Production of fuel cell components by 3D printing for automotive applications

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ABSTRACT

Direct ethanol fuel cells are becoming a promising alternative to their hydrogen counterparts, overcoming the challenges of H_2 storage and distribution. Ethanol has many advantages, but, in practice, its direct oxidation in a fuel cell is still a slower and more complex reaction when compared to hydrogen, reducing the system's efficiency. Different strategies can be considered to overcome this problem, so that ethanol-based fuel cells become the most promising technology for automotive applications, especially in Brazil due to the fuel availability. In this project, we focused on developing a scalable technique to produce lightweight bipolar plates, which are among the bulkiest/heaviest components in polymer-based fuel cell stacks. In this project, we produced bipolar plates from conductive polymer materials through additive manufacturing (3D printing) and assembled and tested direct ethanol fuel cells using the plates produced. Lightweight conductive polymer nanocomposites can be produced by adding carbon-based nanoparticles to a polymer matrix. Additive manufacturing is an important ally in the production of fuel cell parts, as their design can be promptly adjusted and optimized iteratively.

Keywords: DEFC, fuel cells, ethanol, 3D print

INTRODUCTION

Fuel cells (FCs) hold significant promise as energy conversion devices for both stationary power systems and automotive applications, owing to their remarkable energy/power densities. Among the diverse range of FCs, direct-ethanol (EtOH) fuel cells (DEFCs) have emerged as focal points due to their lightweight construction, high energy density, favourable operating conditions, and straightforward system design [1,2]. Typically, two variants of polymer-based direct ethanol fuel cells exist: those employing proton exchange membranes (PEM) and those utilizing anion exchange membranes (AEM) [3]. It is noteworthy that the rate of ethanol oxidation reaction and oxygen reduction reaction is notably accelerated in an alkaline environment. However, for integration into high-power systems, combining multiple modules to form stacks becomes necessary [1,3].

Traditionally, stacks consist of collector plates, bipolar plates, and membrane electrode assemblies (MEA) [4]. Bipolar plates, which typically constitute 80% of the total stack weight, commonly utilize stainless steel due to their superior processability, relatively high electronic conductivity, and corrosion resistance [5]. Consequently, stainless steel bipolar plates find extensive use in transportation fuel cell systems. Indeed, despite the beneficial characteristics of stainless steel, its drawbacks such as high weight, cost, and machining time have spurred the exploration of alternatives [6]. Consequently, numerous studies have deepened the search for materials and manufacturing processes that provide lightweight properties while maintaining compatibility with fuel cell stacks. New materials such as titanium, polymers (e.g., polycarbonate and poly lactic acid), carbon-based materials (e.g., graphene, carbon nanotube), and innovative manufacturing techniques like hot pressing and additive manufacturing have been investigated to produce lightweight bipolar plates suitable for fuel cell stacks [7]. In addition, the 3D printing process is known as the most adaptable and fast manufacturing process.

In this study, we propose the production of filaments by combining various polymers, including polyetherimide, polycarbonate, aliphatic polyamide, polyphtalamide and polyvinylidene fluoride with carbonaceous nanoparticles such as carbon black, single-walled carbon nanotubes, multi-walled carbon nanotubes, and graphene. The resulting electrically conductive nanocomposites can be utilized to produce filaments suitable for printing bipolar plates intended for use in stacks of direct-ethanol fuel cells (DEFCs).

EXPERIMENTAL DETAILS

Materials

All the polymers and nanoparticles used were commercial material grades. Polycarbonate (PC) and polyetherimide (PEI) were supplied by Sabic, aliphatic polyamide (PA66) and polyphtalamide (PPA) were supplied by BASF, and polyvinylidene fluoride was supplied by Arkema.

The carbon black (CB) sample (Vulcan XCmax 22) was supplied by Cabot Corporation. Single-walled nanotubes (SWCNT) were purchased from OCSiAl (Tuball), multi-walled carbon nanotubes (MWCNT) were purchased from NanoView, and graphene nanoplatelets (G) were supplied by 2D Fab.

Composite Formulation

The sequence of processing steps taken to define the best processing conditions and hybrid composition of the target composite filament is presented in Table 1. The selection was based on the electrical properties of the composites produced, a key property for the desired filament to be produced for 3D printing.

Table 1: Nanoparticle concentration used in each composite.

Polymer Matrix	Carbon Black (wt%)	Graphene (wt%)	MWCNT (wt%)	SWCNT (wt%)
PC, PA66, PPA, PVDF, PEI	30	10	1	1

Processing

The nanocomposites were manufactured using an Xplore Micro compounder MC 15 HT co-rotating intermeshing twin-screw extruder. Various screw speeds and time profiles were tested. The parameters tested are presented in Table 2. The materials were extruded in the shape of 1,75 mm thick filaments by passing through a 3 mm die followed by stretching.

Table 2: Processing parameters for each polymer matrix.

Polymer Matrix	Processing time (min)	Screw speed (RPM)	T (°C)
Polycarbonate (PC)	0 5 10	100 200 300	290
Aliphatic polyamide (PA66)	0 5 10	100 200 300	250
Polyphtalamide (PPA)	0 5 10	100 200 300	325
Polyvinylidene fluoride (PVDF)	0 5 10	100 200 300	240
Polyetherimide (PEI)	0 5 10	100 200 300	350

Characterization

To prepare the filament samples for electrical conductivity measurements, their contacts were painted with silver glue to carry out DC (direct current) electrical measurements. The tests were conducted in quintuplicate using the 4-point probe method. Figure 1 presents the experimental setup to carry out the electrical measurements. A Keithley SourceMeter was used to take the measurements and a sample holder was made to hold the samples in position.

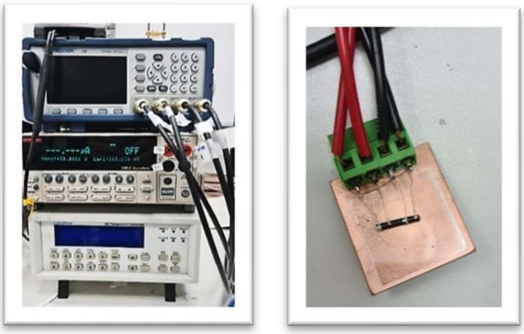

Figure 1: Keithley SourceMeter equipment and sample holder.

3D Printing

After the filaments were obtained, samples were 3D printed using a DDDrop RapidOne 3D printer. Temperature and layer height conditions were established from the software, using and infill of 100%, a raster layer orientation of ±45°, and a printing speed of 20 mm/s.

A bipolar plate model was produced using Free CAD software and the slicing process to generate the G-code was done using the program "Simplify 3D".

3D printed bipolar plates and fuel cell prototype

Bipolar plates were 3D printed with a serpentine channel geometry with an active of 5 cm^2 (Figure 2). For the fuel cell tests a prototype was made and was operated using hydrogen and ethanol as fuels. The bipolar plate prototype was printed using a commercial conductive ABS-based nanocomposite filament.

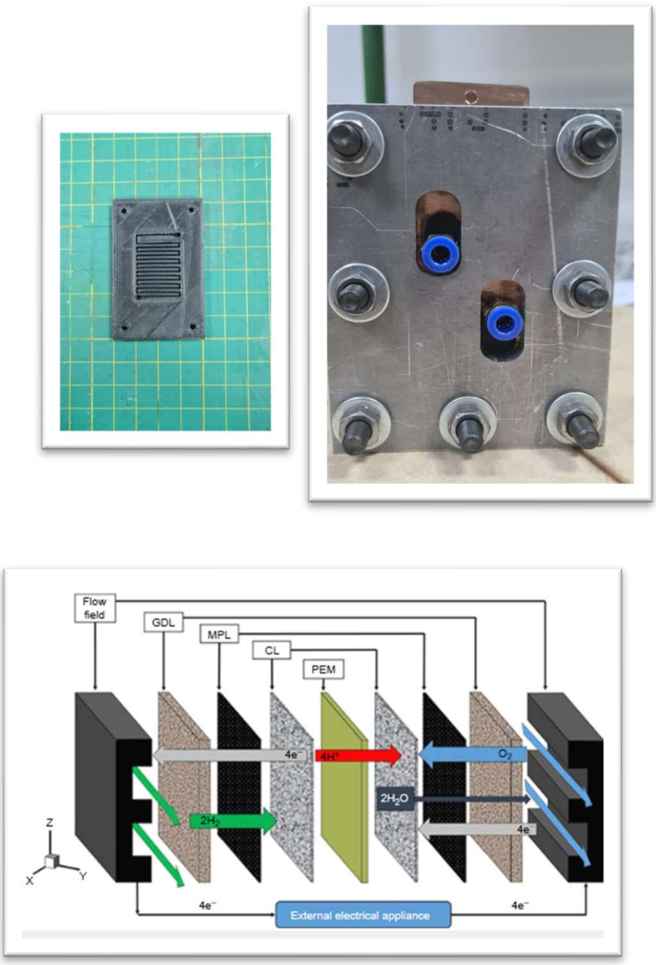

Figure 2: 3D printed nanocomposite bipolar plate, fuel cell prototype and schematic assembly of single PEM fuel cell (GDL: gas diffusion layer, MPL: microporous layer, CL: catalytic layer, adapted from [1].

Results and Discussion

Electrical conductivity of the nanocomposites

Figures 3 through 7 present the effects of composition and processing conditions on the electrical conductivity of the composites produced for each polymer system. By comparing all polymer / nanoparticle systems, some trends can be identified. Firstly, across all polymer systems, samples containing carbon black typically exhibit the highest conductivities. This result is expected, given the high concentration used (30 wt%). The spherical shape of carbon black particles aids in their dispersion within a polymer matrix even at high concentrations, achieving electrical percolation and satisfactory conductivity levels suitable for the proposed bipolar plate application.

However, it is important to consider the potential of other nanoparticles, depending on the chosen polymer matrix. The addition of 5 wt% graphene was generally insufficient to achieve significant electrical conductivity. Among the polymer systems studied, only PEI showed promising results, reaching conductivities on the order of 10^{-5} S/cm (Fig. 7). The highly aromatic structure of PEI may contribute to its strong affinity with graphene, but the conductivity levels are still generally low. Graphene has a lamellar structure that can form a percolating network at relatively low concentrations, provided there is a good degree of exfoliation / dispersion inside a polymer matrix. The results for PEI suggest that lower processing speeds favor the formation of a percolating network, leading to higher conductivities. PEI is a highly viscous, high-temperature thermoplastic, and despite its excellent mechanical and thermal properties, producing functional, conductive 3D printing filaments with PEI may be challenging due to its high viscosity.

Carbon nanotubes are often used as additives to promote electrical conductivity in polymers at low concentrations. However, for most of the polymer systems studied, the addition of 1 wt% multiwalled carbon nanotubes did not significantly increase the electrical conductivity. The only exception was PC+MWCNT mixed at 300 rpm, which reached a conductivity of around 10^{-2} S/cm. More noteworthy results were observed with single-walled carbon nanotubes in two polymer systems, PA66 and PVDF. In these cases, conductivity levels comparable to those obtained with carbon black were achieved, but at much lower nanoparticle concentrations.

In most cases, little influence of the processing parameters could be observed. This suggests that particle concentration and the individual physicochemical affinity between the polymer and the carbon nanoparticles play a more significant role in promoting the formation of percolating networks and achieving high conductivity levels.

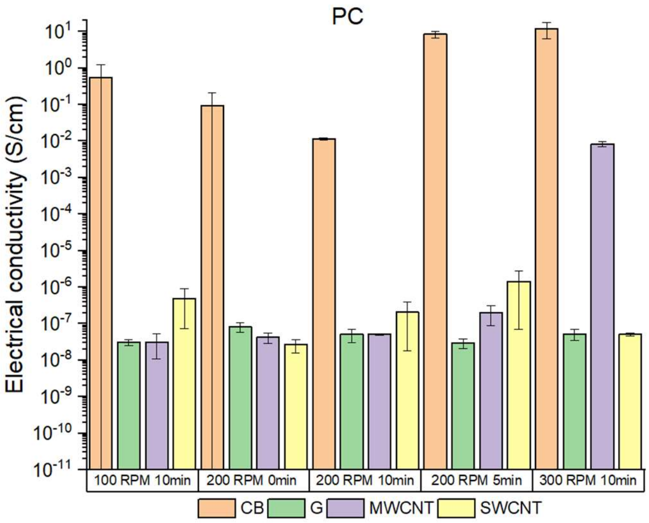

Figure 3: Electrical conductivity of the PC nanocomposites.

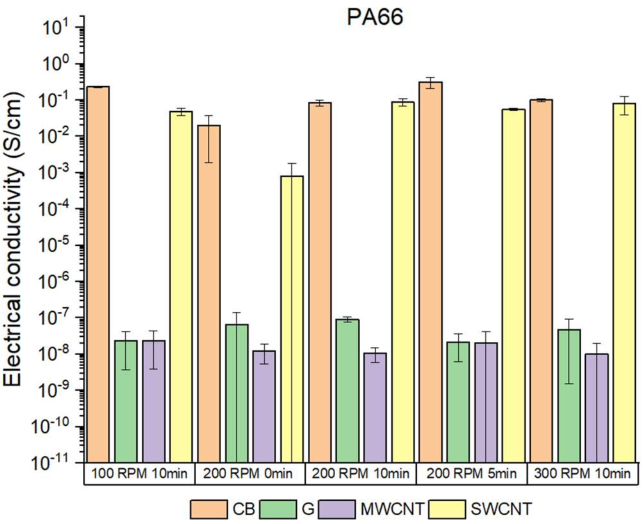

Figure 4: Electrical conductivity of the PA66 nanocomposites.

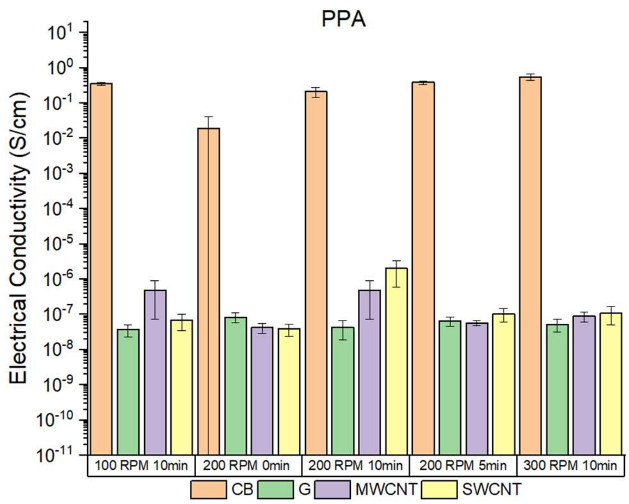

Figure 5: Electrical conductivity of the PPA nanocomposites.

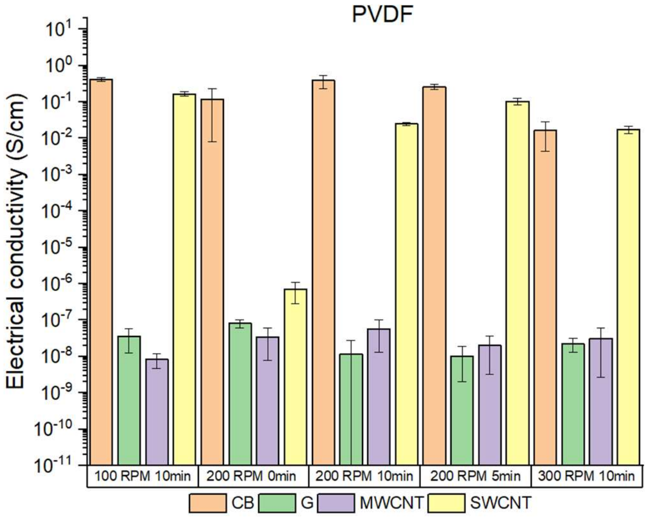

Figure 6: Electrical conductivity of the PVDF nanocomposites.

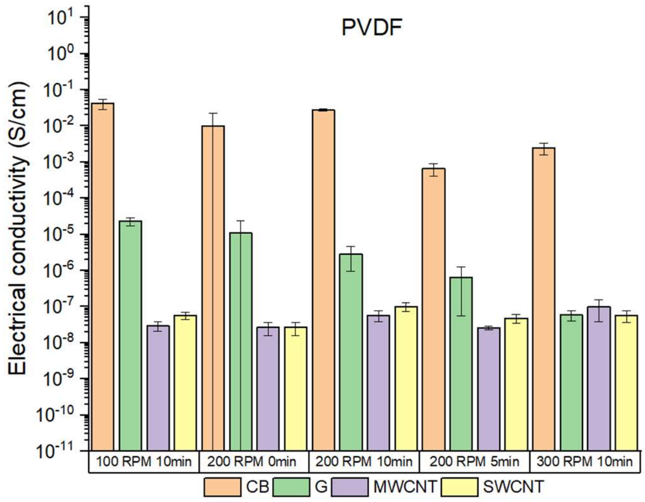

Figure 7: Electrical conductivity of the PEI nanocomposites

Based on the results obtained for each polymer system, Table 3 shows the most promising compositions and processing conditions. These compositions can be selected to produce 3D printing filaments for preparing lightweight, tough bipolar plates for fuel cell applications.

Table 3: Selected nanocomposite systems with the highest electrical conductivities.

Nanocomposite	Speed (RPM)	Time (min)	Conductivity (S/cm)
PC/CB	200	5	$1{,}2\times10^{1}$
PPA/CB	300	10	$5{,}4\times10^{-1}$
PVDF/CB	100	10	$4{,}1\times10^{-1}$
PA66/CB	200	10	$2{,}7\times10^{-1}$
PVDF/SWCNT	200	10	$1{,}0\times10^{-1}$
PPA/SWCNT	200	10	$1{,}5\times10^{-6}$
PA66/SWCNT	200	5	$8{,}8\times10^{-2}$
PEI/CB	100	10	$4{,}2\times10^{-2}$
PC/MWCNT	200	5	$8{,}0\times10^{-3}$
PEI/G	100	10	$2{,}3\times10^{-5}$

Fuel cell performance

The polarization and power density curves for a PEM fuel cell using conductive 3D-printed ABS bipolar plates operating in H_2/Air gas supply mode are shown in Figure 8. Despite the overall performance being affected by the benchtop experimental setup, the cell performed well, as expected. The low gas flow rate into the system resulted in limited current density, as the conversion to electrical current is proportional to the amount of gas supplied to the cell. However, the cell's efficiency was not impacted, since its design takes into account the thermodynamic potential E°=1.229 V and the cell's operating potential E_{cell}=0.7V, despite the significantly lower current density. Equation 1 presents the calculation of the efficiency of the H_2/Air fuel cell

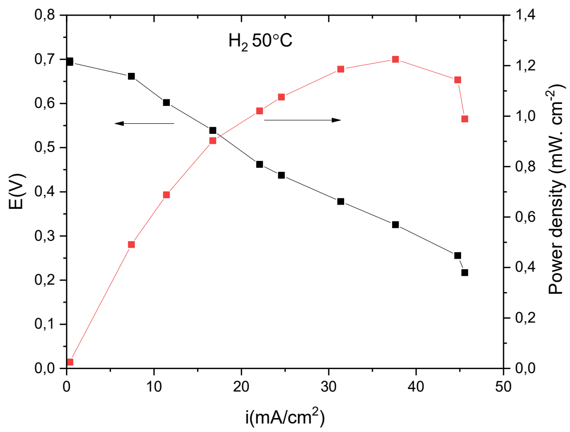

Figure 8: H_2/Air fuel cell performance.

$$\eta = \frac{E_{cel}}{E^0_{cel}} \times 100\% = \frac{0{,}7}{1{,}229} \times 100\% \cong 57\% \qquad (1)$$

Figure 9 presents the polarization and power density curves for the fuel cell operating in the ethanol/air system. Considering that ethanol provides lower power density than hydrogen, the measured values of power and current density in the cell are lower than in the previous system. However, the calculated efficiency was greater than the hydrogen cell, as shown by Equation 2.

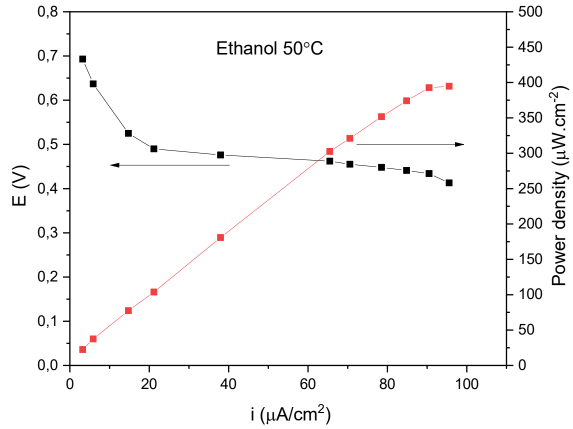

Figure 9: Ethanol/Air fuel cell performance.

$$\eta = \frac{E_{cel}}{E^0_{cel}} \times 100\% = \frac{0{,}7}{1{,}145} \times 100\% \cong 61\% \qquad (2)$$

Both tested systems demonstrated that the 3D printed bipolar plates operated adequately, and new conductive nanocomposite filaments can be used in future developments of such devices aiming for lightweight automotive applications.

CONCLUSIONS

In this research, a series of conductive polymer-carbon nanoparticle nanocomposites were produced to maximize electrical conductivity for developing 3D printing filaments for use in fuel cell applications. These conductive composites were used to print tough, lightweight bipolar plates for ultra-light PEMFCs. A commercial 3D printing system was employed to fabricate bipolar plate prototypes with a serpentine-type flow channel. The cells were tested using hydrogen and ethanol as fuels.
This study provides promising results for creating a roadmap to develop the next generation of fuel cells. These low-cost, lightweight and tough fuel cell components can be scaled up to make direct ethanol polymer-based fuel cells a viable alternative power source for automotive applications. The next steps in this study involve producing high-performance

conductive bipolar plates through 3D printing, utilizing filaments made from the materials developed. Additionally, fuel cell stacks will be assembled using these materials, aiming to obtain lighweight, scaled-up devices that deliver higher power output for automotive applications.

REFERENCES

[1] Akay, R. G., & Yurtcan, A. B. (2020). Direct Liquid Fuel Cells: Fundamentals, Advances and Future. In *Direct Liquid Fuel Cells: Fundamentals, Advances and Future*. https://doi.org/10.1016/C2018-0-04168-7

[2] Pramuanjaroenkij, A., & Kakaç, S. (2023). The fuel cell electric vehicles: The highlight review. In *International Journal of Hydrogen Energy* (Vol. 48, Issue 25). https://doi.org/10.1016/j.ijhydene.2022.11.103

[3] Saisirirat, P., & Joommanee, B. (2018). Study on the micro direct ethanol fuel cell (Micro-DEFC) performance. *IOP Conference Series: Materials Science and Engineering*, *297*(1). https://doi.org/10.1088/1757-899X/297/1/012002

[4] Zhang, J., Wu, J., Zhang, H., & Zhang, J. (2013). PEM Fuel Cell Testing and Diagnosis. In *PEM Fuel Cell Testing and Diagnosis*. https://doi.org/10.1016/C2009-0-63216-5

[5] Kangfu Ruan, Linlin Yang, Hai Sun, Gongquan Sun, (2022) Distribution of relaxation times: A method for measuring air flow distribution in high-temperature proton exchange membrane fuel cell stacks, *Journal of Power Sources*, V 523, https://doi.org/10.1016/j.jpowsour.2022.231000.

[6] Jang, Gye-Eun, and Gu-Young Cho. (2022). Effects of Ag Current Collecting Layer Fabricated by Sputter for 3D-Printed Polymer Bipolar Plate of Ultra-Light Polymer Electrolyte Membrane Fuel Cells" *Sustainability* 14, no. 5: 2997. https://doi.org/10.3390/su14052997

[7] Hyunguk Choi, Dong Jun Seo, Won Young Choi, Seo Won Choi, Myeong Hwa Lee, Young Je Park, Tae Young Kim, Young Gi Yoon, Sung-Chul Yi, Chi-Young Jung, (2021) An ultralight-weight polymer electrolyte fuel cell based on woven carbon fiber-resin reinforced bipolar plate, Journal of Power Sources, V 484, https://doi.org/10.1016/j.jpowsour.2020.229291