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**Design and Construction of a Demonstrative Hybrid System Consisting of a Solar Panel, a Stack of
Regenerative PEM Fuel Cells and Supercapacitors**

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ABSTRACT

The continuous search for improvements in clean energy systems and processes has led to the development of techniques with improved production efficiency and electrical energy storage. Some examples are represented by regenerative fuel cells and supercapacitors.

In this work, we report on a small-scale hybrid renewable hydrogen prototype, which uses a photovoltaic panel to provide electricity (2.8 V) to a regenerative fuel cell stack and also to a supercapacitor module. With the regenerative cell in electrolysis mode, the process of water electrolysis occurs, generating the reactive gases (H₂ and O₂) which are being stored in small water tanks. In fuel cell mode, these gases are fed to the regenerative cell in order to produce electrical energy. The supercapacitors release additional energy when needed.

The electrical energy is sent to a DC engine which allows for the movement of a small toy car. The supercapacitors supply power to the engine at the moment of start when the fuel cell is not able to provide sufficient energy for initial movement. The supercapacitors are rapidly discharged by the engine, and operating depends on the fuel cells until completion of the stored hydrogen.

The fuel cells and supercapacitors were prepared in our laboratory. The fuel cell stack was integrated by two membrane-electrode assemblies (MEA) of 4 cm² active area. Ink loading was performed by the drop method using Pt/Ru catalyst for the cathode and Pt catalyst for the anode (fuel cell mode). The supercapacitor electrodes were prepared from mesoporous carbon, polyvinylidene fluoride, and a liquid electrolyte of sulphuric acid is used.

An electrical circuit was designed to control current flow. The toy car with a total weight of 1.2 kg was shown to move at a speed of 2.0 m/s.



1. Introduction

Global fossil energy consumption has increased in recent years due to population growth, increased development and industrialization, causing environmental pollution, climate change, etc. For this reason, the optimization of alternative technologies for clean energy generation, based on low-cost, low-noise, highly efficient and high quality systems, has become a matter of great interest. In this context, hydrogen as a fuel has received considerable attention for its energetic properties, being the fuel with highest energy density [1]. A device to channel this energy vector into electrical energy is represented by the fuel cells of proton exchange membrane (PEMFC).

The present work implements a regenerative PEM-type fuel cell (RFC), which has the particularity of being able to generate hydrogen and oxygen gases by water electrolysis, using electrical energy from a photovoltaic panel in order to perform the process, as well as to generate electrical current as a conventional PEMFC. In this project, the electrical current is provided to a DC engine in order to move a small toy car. An auxiliary boot-up system was incorporated through a bank of supercapacitors, initially charged by the photovoltaic panel.

2. Experimental

The activities were divided in four parts to accomplish the objective:

1. System design.
2. Manufacturing the RFC components and stack.
3. Electrode manufacturing and assembly of supercapacitor
4. System assembly

2.1. System design

Power requirements for the toy car and engine that were used to calculate the parameters of the RFC, were based on experimental work already performed [2]. Was calculated the gas storage system, the supercapacitor module and electrical circuit. the main goal was to produce the electricity needed to drive a 2V engine, 600 mA and a torque of 2kgF * cm. to move the small car of 1200g. (see figure 1).

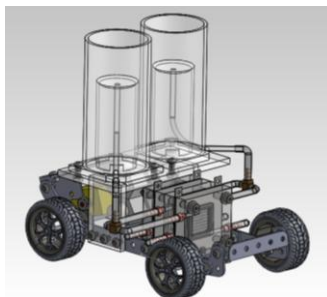


Figure 1. System design

2.2 Manufacturing the components stack URFC

2.2.1 Water storage tanks and gas reactants

Storage tanks were manufactured using acrylic tube of 27.74 mm and 50.80 mm of diameter and with volumetric capacity of 64,16 mm³ for the water container and 26,70 cm³ for the reactant gases. Holes for gas transport were of 2.5 mm diameter, as shown in Figure 2.

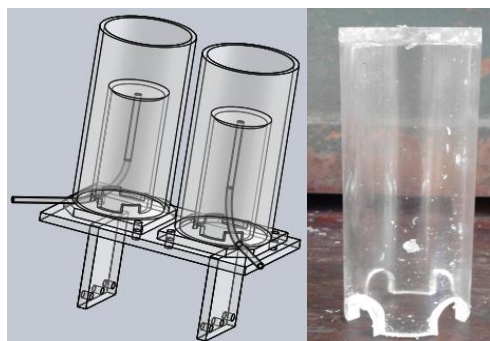


Figure 2. Design and construction of water containers and reactant gases

2.2.2 End plates

The end plates were made of acrylic plate of 1 cm thick using a CNC machine. A channel of 1.5 mm width and perimeter of 80 mm was included for commercial packing in order to prevent leakage of gases and water, as well as holes of 3.18 mm and 0.16 mm for the inlet/outlet of reactant gases and water. Finally, in order to allow compression on the RFC, four holes of 5 mm of diameter were included in the extreme corners of the plates (see figure 3).

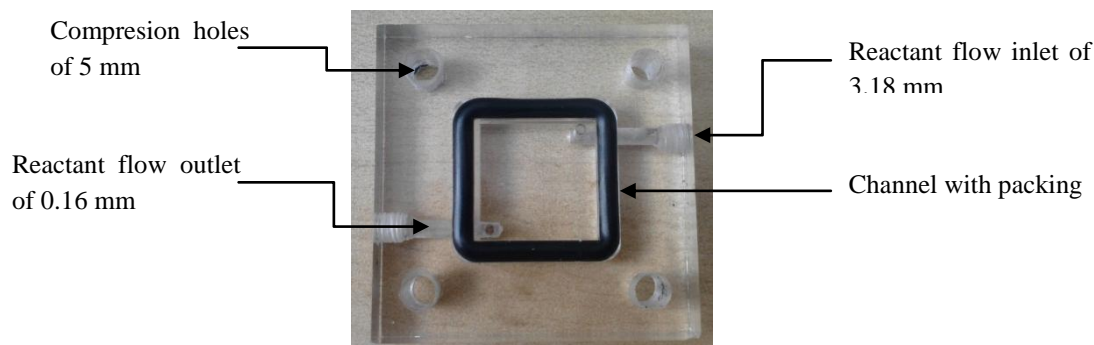


Figure 3. RFC acrylic end plates

2.2.3 Current collector

The current collectors used in the RFC, were machined from a stainless steel (SS316) plate, as shown in figure 4a. The steel provides electrical conductivity in addition to withstand the effects of corrosion from the acid environment. Several holes of 1.98 mm were distributed in the central area of the collector of 4 cm². Also, four holes of 5 mm were incorporated to allow the passage of compression screws. A terminal was machine at the top of the collector for connection to an external load. A silicone gasket (FuelCell) of 0.43 mm thick was used between the surfaces of the collectors in order to electrically insulate and support the commercial packing in the leakage of gases, see Figure 4b.

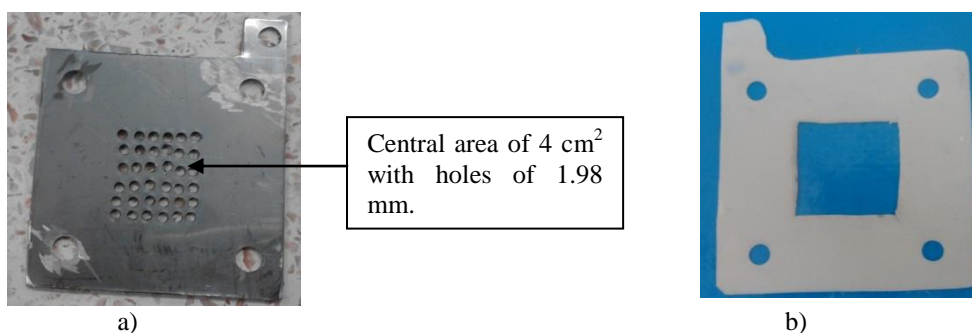


Figure 4a). Current collector y **4b)** Silicone gasket for electrically insulate.

2.2.4 Membrane-Electrodes Assembly

The catalytic layer was applied to an area of 4cm² of the gas diffusion layers (trademark fuelcell) by the drop method. An ink was prepared from carbon supported platinum (Pt) and platinum/rutenium (Pt/Ru - 20% on Vulcan trademark fuelcell), liquid nafion (5%, trademark Electrochem) and isopropyl alcohol. The electrocatalytic ink was deposited with a catalyst load of 0.5 mg/cm². Nafion 115 was used as electrolyte, after activation in H₂SO₄ and H₂O₂. The membrane-electrodes assembly (MEA) was prepared by hot pressing at 120°C with 4000 lb for 4 min [2]. See figure 5.

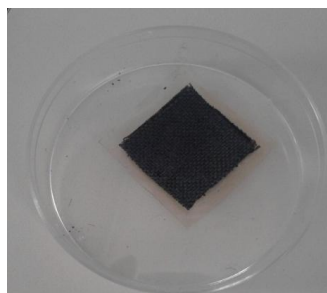


Figure 5. Membrane Electrode Assembly.

MEA's were characterized as conventional fuel cells, injecting a flow of hydrogen and oxygen gas of 0.05 l/min, at a temperature of 25°C in fuel cell test system 850C (Scribner Associates) and using a BioLogic potentiostat/galvanostat.

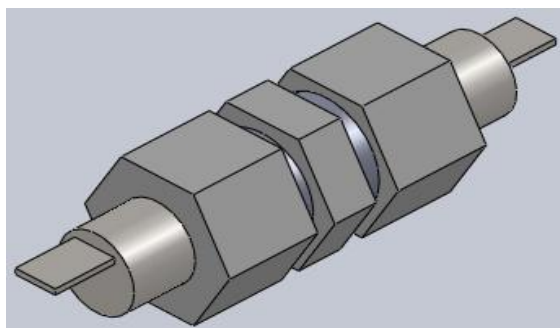
2.3 Electrode manufacturing and assembly of supercapacitor

Supercapacitor electrodes were prepared as cylindrical pellets of 50 mg each, 13 mm diameter and 1 mm thickness, from a homogeneous mixture of 200 mg of electrode power, with the following proportions [3]:

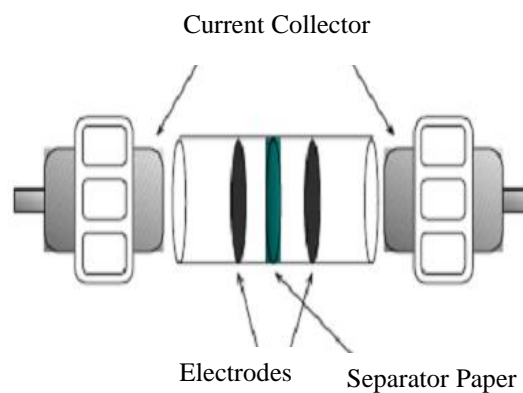
- 75 wt % of mesoporous carbon type Cummings by Asbury Carbon
- 20 wt% of PVDF polyvinylidene fluoride by Aldrich
- 5 wt % of a high electrical conductivity carbon Super P by 3M

by cold compression of 500 kgf for 15 minutes.

Two electrodes of the same material are mounted in a cell made out of teflon (see Figure 6a), separated by paper microfiber discs (Whatman BS45) and with 1.5 ml of 1M H₂SO₄ as electrolyte, as shown in figure 6b. Current collectors were made of stainless steel A20 to resist acid corrosion. Two supercapacitores (SC1 and SC2) were prepared.



a)



b)

Figure 6. Schematic drawing of supercapacitor

Previous to electrochemical characterization, each supercapacitors underwent a pretreatment by cyclic voltammetry (10 cycles, scan rate at 10 mV s⁻¹ and potential range of 0 to 1 V), to improve the interaction of electrolyte ions in the porous structure of the material. The electrochemical analysis of the supercapacitors was performed on the Biologic® potentiostat. Cyclic voltammetry was applied at different scan rates, in a potential range of 0 to 1 V. In

order to obtain the values of specific capacitance for each device, galvanostatic cycles were realized at constant current density. The specific capacitance (C_{esp}) of the material was determined from the following equation 1:

$$C_{esp} = \frac{2 \left(\frac{td * i}{\Delta V_2} \right)}{X * 0.75} \quad (1)$$

Where: i is the current density, t_d is the discharge time, ΔV_2 is the value of the potential, during the discharge process after the collapse due to internal resistance (ESR) of the capacitor, X is the average mass of the two electrodes and 0.75 corresponds to the fraction of active material in the electrode.

2.4 System assembly

For the correct operation of the prototype, it was necessary implement an electrical circuit shown in figure 7, which allows for the different components of the system to be activated and deactivated using four switches. With switches $S3$ and $S4$ opened and $S1$ and $S2$ closed it is possible to perform electrolysis and to load the supercapacitors bank through the photovoltaic panel. Once completed the tasks, the switches $S1$ and $S2$ are opened and $S3$ and $S4$ closed, so the RFC begins to release electrons to the engine while at the same time the supercapacitors are discharged in about 10 sec. Thus, the small car receives the necessary energy impulse and time for the RFC to stabilize the power supply in order to satisfy engine demand.

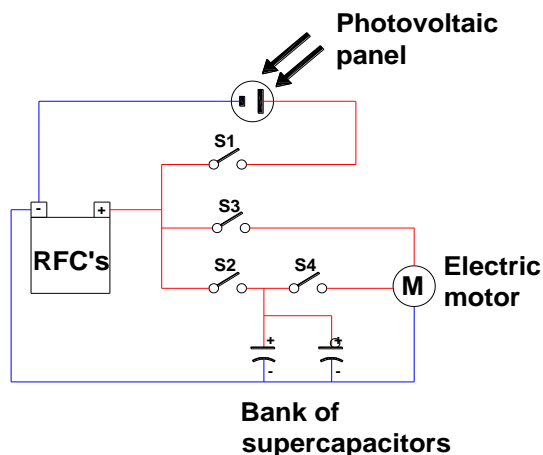


Figure 7 Electric circuit.

All parts of the prototype were assembled (RFC stack with two unit cells, supercapacitor module and the electric engine), as shown in figure 8. The total dry system weight was 940 g and after loading the tanks it was 1200 g. The car speed was 2m/min. Final results are shown in Table 1.

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Table 1. Hybrid system performance

Electrolyzer	
Input voltage of photovoltaic panel	2.8 V
Gas production time	15 min
Volume of hydrogen produced	26 cm ³
Volume of oxygen produced	10 cm ³
Cell PEM	
Stack output voltage	1.3 V
Maximum output current	0.85 A
Output power	2.4 W
Supercapacitors	
Operating voltage	1 V
Capacitancia values	≈ 22 F
System	
Speed	2 m/min
Weight	1200 g

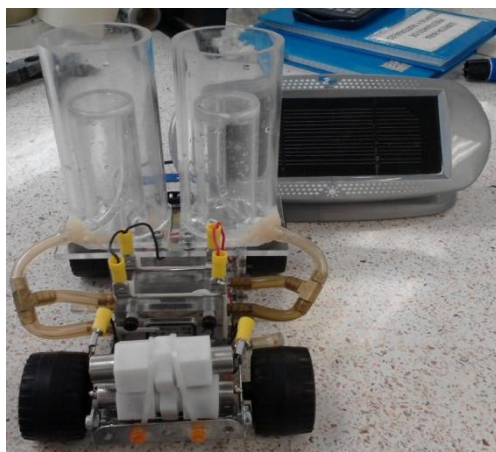
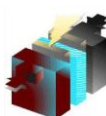


Figure 8. Hybrid renewable hydrogen toy car.



3. Results and discussion

3.1 Characterization of RFC

The results for MEA's characterization (polarization curve and AC impedance spectroscopy) are shown in figure 9. a and b show results the RFC no.1, which has a power of 0.15 W at 0.30 V and 0.50 A with a resistance of 0.75 Ohms. Figure 9 c and d show results for RFC no. 2, which has a power peak of 0.16 W at 0.40 V and 0.4 A. with a ohmic resistance of 0.35 Ohms.

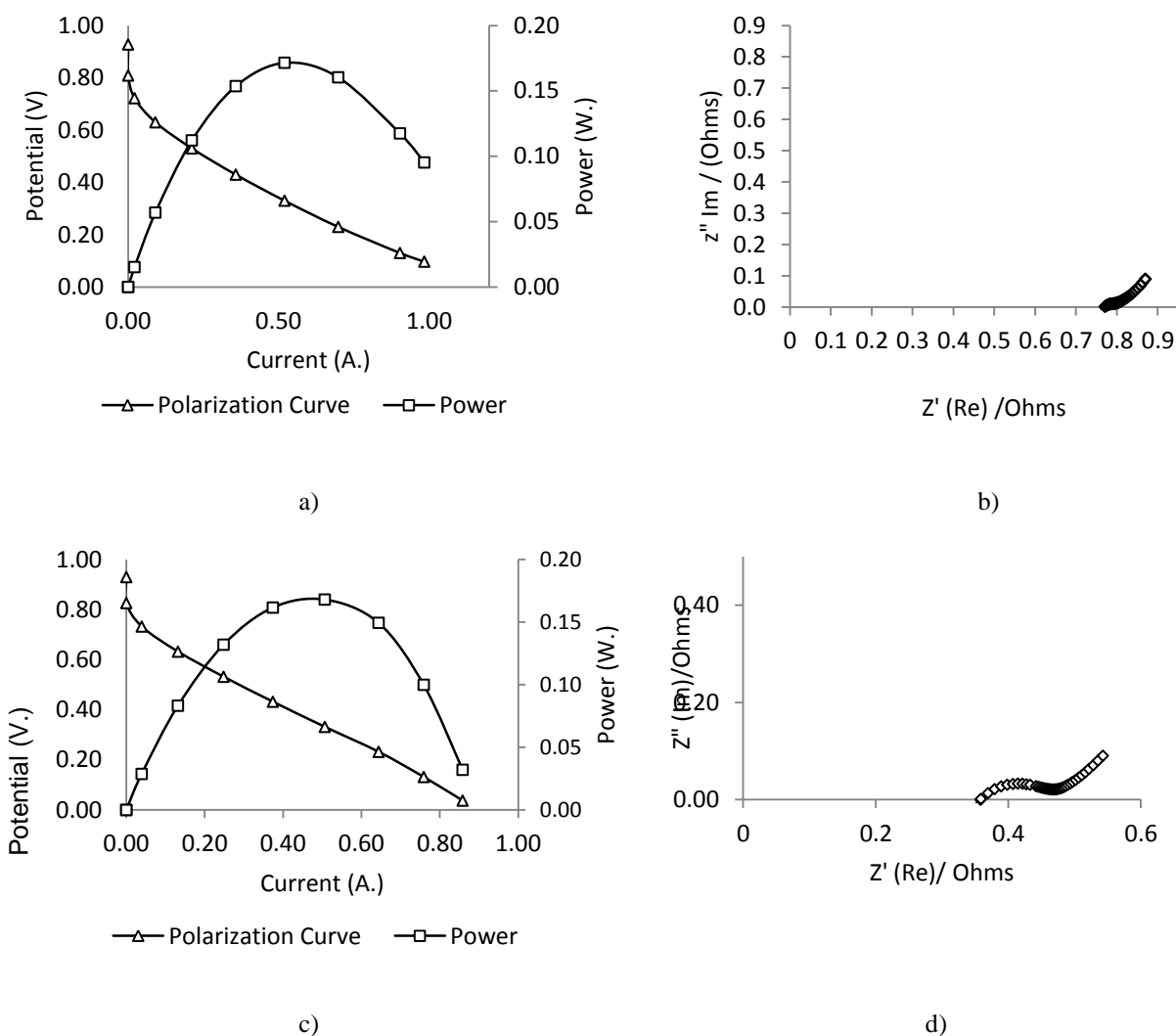


Figure 9. a) Polarization curves and power for RFC 1; b) AC impedance spectrum for RFC 1; c) polarization curves and power for RFC 2; and d) AC impedance spectrum for RFC 2.

3.3 Characterization of supercapacitors

The charge/discharge cycles performed at a constant current density at 10 mA/cm^2 with a potential limit of 1.0 V are shown in figure 10.

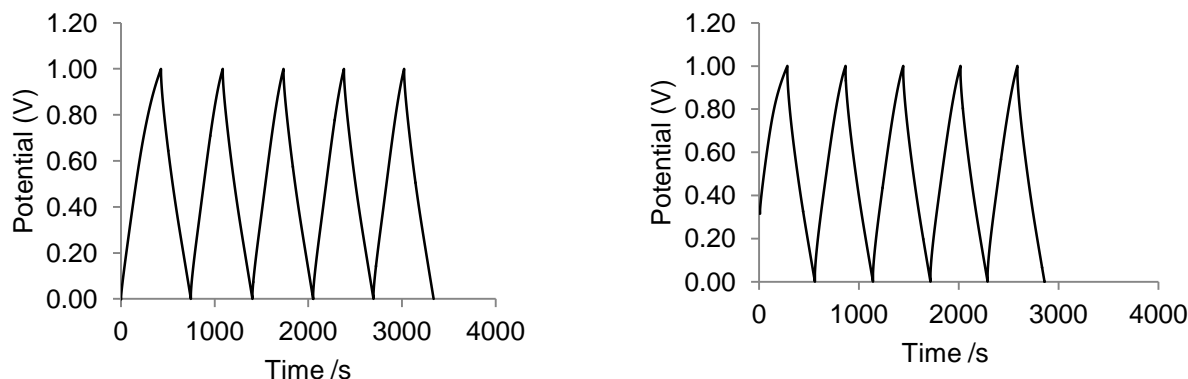


Figure 10. Galvanostatic Charge/discharge cycles for supercapacitors SC1 (left) and SC2 (right).

The SC1 presents a cycle time of 725 s and SC2 of 560 s . The specific capacitance for each capacitor was calculated to be X and Y for SC1 and SC2, respectively.

4. Conclusions

The developed prototype was able to produce, store and consume the gases (hydrogen and oxygen) through the process of electrolysis using electricity from a renewable resource. The implementation of the supercapacitor module allowed increased performance.

The supercapacitors provided the power necessary to the engine at the moment of start, allowing time for the RFC provides the energy sufficient for initial movement.

5. Acknowledgements

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