Synthesis and Evaluation of Carbon Catalyst from Human Urine for Proton Exchange Fuel Cell

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Abstract: *Human urine, a potentially polluting waste, is a universal unused resource in organic form disposed by the human body. This paper presents a convenient, beneficial, and innovative template-free route to synthesize highly porous carbon containing heteroatoms such as N, S, Si, and P from human urine waste and evaluate its performance on a PEM fuel cell. Multiple hetero atoms are naturally doped into the carbon, making it unnecessary to employ troublesome expensive pore-generating templates. The naturally doped conductive porous URC (Urine Carbon) can be utilized as electro catalysts for oxygen reduction reactions in fuel cell due its superior electro catalytic oxidation reduction reaction (ORR) activity. The prepared catalyst showed a promising characteristic curve showing its adaptability in PEM fuel cells. Based on their physical characteristics, it is also expected to act as a very good support medium for electro catalysts. The unexpected capacitance nature may also help in the field of batteries where capacitive nature is the foremost concern.*

Keywords: *Fuel Cell, Human Urine, Carbon catalyst, Heteroatom, Adsorption isotherm*

1. Introduction

Human urine, which was considered as a polluting waste, is a useful organic resource from which a highly porous carbon material was developed. Human urine mainly consists of urea(C, H,N,O). Tyrosine O- sulphate and thiosulfate are daily excreted in considerable amounts in human urine which are key source of S. In addition, Si and P complexes are also present. The presence of all these elements makes urine a vital precursor.

Urine was treated through a series of steps to finally obtain a mesoporous carbon structure.High porosity is created through removal of inherently-present salt particles. The isolated rock salts can be used as de-icing agents. This was a much more cost effective method than preparing any of the conventional catalysts. Moreover, this will surely reduce the environmental issues considered with water pollution like eutrophication, formation of algae etc. to a great extent because the elements present in the urine can be made to a vital precursor rather than grouping them as "pollutants".

Fuel cells produce electricity from the energy of a fuel through a highly efficient direct electrochemical conversion process, resulting in low emissions and low environmental impact. Of the different types of fuel cell under development, the Proton Electrolyte Membrane Fuel Cell (PEMFC) is attracting the most attention[1]. This can start up fast and easily and operates at near ambient temperatures. PEM fuel cells use platinum as the catalyst for anode and cathode side. But using platinum is not economical due to its high cost and low availability. Thus, developing active, inexpensive non-platinum based oxidation reduction reaction (ORR) catalyst materials to replace currently used Pt- based catalysts is a necessary and essential requirement in order to reduce the overall system cost. Thus the developed catalyst was tested and evaluated on a fuel cell.

Three catalysts which differed in the heating procedure during carbonization were prepared. These catalysts were then evaluated on a proton exchange membrane (PEM) fuel cell to measure the electrochemical activity. The three different catalysts were compared and the most active one was found out. It has shown a comparable activity in terms of ORR with platinum. These cost effective catalysts are believed to be useful for various fuel cell application such as space, automobile, portable power systems.

2. Methodology

2.1. Synthesis of Catalyst

Healthy human urine approximately 5 L was collected and a few ml was used to test pH. The pH was tested using universal pH indicator and it showed about 6.5 -7 which shows slightly acidic nature. The urine was taken in beaker and dried in

hot air oven for 4 days to remove the water present in it. A brownish yellow powder was obtained and traces of moisture present in it was removed and dried completely by placing it in a desiccator (Fig 1). The sample was weighed.

Figure 1. Dried Urine

Prior to heating in the tube furnace, TGA analysis was conducted for the catalyst in order to understand the weight loss at different temperatures. The results showed 2 dips (fig 2). The first dip occurred at 200 C (12mins) which is mainly due to the loss of moisture present in the sample and the second at 600 C (36 mins) is due to the carbonization reaction. As the results suggested, approximately 23.7% of the sample could only be recovered
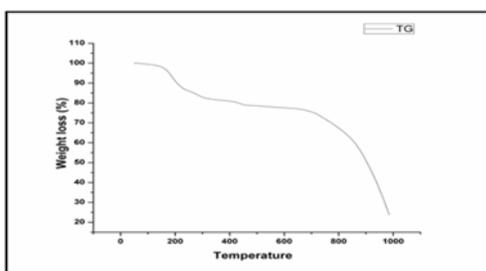

Figure 2. TGA Curve

Three catalysts which differed in the way they were carbonized were prepared. The first catalyst named 'Catalyst A' was prepared by carbonizing the sample at 700°C. The second named 'Catalyst B' was prepared by first heating the sample from room temperature to 600°C at the rate of 10°C/min and a holding of 30mins, and again heating from room temperature to 1000°C at the rate of 10 °C/min and a holding of 15mins. The third sample named 'Catalyst C was prepared by first heating the sample from room temperature to 600 C at the rate of 10°C/min and a holding of 30 mins, and again heating from 600°C to 1000°C at the rate of 10°C/mins and a holding of 15 mins[2].

Figure 3. Carbonized urine

Catalyst B and C were given a ramped heating so as to reduce the mass loss. A fine powdered sample of greyish black powder (Fig 3) was obtained after carbonization.The prepared carbonized urine was then subjected for HCL washing so as to neutralize the rock salts present. 300 ml of 0.1 M HCL was used for washing. We could sense the smell of H2S gas (due to neutralization of S by HCL) during washing.The black liquid obtained was then subjected for sonication for 30 mins followed by vacuum filtration. The filter paper used was GSF filter paper.The wet filter paper with the porous carbon was then dried at 100°C for about 30mins.
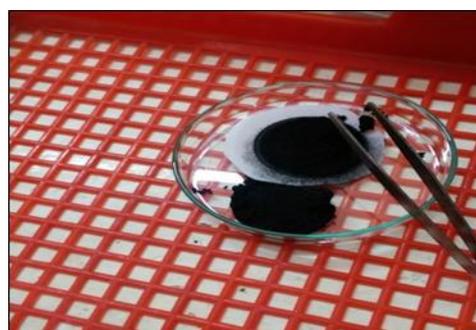

Figure 4. Urine Carbon

2.2. Fuel Cell Testing

2.2.1. Membrane Coating and Electrode Preparation:

The fuel cell testing was done with 3 samples of prepared catalyst labeled as sample 'A', sample 'B' and sample 'C'. For the membrane coating, three 1*1 cm^2 electrode was taken from the carbon paper for each sample.

In a pestle and mortar, first 0.36 Pt/C catalyst was mixed with water, 0.05g nafion solution and alcohol for the anode side preparation. Water is added so as to prevent burn out of Pt when it comes in direct contact with alcohol. Three frames each fitted with a 110*110 mm^2 membrane were taken

for the 3 samples to be tested. The prepared Pt/C catalyst ink was brushed on the H_2 side of the membrane fitted frames.

For cathode preparation of sample 'A', 0.0178 g of sample was mixed with 0.14 g of nafion solution, for sample 'B', 0.38 g of sample was mixed with 0.0502g of nafion solution and for sample 'C', 0.3841 g of sample was mixed with 0.0510g of nafion solution. These 3 catalyst inks were then coated by brushing on the O_2 side of each of the three membranes fitted on frames. After brushing, the frames were kept for fan drying.

For electrode preparation, carbon paper was taken and dipped in 30 wt% PTFE solution followed by drying at 120° C for about 10-30 minutes and sintering at 300 – 350 °C for 10 minutes. A $1*1cm^2$ piece was cut out and was used as the electrode. The prepared electrode was the left for drying. For sample A, 1.47 mg/cm^2 was the catalyst loading rate. For sample B and sample C, 1.54 mg/cm^2 were the catalyst loading rate.
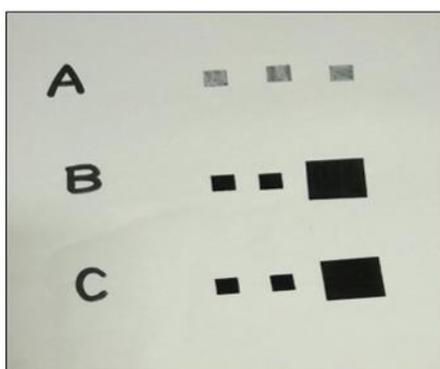

Figure 5. Electrode coated with catalyst

2.2.2 Membrane electrode assembly (MEA) Preparation:

First, a 5.8 cm^2 carbon paper was dipped to 60 wt% PTFE solution followed by drying at 120 C for about 10-30 minutes and sintering at 300 – 350 C for 10 minutes. A $1*1cm^2$ piece was cut out from the centre.

The remaining portion served as the GDL (Gas Diffusion Layer). PTFE is used to provide a hydrophobic nature to prevent the rupturing of GDL while washing the MEA before assembling in fuel cell stack. A GDL of 0.37 mm thickness was used. The GDL was then placed onto both the sides of the membrane fitted on frame in such a way that the catalyst coated on the membrane was completely visible through the $1 *1 cm^2$ cut out area. Into the $1*1 cm^2$ hole of the GDL, the dried electrode coated with catalyst was attached with

special taping mechanism on both the sides of the membrane. This way, all the three MEA's for all the 3 samples was prepared.

2.2.3. Compression:

Each of the three MEA's were then subjected to cold pressing using a hydraulic press. A total load of 210 kg/cm^2 was applied on the 5.8 cm^2 of MEA for 5 minutes.

2.2.4. Fuel Cell Stack Assembling:

Before assembling, the MEA has to be removed from the frame by immersing it in water because the membrane stretches only in hydrated condition. The MEA is then placed on silica sheet and an EPDM gasket layer was placed above it so that the GDL just fits to the inner square of the gasket. Here, the gasket used had an external dimension of 110*110 mm2 and an internal dimension of 59*59 mm2. The gasket was then cut from the outer area so as to fit into the stack.
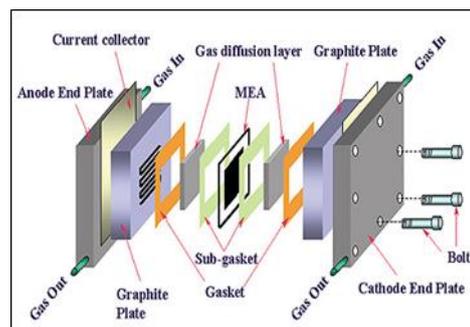

Figure 6. Schematic representation of a fuel cell[6]

For the assembly (Fig 6), a stack was placed. Starting from the H_2 side, initially an end plate was placed followed by a bipolar plate which was glued to the end plate using RTV. The MEA was then glued to the sides of the bipolar plate using RTV such the Pt/C catalyst side was facing to the bipolar plate. The second bipolar plate was placed on the O_2 side where the sample catalysts were brushed. Bridges were provided on the bipolar plates for proper channeling of gases. Finally the assembly was complete by placing the second end plate and screwing the stack together. The assembly was then tightened using a torque wrench by applying 10 N/m on the bolts. The completed assembly is shown in figure7.
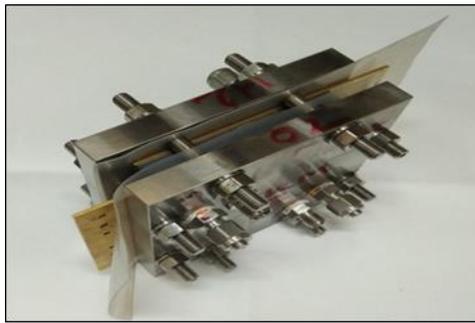
Figure 7. Assembled Fuel Cell Stack

2.2.5 Fuel Cell Testing:

Initially through both the fuel channels, nitrogen gas was passed at a pressure of 0.2 bars so as to remove any trapped gases. This is done as part of safety considerations because direct contact of hydrogen and oxygen gases may lead to explosions. From the outlet of both the sides, the outlet tubes were dipped in a beaker of water to check if the flow of gas is proper and to ensure no leakage. The entire fuel cell stack was also dipped into water to check for any leakages in membrane or gasket. Bubbles arise if such leakages are seen.

3. Characterizations of Catalyst

3.1. Scanning electron microscopy

The surface characters of the samples were analyzed using SEM and the fibre like structures emphasized the porous nature of the prepared catalyst.Since the SEM image for solid particles tends to be non-uniform, the carbon powder was dispersed in acetone prior to SEM analysis.A process called sputtering was done just before SEM analysis, where a gold coating was provided over the surface to prevent electron accumulation and thereby a probable charge build-up.
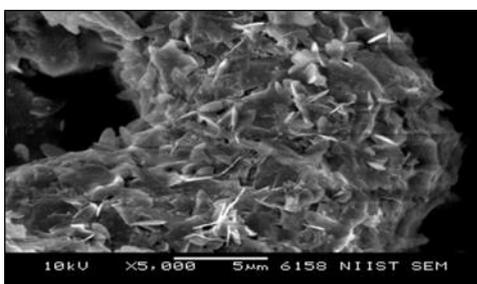

Figure 8.SEM Images of catalyst

3.2. Surface measurements

Surface properties of the as-obtained carbon materials are very important for the electrochemical performance when used as an electrode material for ORR.Figure 9 reveals nitrogen isotherm.N2 isotherms for both the URC carbons exhibit more or less similar type I isotherm typical of microporous carbon materials.The presence of a hysteresis loop is indicative of a solid containing both micropores and mesopores. The catalyst B shows a limited hysteresis loop which indicates parallel or slit like pores, whereas catalyst C has got more pronounced hysteresis loop which indicates cage like pores.
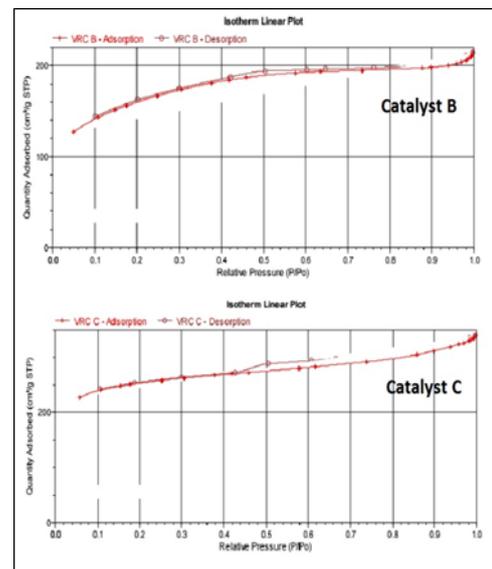

Figure 9. Linear Isotherm

Table 1 summarizes the BET surface area, pore volume and pore size. BET surface area is an important analysis technique for measurement of surface area. Surface area of catalyst is an important factor in catalytic activity.Nitrogen was used as the adsorbate as it is a non-corrosive gas. It was observed from the analysis that the catalyst C has got BET surface area of 826.17 m^2/g and catalyst B has got BET surface area of 552.01m^2/g. From this it can be interpreted that catalyst C has more surface area than B. The large surface area is overestimated due to enhanced adsorption in the micro- pores. Thus catalyst C shows an extraordinary catalytic effect, which increases its possibility of being used in fuel cells.

Table 1. Surface Characteristics

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
B	552.0115	0.1984	32.5075
C	826.1763	0.2304	45.117

The Poresizedistribution and pore volume was calculated by Barrett Joyner Halenda (BJH). From the pore size distribution it can be interpreted that both the catalysts have mesopores (2-50nm).Mesopores are mainly created by the evaporation of salts during the carbonization at higher temperature The pore volume and pore size is greater for the catalyst C compared to catalyst B, thus making catalyst C much more efficient in catalytic activity

4. Results and Discussions

The fuel cell was connected to the gas cylinders after the assembly. Hydrogen was passed to the anode side and oxygen was passed to cathode side. The fuel cell setup was then connected to electrochemical impedance spectroscopy equipment for measuring the current produced by connecting the probes to the current collectors. Initially the fuel cell was operated in open circuit condition for 10 mins, during which no current was withdrawn. The open circuit voltage (OCV) for Catalyst A was 2mV and that for catalyst B was 5mV. Since their OCV was very low, polarization could not be done. Therefore current could not be drawn for Catalyst A and B.

Next fuel cell containing catalyst C was connected to EIS, and open circuit voltage was found to be 0.425 V. This shows higher activity for catalyst C compared to the catalyst A and B. Polarization was done for catalyst C and it was observed that a current of 400mA and a voltage of 0.375 were obtained. Normally a voltage of 0.8 V to 0.9 V is obtained with platinum as catalyst. Theoretically the voltage obtained from a single fuel cell is 1.23 V.

4.1. Performance Curve

Different operating regimes of the fuel cell are identified with the help of the polarization curve. At open circuit, no current flows between anode and cathode. With a finite load resistance, current flows; an electron current goes through the external circuit, which is balanced by an ion current going through the electrolyte. At large load resistances the voltage drops rapidly with increasing current; the steep initial decrease is attributed to the barrier for the electron transfer reactions occurring at the electrodes. This is referred to as the activation polarization region. As the load resistance is decreased further, there is a range of load resistances where the voltage decreases almost linearly with the current. This is referred to as the "Ohmic polarization region", where the current is

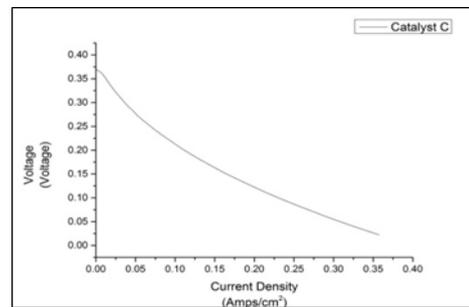limited by the internal resistance of the electrolyte to ion flow.

Figure 10. Performance curve

The Ohmic region is the desirable operating regime for a fuel cell. As the external resistance is decreased further, the current reaches a limiting value where the mass transfer of reactants to the electrode/electrolyte interface limits the reaction. This is known as the concentration, or mass transfer, polarization region [5]. The performance curve for Catalyst C is shown in figure 10. Since the catalysts A and B could not be polarized, performance curve for catalyst C is only obtained.

4.2. Cyclic Voltammetry

Cyclic voltammetry and isan useful tool to analyze electric properties of different materials and interface reaction mechanisms. Cyclic Voltammetry of the three catalysts were done under flooded condition where the fuel atmosphere wasmimicked. It was assumed that the oxygen present in the electrolyte provides the oxygen required for the reaction.

The cyclic voltammetry was done at a scan rate of 50 millivolts per second (mVps). Silver-silver chloride electrode was taken as the reference. In figure 11, curve from 0 V to 1.2 V shows the oxidation reaction, while the curve from 1.2 V to 0 V shows the reduction reactions. From the graph it was observed that the catalyst A shows purely capacitance behavior, while the catalyst B also shows slight capacitance but compared to catalyst A it has better activity The curve at the bottom for catalyst C is mainly due to evolution of hydrogen.
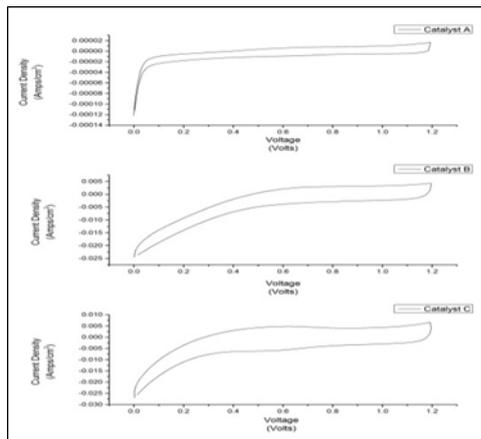
Figure 11. Cyclic Voltammetry

4.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool that you can use to characterize limitations and improve the performance of fuel cells.The EIS of the three catalysts were done in flooded condition at 0 V, and the result is obtained as in Figure12. EIS shows the capacitive, resistive and inductive nature of the catalyst. As it can be seen the catalyst A has got a straight line, which shows that it is of capacitive nature. The actual fuel cell catalyst must have an EIS of curved shape.
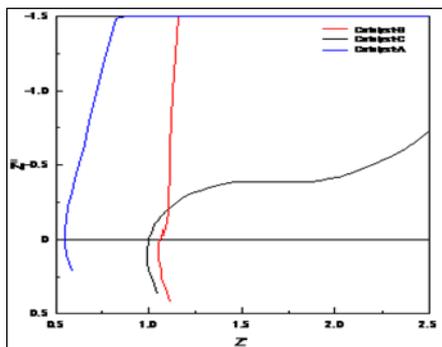

Figure 12. EIS of the catalysts

The catalyst C shows somewhat this behaviour at lower values, but at higher values it shows a capacitive behaviour. The capacitive nature of Catalyst A is greater than B and C. Therefore Catalyst A has least activity. From this it can be understood that catalyst A can be used in storage batteries due its capacitive nature, as fuel does not require much capacitance as storage batteries. Catalyst C has both capacitive and kinetic resistance nature.

4.4. Verification of Tafel Equation

The Tafel equation is an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential. It is derived from the famous Butler-Volmer equation, expressed as below:

When the over potential is very large, the second exponential term of the Butler-Volmer equation is neglected, which results in to the Tafel equation. The Tafel equation after further simplification is shown below:

$$\eta = \frac{2.303 \, k \, T \, log(-Io)}{\alpha \, n \, e} - \frac{2.303 \, k \, T \, log(Ic)}{\alpha \, n \, e}$$

Where,
η:Over potential (Volts
T: Absolute temperature = 303K
k: Boltzmann const.= 1.38 x 10^{-23} J/K
α: Charge transfer coefficient
(Generally between 0.2 and 0.5)
n: Number of electrons = 2 (PEMFC)
e: electron charge =1.602 x 10^{-19} C

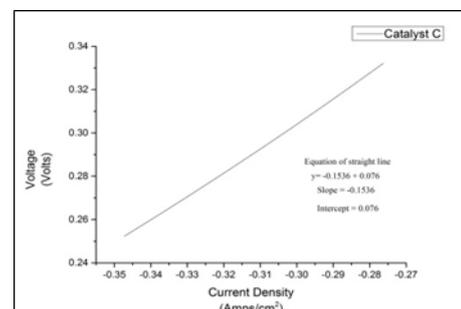I_0: Exchange current density(Amps/cm^2)

Figure 13. Tafel Plot

Current values are taken for several over potential values and the log values of these current values are plotted against the over potential. Since the activation region is from 0.25 – 0.32, Tafel plot is drawn using this region.
From figure 13,
Slope = - 0.1536 V
Intercept = 0.076
From Tafel equation,

$$\text{Slope, A} = -\frac{2.303 \, k \, T}{\alpha \, n \, e},$$

Intercept, B=$\frac{2.303 \, k \, T \, log(Io)}{\alpha \, n \, e}$

Therefore,

$$\alpha = -\frac{2.303 \, k \, T}{A \, n \, e}$$

$$= -\frac{2.303 * 303 * 1.38 \, X \, 10 \, \hat{} -23}{-0.1536 * 2 * 1.60 X \, 10 \hat{} -19} = 0.2 log (I_0) =$$

$$\frac{B \, \alpha \, n \, e}{2.303 \, k \, T}$$

$$= \frac{0.076 * 0.2 * 2 * 1.60 \, x \, 10\char`\^{}-19}{2.303 * 1.38 \, x \, 10\char`\^{}-23 * 303}$$

$$I = I_0 \cdot \left\{ \exp\left[\frac{\alpha_A nF\eta}{RT}\right] - \exp\left[-\frac{\alpha_C nF\eta}{RT}\right] \right\} =$$

3.199 Amps/cm^2

Table 2: Summary of Tafel equation

Charge transfer coefficient, α	0.2
Exchange current density, I_0	3.199 Amps/cm^2

5. Conclusions

The proposed technique offers naturally doped porous carbon material without the usage of expensive artificial pore-generating templates like sacrificial inorganic hard templates or polymer/polymers precursors-based soft templates. The ORR activity can be addressed in terms of heteroatom doping, surface properties and electrical conductivity of the carbon framework. The urine catalyst acts as the best substitute to the costly conventional catalyst.

The foremost prepared catalyst 'A' showed very low activity as low as 2 mV and the second catalyst 'B' showed more or less a capacitive behavior which maybe suitable for usage in batteries where capacitive nature is of great importance. This sample can also be a promising catalyst in fuel cell applications after undergoing certain activation processes. Also on the basis of physical considerations, they may also act as a great support for catalysts in fuel cells. The finally prepared catalyst 'C' showed an exceptional ORR activity in fuel cell evaluation and approximately 400 mA current (0.375 V) was obtained with a single cell. Stacking up of 2 or more cells in series may lead to even higher activity. The difference in the above three catalysts must be because of the different heating schemes employed. Since the urine catalysts are prepared out of an extreme waste, their performance can bring revolutionary scientific, technical and economic changes in the field of fuel cells.

6. Acknowledgements

7. References

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