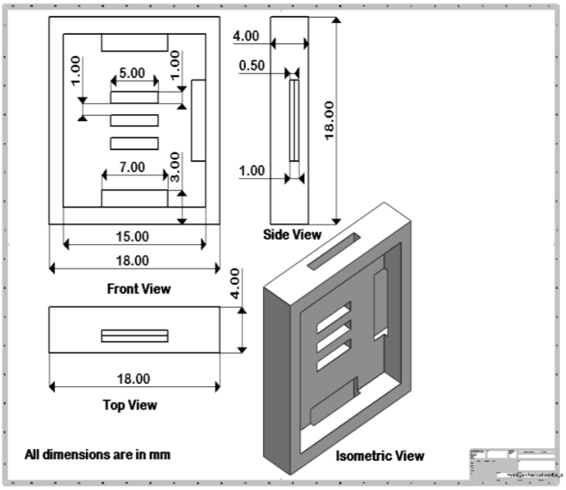

Fig 2a): Bottom base hydrogen fuel cell

SOLIDWORKS software and printed using a tabletop 3D printer (Flashforge) with Polylactic acid (PLA) filaments dimensions to fit the electrodes (Fig.1I). The copper tape was used as a current collector for the electrodes[17]. Aluminum foil (3.5 mg (1 cm 11-micron) thickness was enclosed in a paper substrate to reduce the rate of corrosion during the H_2 generation (Fig.c). NaOH electrolyte (100 µl) was supplied with the help of an inlet present on the grade 1 filter paper. The 3D printed top (Fig. 1f, Fig.2b) was completely sealed so that there is no intrusion of air in the anode side. However, the 3D-printed bottom (Fig.1g, Fig.2a) had a window to allow oxygen from the atmosphere to enhance the power output from the mHFC[18].

4. Electrochemical Technique:

Electrocatalytic analysis of the electrodes was executed using a potentiostat/Galvanostat (SP- 150 from Biologic, France). Open circuit voltage (OCV) was initially measured by a multimeter for up to 10 minutes for OCV stabilization. Using a two-electrode configuration where the anode is connected with the counter and reference electrode and the cathode is connected with the working electrode was used for recording power performance values [19].

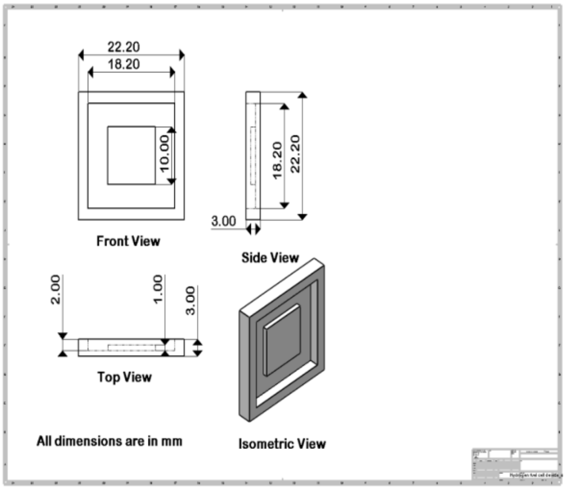

Fig 2b): Top base hydrogen fuel cell

4.1. Hydrogen fuel cell operation and performance

After optimization, the HFC configurations were realized on a miniaturized 3D printed platform for different polarization studies. This HFC will take time to produce a stable performance due to self-pumping and air-breathing Fig. (3a). The hydrogen fuel cell device is connected to two series and two parallel connections. HFCs were evaluated by connecting anode MFC1 to cathode MFC2. In the series configuration, the current will be the same and voltage will be added Fig. (3b). The parallel configuration is operated opposite to the series, instead of adding voltage, the current is added and the voltage is the same as the single MFC Fig. (3c).

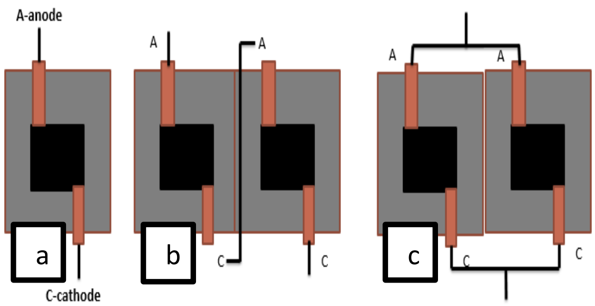

Fig 3: Carbon cloth-based HFC a) single HFC b) series HFC c) Parallel configuration

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5. Results and Discussion

5.1 Structural characterization:

Scanning electron microscopy (SEM) of the CC electrodes shows that the CC has a textile-like structure (Fig. 4a). The anode catalyst cobalt oxide–rGO coated CC electrodes were analyzed by using the SEM (Fig.4b) and cathode catalyst Platinum-carbon coated CC electrodes were analyzed by using the SEM (Fig.4c). Cobalt oxide-rGO synthesized nanoparticle image analysis (Fig 4d) Also, the electrodes were analyzed by Energy Dispersive X-Ray Analyzer (EDAX) for their elemental composition. The EDAX analysis of the anode confirmed the presence of Co-12.96%, O-32.84%, and C-54.20%. The cathode consisted of elements Pt-20.16% and carbon -79.84%.

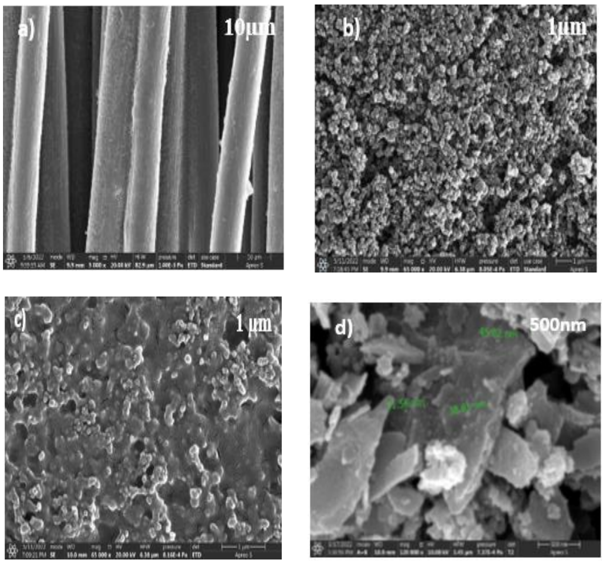

Figure 4(a): Bare carbon cloth, (b) SEM and EDAX analysis of cobalt Oxide-graphene, (c) SEM and EDAX analysis of Platinum-carbon coated, (d) Synthesized Cobalt Oxide-rGO SEM analysis.

5.2 Aluminum foil study

The aluminum foil affects the hydrogen supply rate in process of the device running. The higher the aluminum foil thickness reduces the hydrogen supply. To investigate this effect, two Al foil studies were adopted for HFC, and performance was compared. The 11-micron Al foil achieved a higher peak power density than the 18-micron Thickness. The 11-micron thickness of 4.5mg of Al foil is used max OCV is 255 mV Fig. 5(a) and max power density is 8 µW/cm^2. The 18-micron thickness is used to find the hydrogen peak power density of the polarization

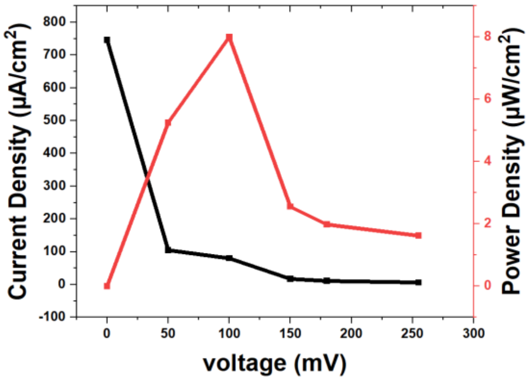

Fig 5a): Effect of 11 microns Al foil

curve max OCV is 325mv Fig. 5(b) and max power density is 2.21µW/cm^2. To increase the thickness, the size will be reduced, then the aluminum foil was corroded as soon as early. So, hydrogen production was stopped during that time.

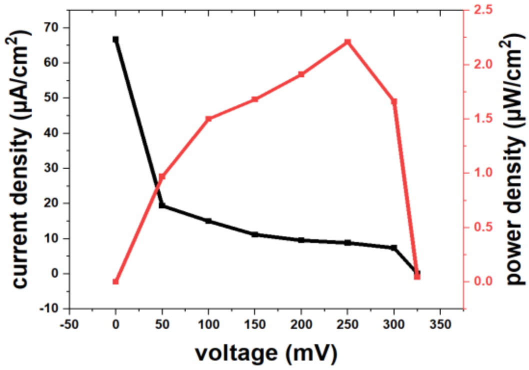

Fig 5b): Effect of 18 microns Al foil

5.3. Effect of electrolyte and catalyst concentration

The performances of anode and cathode, with a surface area of 0.25 cm^2, were analyzed using chronoamperometric (CA) analysis to find the power output. The concentration effect of NaOH was studied for a range of 0.2 mM - 3 mM and its corresponding power density values were plotted. The hydrogen generation rate was decreased while the concentration of NaOH increased due to faster corrosion of Al foil because of which the performance of the device was also reduced. Finally, it was observed that 0.5 M NaOH concentration produced a high peak power density at an open-circuit voltage of 440 mV (Fig 6a). The catalyst study of 0.5 mg/ml to 3.5 mg/ml was used to analyze the

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power density at each loading denoted by different catalytic responses on carbon cloth electrodes. The fuel cell performance decreased at a higher Catalyst loading because of diffusion of the reacting molecule's adsorption is low at higher loading and it reduced the activation energy[20].

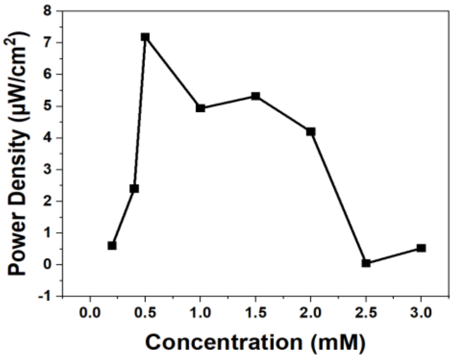

Figure 6: (a) Concentration Study

It was clear from these (Co_3O_4 – rGO) that 3 mg/ml of catalyst loading delivered more power density is 15.4 μW/cm^2(Fig.6b).

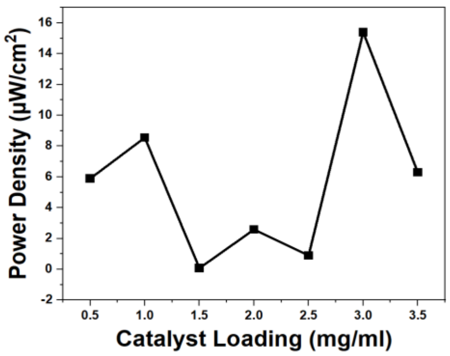

Figure 6: (b) Catalyst loading

5.4 Polarization performance:

The optimized parameters, such as electrolyte concentration and catalyst loading, were used to study the performance of the HFC. The power curves were plotted with the help of the chronoamperometry technique by decrement of voltage until 0 mV from the open circuit potential. The developed HFC delivered a stable voltage of 480 mV within 10 minutes of electrolyte supply through For the capillary action of the paper-based inlet. A high-power density of 25.6 μW/cm^2 was observed at a potential of 400 mV with a maximum current density of 175 μA/cm^2. The polarization curves (Fig.7) show that there exist activation losses and mass transfer losses during the hydrogen generation.

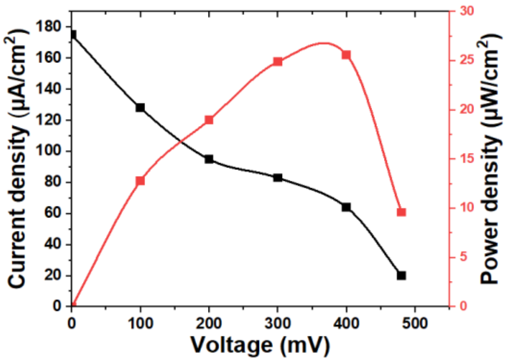

Figure 7: Polarization performance of mHFC using optimized parameters

5.5 Discharge analysis

The stability of the device is analyzed with open circuit potential 435 mV OCV of the cell was measured over time 160 minutes almost linear. Based on this analysis, the fuel cell has been provided with a consistent and stable OCV up to 2.4h after a gradual decrease in yield. This carbon cloth-based fuel cell is stable more time comparatively than paper (Fig.8).

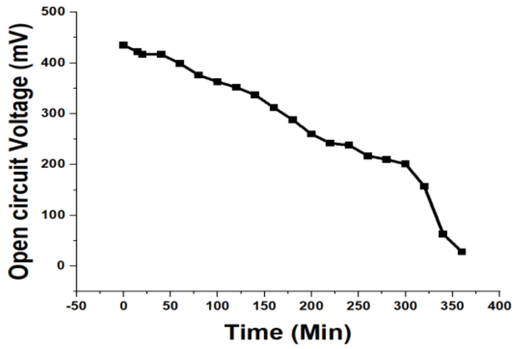

Fig. 8 Discharge analysis

6. Conclusion

In this work, carbon-cloth (CC) based electrodes were fabricated and tested for their efficiency in a miniaturized HFC 3D printed device. Al foil was embedded inside the paper as a hydrogen source and CC modified with catalysts were used as the anode and cathode electrodes. The HFC was capable of energy harvesting a power density of 25.6 μW/cm^2 with a max OCV of 480 mV which could be a suitable energy source for small power applications. However, further power output and stability can be increased with a change in the amount of aluminum foil used for hydrogen generation and electrolyte used.

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