Project Title: Microbial fuel cell development for production of electricity from waste biomass. **DST No**: DST/TSG/AF/2010/09 Dated. 01-10-2010

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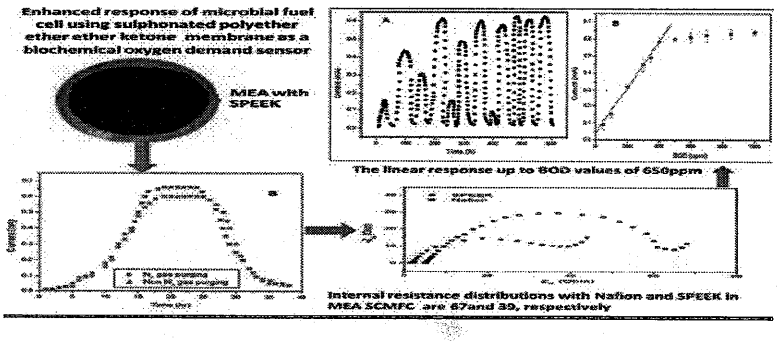
Highlights of the Project

The performance of synthesized non-fluorinated hydrocarbon based sulfonated membranes, including cation exchange membranes (sulfonated polystyrene- ethylene –butylene-polystyrene (SPSEBS), sulfonated polyether ether ketone (SPEEK)), anion exchange membranes (quaternized poly ether ether ketone (QPEEK)), novel composite membranes (SPEEK-sulfonated TiO_2-SO_3H, Chitosan–MWCNT and SPEEK- Fe_3O_4 were systematically compared with commercially available membranes such as Nafion 117 (CEM) and AMI-7001(AEM) in a single microbial fuel cell (28 ml). The study also extended to MFC bio cathode for the replacement of costlier platinum catalyst in cathode part of MFC. The prepared membranes were characterized by FTIR, XRD, NMR, SEM-EDX etc. The synthesized membranes showed excellent static and kinetic properties such as ion exchange capacity (IEC), water absorption, lower oxygen cross over and better durability. The use of hydrocarbon based membranes has been demonstrated to be environmentally safe, efficient and a cheap alternative for the respective commercially available membranes in MFCs.

Additionally, Flat Plate Microbial Fuel Cell (FPMFC) was constructed using graphite material and elevation in performance using sulfonated polyether ether ketone membrane for electricity generation was achieved. In our scalable stack design of the MFC, anode and cathode were close together and a large membrane area was used than the traditional one. The larger surface-area-to-chamber volume ratio and decreased average distance from any point in the fluid to an electrode surface improved the charge transport efficiency for electrons generated inside the anode chamber. This ratio was 10-50 times larger than many traditional MFCs. A Nyquist plot for single unit of the stack revealed that the overall *R* int of 8.5 Ω observed here was actually lower than the majority of previously reported values. The lower oxygen mass crossover of SPEEK based system produced higher power densities with low substrate loss.

(1) Enhanced response of microbial fuel cell using sulfonated poly ether ether ketone membrane as a biochemical oxygen demand sensor

(1) Sulfonated poly ether ether ketone (SPEEK) membrane in SCMFC was also used to determine the BOD. (2) The biosensor produced a good linear relationship with the BOD concentration up to 650 ppm. (3) This sensing range was 62.5% higher than that of Nafion®. (4) SPEEK exhibited one order lesser oxygen permeability than Nafion®. (5) Nafion® showed higher anodic internal resistance (67Ω) than the SPEEK (39Ω).



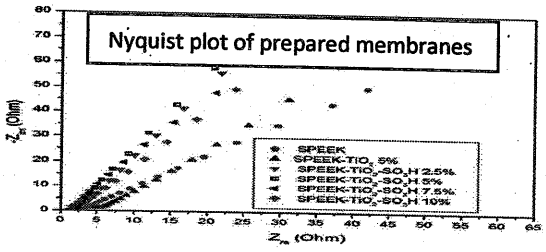
Reference: "Enhanced response of microbial fuel cell using sulfonated poly ether ether ketone membrane as a biochemical oxygen demand sensor", Sivasankaran Ayyaru, **Sangeetha Dharmalingam, Analytica Chimica Acta 818 (2014) 15–22**

(2) Improved performance of microbial fuel cell using sulfonated polyether ether ketone (SPEEK) TiO_2–SO_3H nanocomposite membrane

Novel SPEEK-TiO_2-SO_3H membrane was prepared by solution-casting method.
The composite membrane exhibited highest IEC value, proton conductivity and MFC performance at wet condition.
The improved performance was due to the sulfonation effect of TiO_2-SO_3H particles.
The oxygen mass transfer coefficient (K_O) of composite membranes was lower than SPEEK.
The sulfonated composite membrane delivered 4 –fold higher power output than Nafion 117.

Table 2 Comparison of a sulfonated nanocomposite with a commercial Nafion membrane

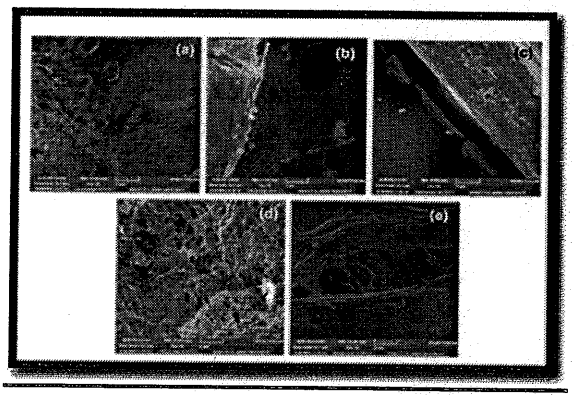
Membrane specifications	SPEEK–TiO_2–SO_3H (7.5%)	Nafion®[16,17]
Proton conductivity (S cm $^{-1}$)	1.382×10^{-2}	0.30×10^{-2}
Water uptake (%)	39	22
Thickness (μm)	120	183
K_O (cm s $^{-1}$)	0.8×10^{-6}	1.6×10^{-5}
Performances (mW m $^{-2}$)	1202.5	300
Internal resistance (Ω)	37	125



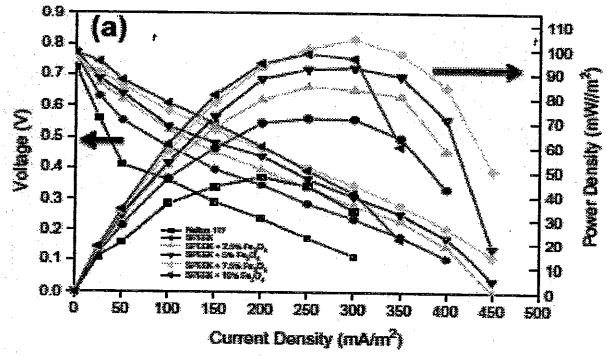
Reference: "Improved performance of microbial fuel cells using sulfonated polyether ether ketone (SPEEK) TiO2–SO3H nanocomposite membrane" RSC Adv., 2013, 3, 25243, Sivasankaran Ayyaru, **Sangeetha Dharmalingam.**

(3) Characterization and performance study of sulfonated poly ether ether etone/Fe_3O_4 nano composite membrane as electrolyte for microbial fuel cell.

Use of SPEEK/Fe_3O_4 composite membrane as an alternate for the Nafion 117 was demonstrated.
Higher power production was observed in SPEEK/Fe_3O_4 than Nafion® 117.
SPEEK/Fe_3O_4 has lower oxygen diffusion property.
Improved Performance was due to the inverse spinel structure of iron oxides that have the unique property of facilitating proton migration through water mediated hopping mechanism which in turn favors the rapid movement of protons through the porous polymer membrane.



SEM images of (a) SPEEK, (b) 2.5%, (c) 5%, (d) 7.5%, and (e) 10% Fe_3O_4 in SPEEK



Polarization Graph

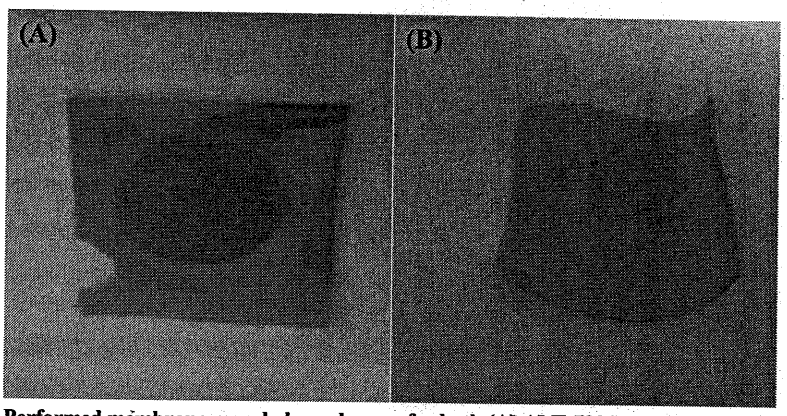
Reference:"Characterization and performance study of sulfonated poly ether ether ketone/Fe3O4 nano composite membrane as electrolyte for microbial fuel" *cell, N. V. Prabhu*, **Dharmalingam Sangeetha**, Chemical Engineering Journal, 243 (2014) 564–571.

(4) Increased microbial fuel cell performance using quaternized poly ether ether ketone anionic membrane electrolyte for electricity generation

Synthesized QPEEK membrane showed excellent electrical cell performance over the commercially available anion exchange membrane (AMI-7001).

The Oxygen mass transfer coefficient for QPEEK was lesser as compared to AEM in the same MFC reactor.

The MFC with QPEEK showed stable electrical cell performance over 250 days, while MFC with AEM- 7001 significantly deteriorated.



Performed membrane morphology changes for both (A) AMI-7001 and (B) QPEEK.

Table 1 – Comparison of membrane properties.

Membrane specifications	QPEEK	AMI-7001
Hydroxide conductivity (mS cm^{-1})	12	0.6
Thermal Stability (°C)	150	90
IEC (meq/g)	1.39	1.3
Water swelling (%)	24	22
Thickness (mm)	0.0002	0.45
K_O (cm/s)	2.1×10^{-5}	1.03×10^{-4}
K_A ($\times 10^{-8}$ cm^2/s)	5.2	4.6

Reference : Increased microbial fuel cell performance using quaternized poly ether ether ketone anionic membrane electrolyte for electricity generation. Mahendiravarman Elangovan and **Sangeetha Dharmalingam**, International Journal of Hydrogen Energy 38 (2013) 2471-2479.