

Generation of Energy from a Single Fuel Cell Using Synthesized Solid Electrolyte Membrane from Functionalized Polyisoprene/Carbon Nanotubes

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Abstract: Study on the electrical energy generated from a single fuel cell using a synthesized solid electrolyte membrane from polyisoprene that was impregnated with carbon nanotubes was carried out. The initial functionalization of the polymer yielded an ion exchange capacity (IEC) of 4.04, 7.82, 11.1 and 15.53 mmol/g with their corresponding degrees of sulphonation (DS) of 10.93, 21.1, 30.03 and 42.02 %, respectively. The later but highest DS achieved water uptake of 49.23 wt % and proton conductivities of 4.3×10^{-3} , 1.2×10^{-3} and 2.6×10^{-2} S/cm for membrane of thickness 250, 215 and 120 mm, respectively. The performance testing of the membrane in a single fuel cell achieved an open circuit voltage (OCV) of 647.23 mV with the synthesised membrane of 35 wt % catalyst loading, 589.79 mV and 410.48 mV of 25 wt % and 15 wt % catalyst loading, respectively at constant DS (42.02 %). Their corresponding power densities achieved were 68.67, 49.20 and 35.83 Mw/cm², respectively. Thus the functionalization of polyisoprene impregnated with carbon nanotubes through the process of sulphonation with chlorosulphonic acid resulted into the development of solid polymer electrolyte membrane for fuel cell application.

Keywords: Energy, sulphonation, polyisoprene, carbon nanotubes, fuel cell.

1. INTRODUCTION

The drift from the over dependency of fossil fuel to generate energy is presently on the increase, majorly because of its finite nature, pollution, and unsteady market prices. The shift now is towards clean energy sources that are not just efficient, environmentally friendly but renewable [1,2]. In the midst of this, Fuel cell systems especially proton exchange membrane fuel cell (PEMFC) is considered as one of the most promising alternative sources of energy, because it is not only found to be an efficient and portable power source that is convenient for vehicular transportation, devices for residences, homes and institutions, mobile electronic devices but also for industrial applications [3-5]. These sterling qualities are due to their high-power density, making them compact and lightweight, as well as their rapid response to varying load, relatively quick start up, low operating temperature and environmental friendliness [6,7].

Generally fuel cells are electrochemical devices that convert the chemical energy of reactants (both fuel and

oxidant) directly into electrical energy [8]. In other words, the direct chemical conversion into electricity and heat does not involve combustion cycles, and as such, the use of the thermal-mechanical-electric sequence with Carnot's theorem limitation in the conventional indirect technology is avoided. Fuel cells do not require recharging because they do not run down or undergo material changes. In principle, they have unlimited lifetime as long as the reactants are supplied and products removed continuously.

The basic structure of the PEMFC involves an anode electrode, a cathode electrode and a solid polymer membrane that acts as an electrolyte [9-11]. The central component of the PEMFC is the polymer membrane which performs the functions such as, a conductor of protons generated at the anode, opposes direct contact between the fuel and the oxidant in order to avoid oxidation of the fuel, as well as a barrier against the passage of electron [5,11]. It is therefore recognized that since PEMFCs operate electrochemically, the performance of the proton exchange membrane (PEM) synthesized from an appropriate polymer, becomes crucial for fuel cells of this type to function properly and maximally [12]. However, a good PEM is expected to exhibit chemical stability especially against the attack of oxygen and

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strong acids, high proton conductivity, suitable water uptake, resistance to fuel crossover especially for those using methanol as their source of fuel, and adequate mechanical properties [5]. Previous work on the properties of sulphonated polyisoprene elastomer for possible proton exchange membrane fuel cell has been investigated [3], and the choice of this synthetic polyisoprene for this study is as a result of some its excellent properties such as resilience, low hysteresis, high fatigue resistance, hence its uses include, shock absorbers, tires, gaskets, automotive mounts, sporting goods, coating, healthcare items and adhesives etc [3]. This work, therefore, is aimed at investigating energy generation from a single fuel cell using synthesized solid electrolyte membrane from polyisoprene that is impregnated with carbon nanotubes, a hard material that will reinforce the polymer membrane hydro and mechanical properties as well as enhancing its conductivity.

2. MATERIALS AND METHODS

Materials and Equipment: Analytical grade (> 98 %) chemicals are used in this study. These are chlorosulphonic acid (Charlec, Nigeria), toluene (Steve Nicholas, Nigeria Charlec), ethanol (Charlec, Nigeria), commercial polyisoprene (Karbochem RSA), carbon nanotubes and single fuel cell (Wits, RSA), and a fabricated four neck reactor.

2.1. Sulphonation of Polyisoprene with Concentrated Chlorosulphonic Acid

Polyisoprene (PI) (15 g) was dissolved in a beaker using toluene (250 ml). This was followed by the gradual and drop-wise addition of concentrated chlorosulphonic acid of different initial concentrations (0.0008, 0.0014, 0.0017 and 0.0022 mol/L.), initially chilled in an iced bath into a solution mixture undergoing vigorous stirring in a four-neck round bottom flask reactor. This was carried out under argon atmosphere at room temperature. The reaction proceeded at varying time of 1, 3, 6, 9, 12, 15 and 18 hours, respectively. The reaction was thus terminated with the addition of ethanol and the precipitated sulphonated polyisoprene (SPI) was recovered and washed with deionised water until a pH tending towards neutral was achieved. Thereafter the SPI was dried in an oven at 80°C for 3 hours.

2.2. Impregnation of Carbon Nanotubes into Sulphonated Polyisoprene

The essence of this process is to use this hard material (carbon-nanotubes) to improve the hydro and

mechanical properties of the membrane from any possible solubilization/weakness effects of water, and of course, previous study has also shown that the carbon-nanotubes (CNTs) incorporated into the membrane were able to reinforce it, as well as increase the conductivity by one order (10^{-3} to 10^{-2} S/cm) [12]. The impregnation of carbon nanotubes (CNTs) (predetermined 1.2 g) into the matrix of sulphonated polyisoprene was carried out by first, functionalizing the CNTs in a solution of sulphuric acid. This was later introduced into a solution of previously dried SPI that was dissolved in a 150 ml toluene and equipped with a magnetic stirrer, in a four-neck round bottom flask reactor under an argon atmosphere at room temperature. The reaction proceeded for a period of 5 hours to allow the CNTs mix thoroughly and well enough inside the matrix of the sulphonated polymer (SPI) [12], and at the end of the reaction the viscous dark solution derived was cast into a thin film.

2.3. Membrane Fabrication into Thin Films

The derived dark, viscous polymeric solution was cast into thin film by pouring it onto a clean polymer paper support and using a laboratory doctor blade casting machine set at appropriate thickness with the aid of feeler gauges. The casting process involves drawing the casting head of the blade along the length of the substrate, and allowed to cure for 5 days by exposing it to air. It was subjected to further drying in the oven at temperature below 80°C for about 3 hours in order to remove any trace of residual solvent and later, the cast membrane was vacuum dried for 2 hours.

2.4. Degree of Sulphonation and Ion Exchange Capacity

The degree of sulphonation (DS) was calculated from the Ion Exchange Capacity (IEC) that was determined from the percentages of sulphur in the dry samples of SPI via the method of elemental analysis. Equation (1) [13] was used to determine the IEC:

$$IEC = \frac{1000 \times S_c}{MW_s} \quad (1)$$

where: S_c , and MW_s , represent the sulphur content in percentage weight rate and the molecular weight of sulphur, while 1000 is the multiplication factor to have IEC value in mmol/g.

The values of IEC obtained above was then used to arrive at the DS using Equation (2) [3]:

$$DC = 100 \times \frac{MW_{SPI} \times IEC}{MW_{PI} \times MW_{OS O_2H}} \quad (2)$$

where: MW_{SPI} , IEC , MW_{PI} and $MW_{OS O_2H}$ represent the molecular weight of the sulphonated polyisoprene repeat unit, the ion exchange capacity, the molecular weight of unsulphonated polyisoprene and the molecular weight of OSO_2H .

2.5. Hydro Property of Synthesized Solid Electrolyte Membrane

The water uptake ability of the synthesised solid electrolyte membrane of different thicknesses was determined by immersing them in distilled water for a few days until they became saturated. The water uptake was thus determined from the weight difference between the wet and dry membranes according to Equation (3) [5]:

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3)$$

where: W_{wet} and W_{dry} represent weights (g) of the wet membranes and dry membranes, respectively.

2.6. Measurement of Proton Conductivity

Measurement of the proton conductivity of the synthesized membrane was carried out using alternating current impedance over a frequency range of 1-106Hz in 1M H_2SO_4 as an electrolyte. In the process, the intersection value of the high frequency impedance curve was taken as the membrane resistance and the proton conductivity was thus calculated using Equation (4):

$$\sigma = \frac{T}{RS} \quad (4)$$

where: σ = the proton conductivity (S/cm), T (cm) = the thickness, S (cm^2) = the surface area of the membrane and R = the resistance determined from the impedance plane.

2.7. Performance Testing of Synthesized Solid Electrolyte Membrane

The electrochemical activity test using the synthesized membrane in a fuel cell system was carried out where the fuel gases (hydrogen and oxygen) were allowed to diffuse through the porous backing layer, and at the gas/electrolyte interface the gases dissolved and then diffused to the electrolyte/electrode interface. Electro catalytic reaction

on the catalyst layer preceded the gas adsorption at the electrode surface, and while the ionic transport occurs in the electrolyte, the electronic transport takes place in the electrode. However, before installing the membrane electrode assembly (MEA) in the fuel cell testing apparatus, the MEA was hydrated for 36 hrs with demineralised water. The single cell was then installed in a fuel cell testing apparatus equipped with gas sources, temperature control, and gas flow-rate control rotameters, back pressure regulators for both hydrogen and oxygen, and a load of resistant box. The fuel cell tests were carried out using Pt/C catalyst in order to determine the distribution of reaction products which involves passing hydrogen through a humidifier to wet the gas and got into the anode at a flow rate of 612 ml/min and 20 kPa. Oxygen entered the fuel cell through the cathode at a flow rate of 373 ml/min and 15 kPa. The electrons generated from the anode were connected to a digital multimeter, with an external variable resistance to measure the current and voltage produced by the cell.

3. RESULTS AND DISCUSSION

3.1. Ion Exchange Capacity and Degree of Sulphonation

For polymeric ionic membrane, the ion exchange capacity (IEC) is a function of the membrane's acid concentration, usually achieved through the process of sulphonation. Meanwhile the acid concentration of the membrane is related to the amount of ionic groups in the membrane; hence its measure is associated with the degree of sulphonation (DS) [14]. Figures 1 and 2 present the results of both the IEC and DS which increase with both sulphonation time and the acid concentration used for the sulphonation process, where the acid concentrations used; 0.0008 mol/L achieved IECs of 1.02 mmol/g and 4.04 mmol/g, 0.0014 mol/L, achieved IECs of 1.80 mmol/g and 7.82 mmol/g, 0.0017 mol/L achieved 2.74 mmol/g and 11.10 mmol/g and 0.0022 mol/L achieved 4.12 mmol/g and 15.53 mmol/g at at both 1hr and 18 hrs, with their corresponding DS of 2.76 % and 10.93% (for 0.0014 mol/L), 4.89 % and 21.10 % (for 0.0017 mol/L), 7.41 and 30.03 % (for 0.0017 mol/L) and 11.15 % and 42.02 % (for 0.0022 mol/L), respectively. The increase in DS is an indication that the presence of the acid group in the polymer matrix is proportional to the ion exchange capacity of the sulphonated polymer, which usually increases with time and acid concentration [1]. However, above 15 hrs, the process of sulphonation became very slow and subsequently levelled out.

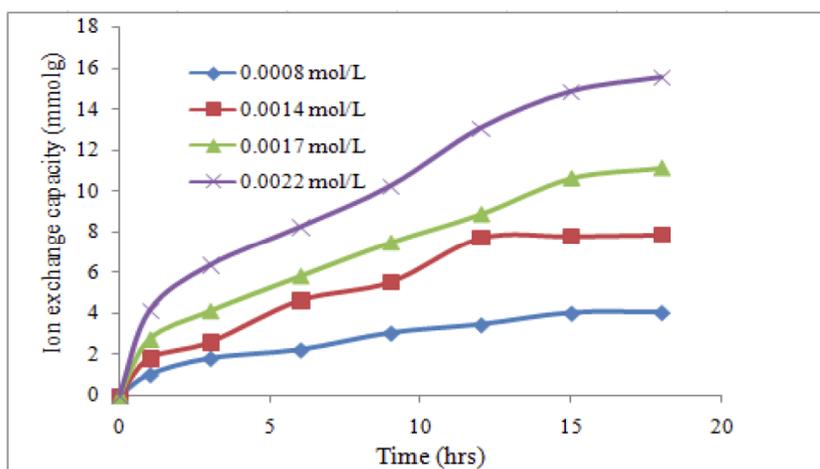


Figure 1: Ion exchange capacity versus of time.

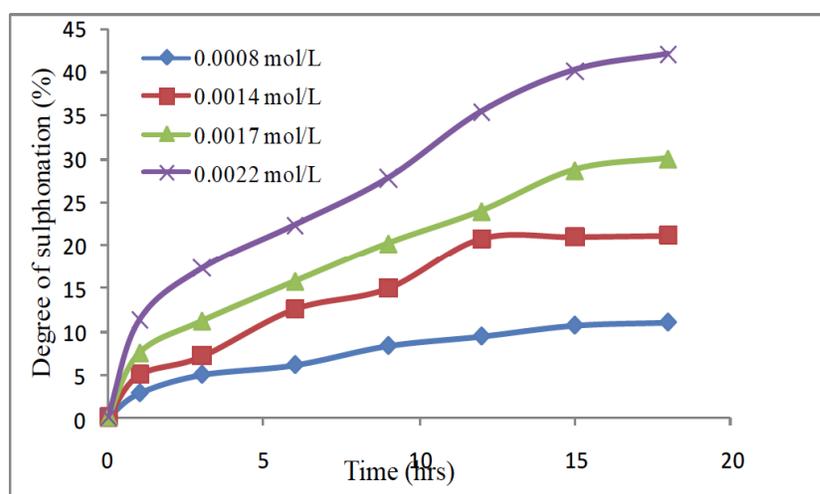


Figure 2: Degree of sulphonation versus time.

3.2. Hydro Property of Synthesized Solid Electrolyte Membrane

The hydro property of an ionic membrane is its water uptake ability. Water uptake is the weight percent of water absorbed by the dry membrane [14,15], and is an important characteristic necessary in providing the medium for the movement of ions [12]. Figure 3 presents the water uptake at different membrane thicknesses at constant degree of sulphonation of 42.02 %. Result shows that water uptake is inversely proportional to membrane thickness, where the smallest thickness (120 mm) achieved the highest but moderate water uptake of 5.47 and 49.23 weights % for 1 day and 6 days, respectively. While membrane of 215 mm achieved 5.49 and 32.99 weights % for 1 day and 6 days respectively, the membrane with the highest thickness (250 mm) achieved water uptake of 1.08 and 13.78 weights % for 1 day and 6 days, respectively.

3.3. Proton Conductivities of Synthesized Membrane

The conductivities of the synthesized membranes presented in Figure 4 follow the same trend with that of the water uptake ability of the membrane as conductivity is also inversely proportional to the membrane thickness but directly proportional to DS, where the membrane with the smallest thickness (120 mm) exhibited the highest conductivities of 4.6×10^{-3} and 2.6×10^{-2} S/cm at 4.90 and 42.02 % DS, 215 mm exhibited conductivities of 3.95×10^{-3} and 1.2×10^{-2} S/cm, and 250 mm exhibited 3.1×10^{-3} and 4.3×10^{-3} S/cm, all at the same DS, which is in agreement with previous work [1,3,5].

3.4. Performance Testing of Synthesized Solid Electrolyte Membrane

The polarisation tests were started when the open circuit voltage (OCV) stabilized. Figure 5 shows the

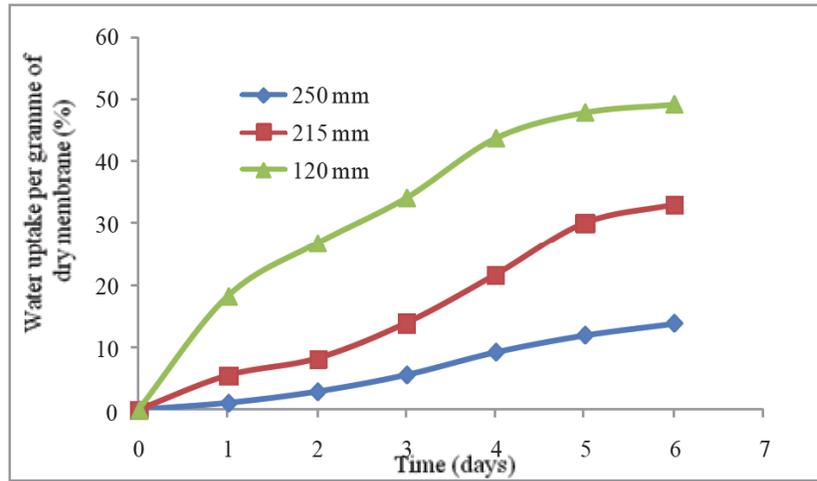


Figure 3: Water uptake of synthesized membrane against time.

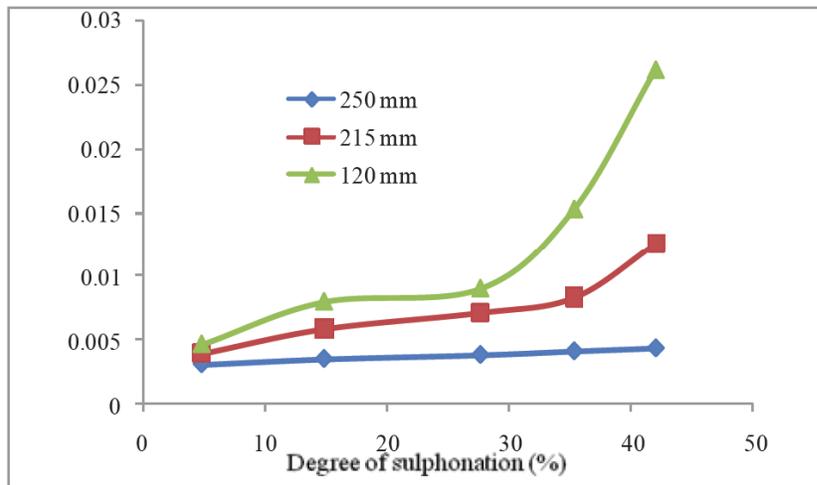


Figure 4: Proton conductivity versus degree of sulphonation at varying membrane thicknesses.

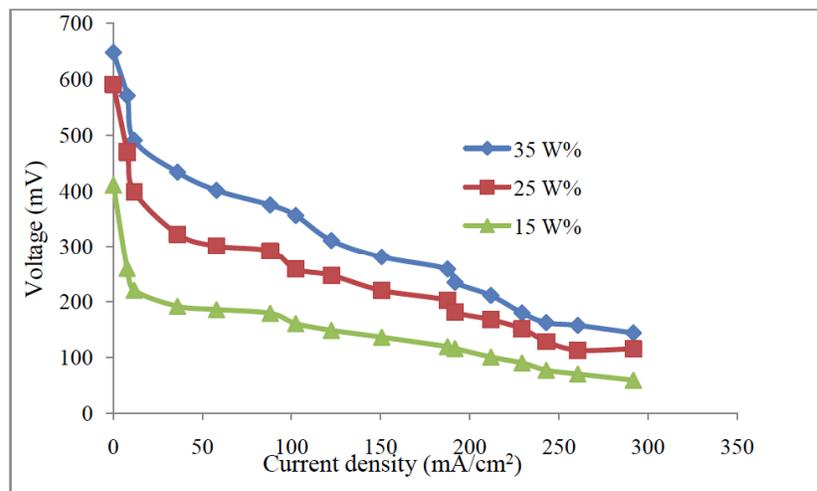


Figure 5: Cell potential versus current density for a single cell (25 cm²) for electrodes operated at 25°C with H₂:O₂ ratio of 1:2.

polarisation curve where a performance of an OCV of 647.23 mV was achieved with the synthesised

membrane of constant degree of sulphonation (42.02 %) with 35 wt % catalyst loading, 589.79 mV was

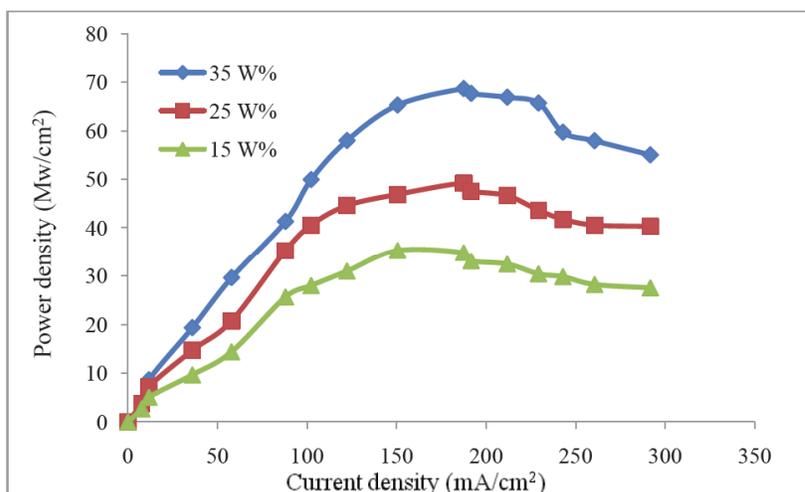


Figure 6: Power density versus current density for a single cell (25 cm²) for electrodes operated at 25°C with H₂:O₂ ratio of 1:2.

achieved at 25 wt %, and 410.48 mV at 15 wt %, respectively. The result also showed that as current density increases the electrical performance decreases and, thus creating a linear fall in voltage as the current density increases. This is due to resistance to current flow within the fuel cell.

The polarisation curves obtained from the electrochemical activity of the cell is as shown in Figure 6. The results showed that increasing current density correspondingly increased the power density of the cell system. This shows that at high current densities (187.52 mA/cm²), the hydrogen reaction rate was high, where a maximum power density of 68.67 mW/cm² was recorded with a catalyst loading of 35 w %, 49.20 mW/cm² with a catalyst loading of 25 w %, and 34.83 mA/cm² with a catalyst loading of 15 w %, all at constant DS of 42.02 %.

After this point the performance dropped even at higher current density considered. The drop could be associated to several factors such as decrease in catalyst active surface, drying of both the membrane and the catalyst layer, decrease in O₂ and H₂ partial pressures [16].

CONCLUSION

Functionalization of polyisoprene impregnated with carbon nanotubes via sulphonation with chlorosulphonic acid resulted into the development of solid polymer electrolyte membrane for proton exchange membrane fuel cell, achieving a maximum performance of an open circuit voltage (OCV) of 647.23 mV and power density of 68.67 mW/cm².

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