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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the degree of a Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

…….Signature of candidate……..day of ……2009

DEDICATION

This thesis is dedicated to the loving memory of my late wife, Mrs. Abdulkareem Ajobi Ashiat who passed away on the 12th of March, 2006 and our unborn child; may their souls rest in perfect peace. Your love, support, hospitality and kindness will forever remain in my memory.

To my late Father, Alhaji Ambali Adisa Abdulkareem who passed away on the 20th of May, 2009, may his soul rest in perfect peace. Your love, support, hospitality and kindness will forever remain in my memory.

ABSTRACT

The need for an alternative source of energy is very urgent. The challenges are to develop a new technology that will produce an efficient and environmentally friendly source of energy other than fossil fuel. A fuel cell system especially proton exchange membrane fuel cell is considered the most promising alternative method of converting and exploiting energy with many benefits including low pollutant emission, sustainability and reliability. However, a number of issues need to be resolved before the proton electron membrane fuel can become commercially and technologically viable. These include the durability and the availability of the membrane among many other factors. In this research, Proton Exchange Membrane (PEM) was synthesized by sulphonation of polystyrene butadiene rubber that is readily available in South Africa, using chlorosulphonic acid as the sulphonating agent. The synthesized membrane was blended with carbon nanoballs (CNBs) produced by the swirled floating catalytic chemical fluid deposition (SFCCVD) method designed and conceptualized by Iyuke (2005). Synthesis of carbon nanoparticles with this reactor was optimized using different experimental conditions of pyrolysis temperature, flow rates of acetylene, hydrogen and argon gases. A maximum production rate of 0.35 g/min was obtained at 1000^{o}C, acetylene flow rate of 370 ml/min, hydrogen flow rate of 180 ml/min and a flow ratio of acetylene to hydrogen equal to five. Since clean nanoparticles are required in this work for membrane synthesis, the SFCCVD reactor was modified to synthesize clean carbon nanoballs via a non-catalytic method. The carbon nanoballs produced were used in the formulation of sulphonated polystyrene butadiene rubber–carbon nanoballs composite membrane. The synthesised membranes and the composite membranes were characterized to determine the ion exchange capacity, degree of sulphonation, thermal stability, water uptake,

porosity, proton conductivity, solvent uptake, and morphology and methanol crossover. The characterization of the synthesized membrane for methanol cross over is to determine the suitability of the membrane for possible application in direct methanol fuel cell; however hydrogen fuel is used in this work. The results obtained revealed that the blending of the membrane with CNBs improved the thermal stability, water uptake, porosity, solvent uptake, methanol crossover and proton conductivity of the membrane with more than 50 % increase in proton conductivity. The results of various analyses conducted on the synthesized membrane revealed that the synthesized membrane shows better qualities in terms of thermal stability, solvent uptake, porosity to solvent, methanol crossover and water uptake than Nafion 112, which is the commercially available membrane. The synthesized and composite membranes were sandwiched between two electrodes to produce a membrane electrode assembly (MEA), using the hot press method at constant temperature, pressure and time. The performance of the fabricated MEA was tested in a single PEM fuel cell using hydrogen as the fuel gas and oxygen as oxidant at room temperature (about 25^{o}C). The results obtained revealed that the utilization of sulphonated PSBR resulted in higher performance compared to Nafion 112. Nafion 112 produces a maximum power density of 67 mW/cm^2 while the membrane synthesized from PSBR generated a maximum power density of 74 mW/cm^2. This difference is corresponding to about 10% increment. Also the membrane blended with CNBs exhibited a superior performance to a non-blended membrane. The former gives a maximum power density in the range of 74-97 mW/cm^2 depending on the mass of CNBs. These values are about 7-32 % higher than the non-blended membrane.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation	
A	Tafel constant
AC	Alternate current
AFC	Alkaline Fuel Cell
BET	Brunauer, Emmett and Teller
BPS	Ballard Power System
CCVD	Catalytic chemical vapour deposition
CNBs	Carbon nanoballs
CNTs	Carbon Nanotubes
CSs	Carbon spheres
CVD	Chemical vapour deposition
DC	Direct current
DS	Degree of sulphonation
DMFC	Direct Methanol Fuel Cells
DOE	Department of Energy
DWCNT	Double walled carbon nanotubes
E (or V)	Cell potential
E^0	Open cell voltage
EDX	Energy Dispersive X-ray Analysis
EW	Equivalent weight
F	Faraday constant

fcc	Face centered cubic
FT IR	Fourier transformation infrared
FWHM	Full width at half – maximum
GDL	Gas diffusion layer
HP	Horse power
HRTEM	High–resolution transmission electron microscope
IEC	Ion exchange capacity
IEMFCs	Ion Exchange Membrane Fuel Cells
IFC	International fuel cells
i	Current density
io	Exchange current density
kW	kiloWatt
MCFC	Molten Carbonate Fuel Cells
MEA	Membrane Electrode Assembly
mV	millivolts
MWCNTs	Multi–Walled Carbon Nanotubes
NASA	National Aeronautics and Space Administration
NNI	National Nanotechnology Initiative
ORR	oxygen reduction reaction
PEM	Proton Exchange Membrane
P	Pressure of the gas
P^0	Standard pressure

PEMFC	Proton Exchange Membrane Fuel Cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PFSI	perfluorosulphonated ionomer
PPV	Poly-p-phenylene vinylene
PSBR	Polystyrene butadiene rubber
PTFE	Polytetrafluoroethylene
PXRD	Powder X–ray diffraction
ppm	parts per million
ppm/s	parts per million per second
R	Universal gas constant
R_T	Total ohmic resistance
R_M	Ionic resistance of membrane
R_{ec}	Electronic resistance electrode
R_i	Ionic resistance of MEA
RFC	Regenerative Fuel Cells
RS	Raman Spectrometer
S	Surface area of membrane
Sc	Sulphur content
SEM	Scanning Electron Microscopy
SiNWs	Silicon nanowires
SFCCVD	Swirled floating chemical vapour deposition
SOFC	Solid oxide fuel cells
SPEFCs	Solid polymer electrolyte fuel cells

SPBSR	Sulphonated polystyrene butadiene rubber
STM	Scanning tunneling microscope
SWCNTs	Single–walled carbon nanotubes
T	Temperature
TEM	Transmission electron microscopy
TGA	Thermo–gravimetry analysis
TPR	Temperature programmed reduction
US	United States
mV	milliVolts
V	voltage (or Volts)
V-I	voltage-current
UV	Ultra violet
XRD	X-ray diffraction

Greek

η	Efficiency
δ_f	Fuel utilization coefficient
ΔG_f	Gibbs free energy
a	Associated activity
Φ	Relative humidity of air
σ	Proton conductivity
ε	Membrane porosity to methanol
λ_{total}	Overall uptake of solvent molecules

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