Supporting Information

Analysis of partially sulfonated low density polyethylene (LDPE) membranes as separators in microbial fuel cells

Vikash Kumar[a], Ruchira Rudra[b], Arpita Nandy[b], Subrata Hait[a*], Patit P. Kundu[b*]

[a] Department of Civil and Environmental Engineering, Indian Institute of Technology, Patna (Bihar), India.

[b] Advanced Polymer Laboratory, Department of Polymer Science and Technology, University of Calcutta, India.

Figure S1. FTIR analysis of cross-sectional LDPE membranes

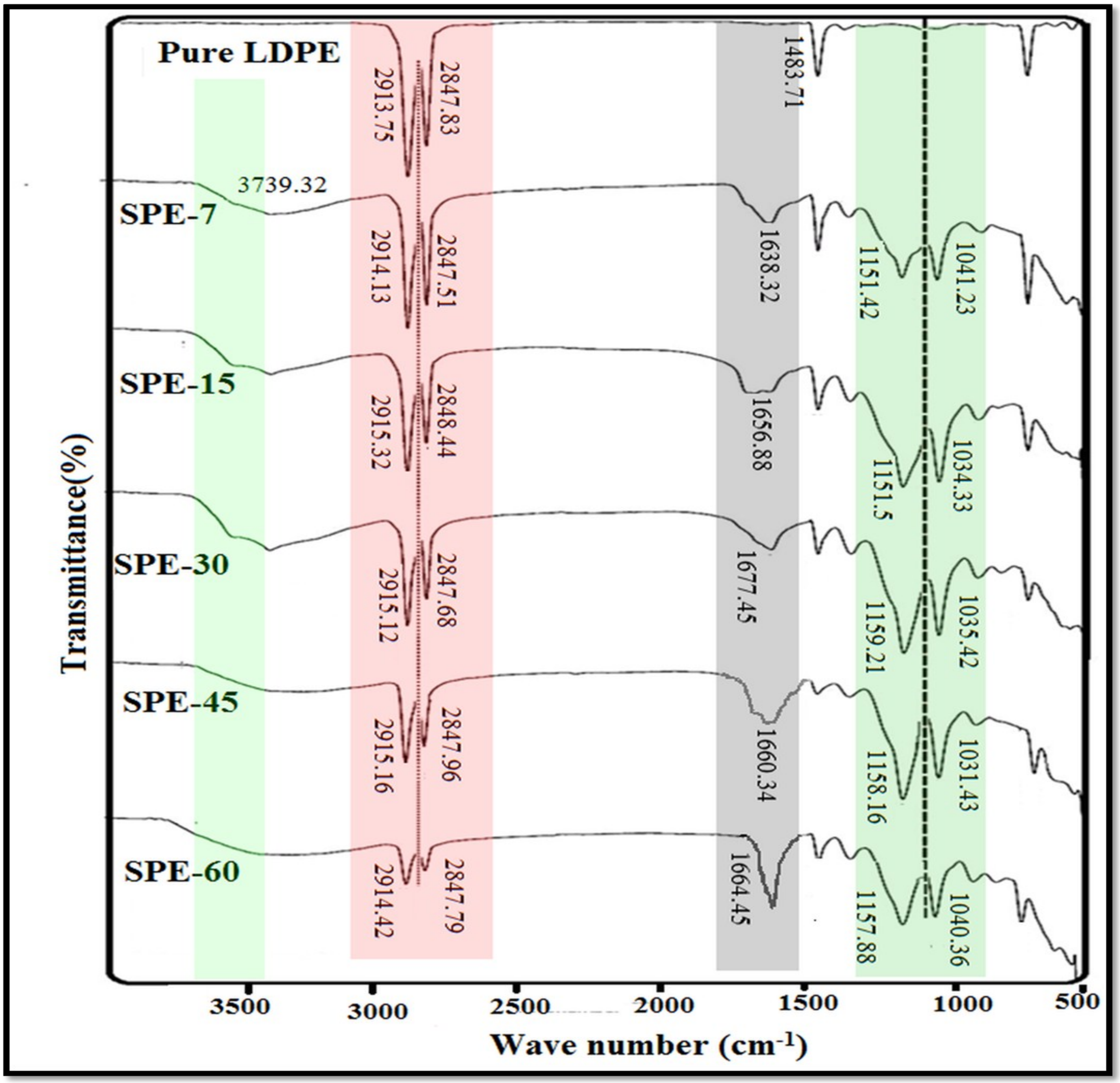


Figure S2: Cell performances at different resistances.

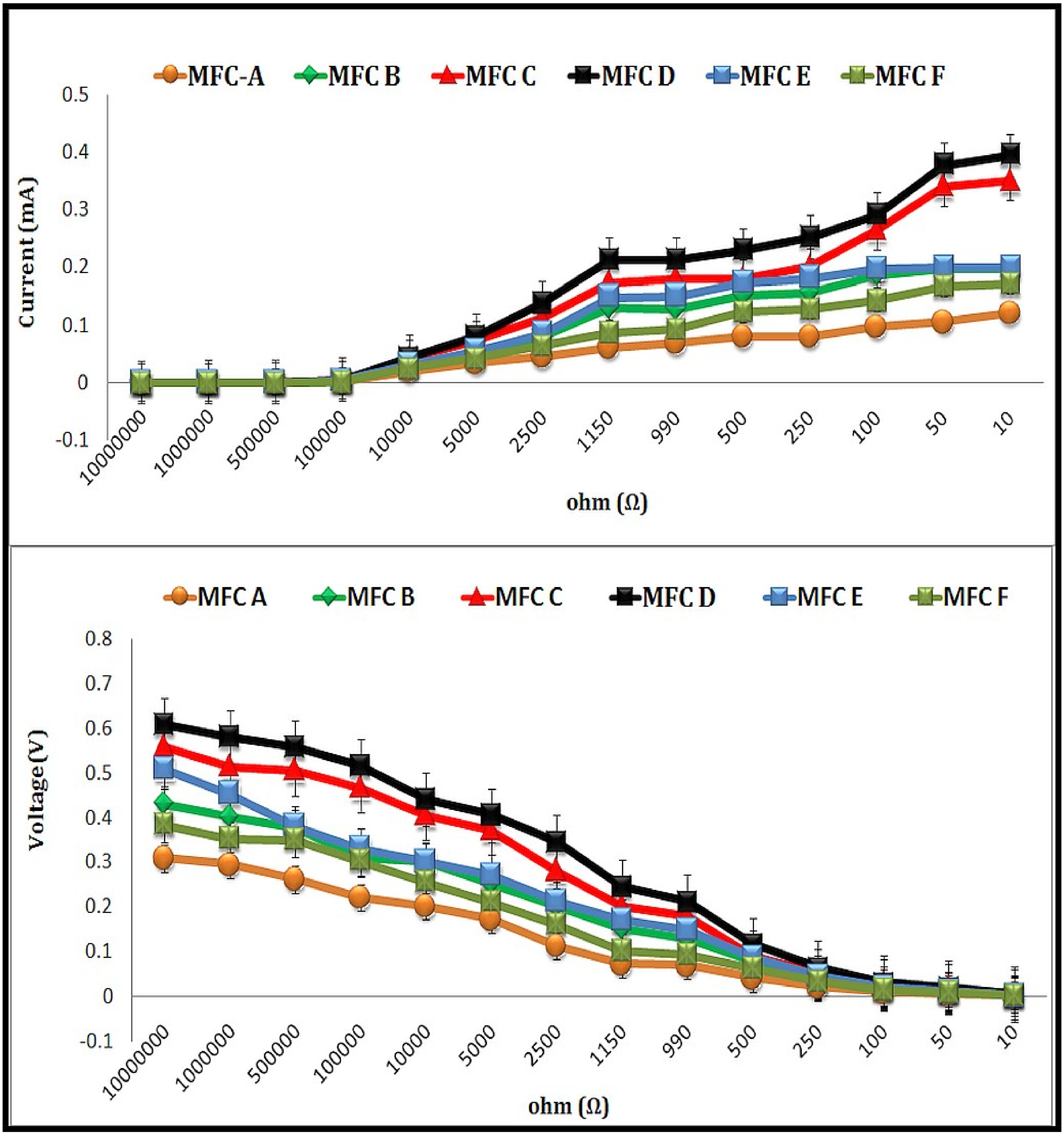
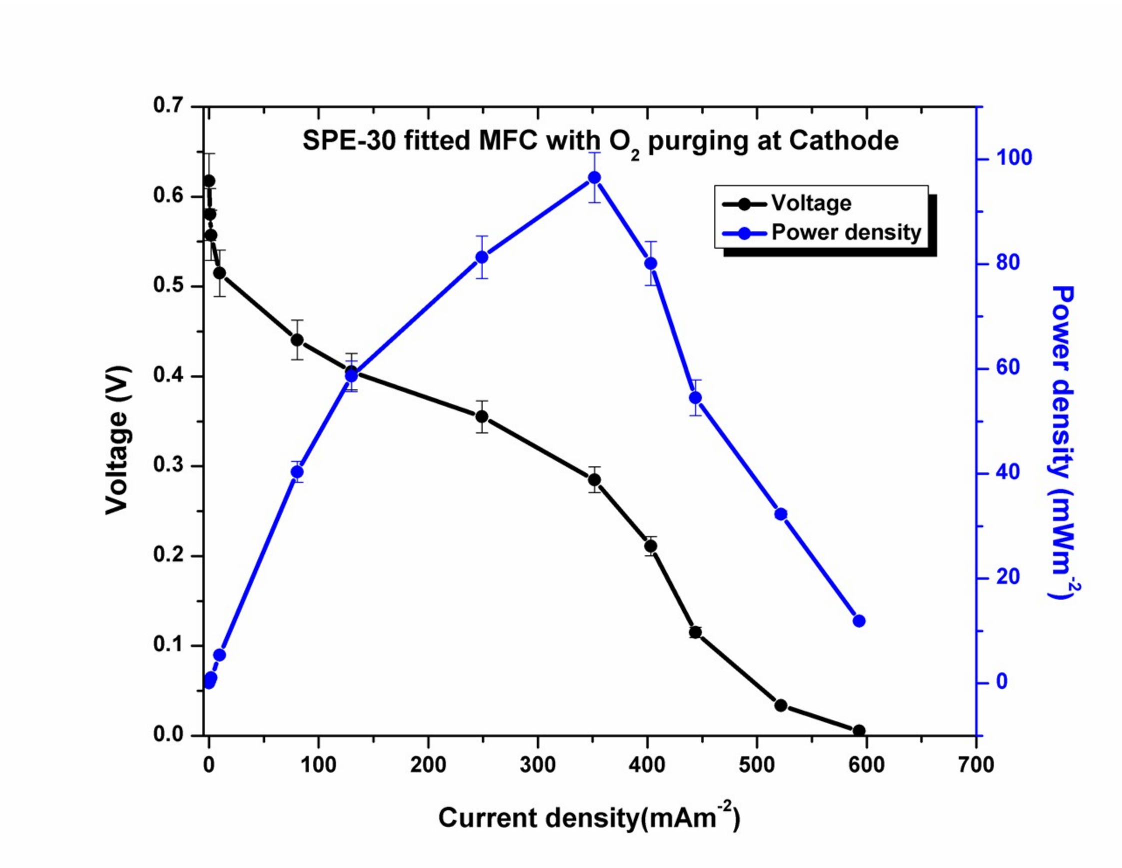


Figure S3: Polarization curve of SPE-30 fitted MFC with O_2 purging at cathode.



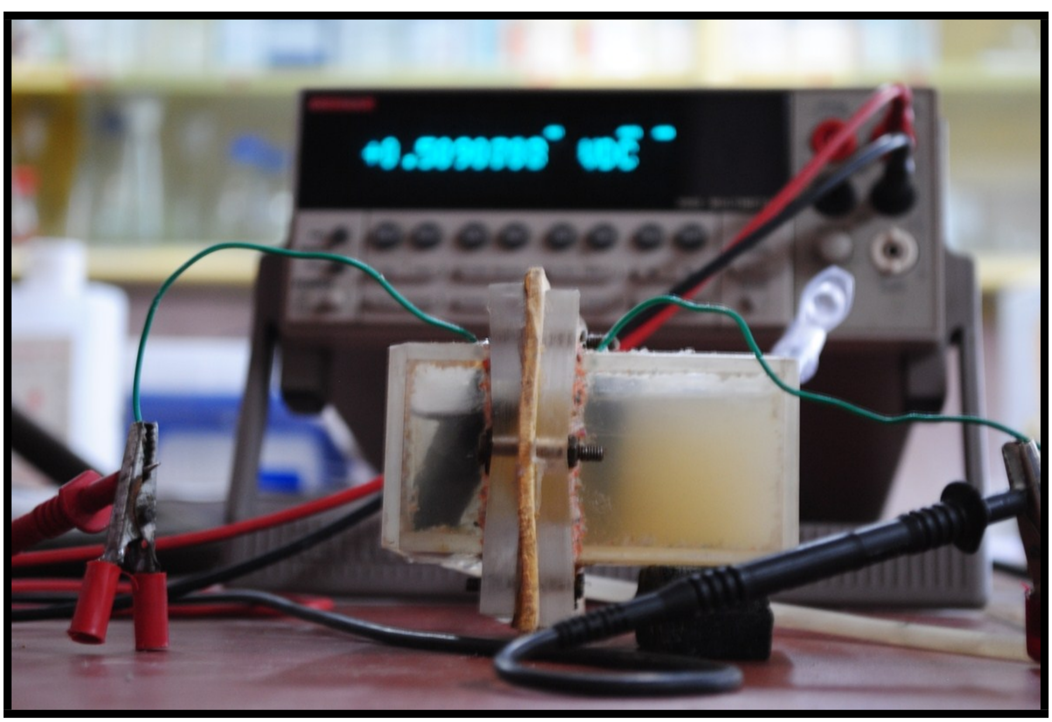


Figure S4: Schematic illustration representing the proton conductivity measurement of membranes.

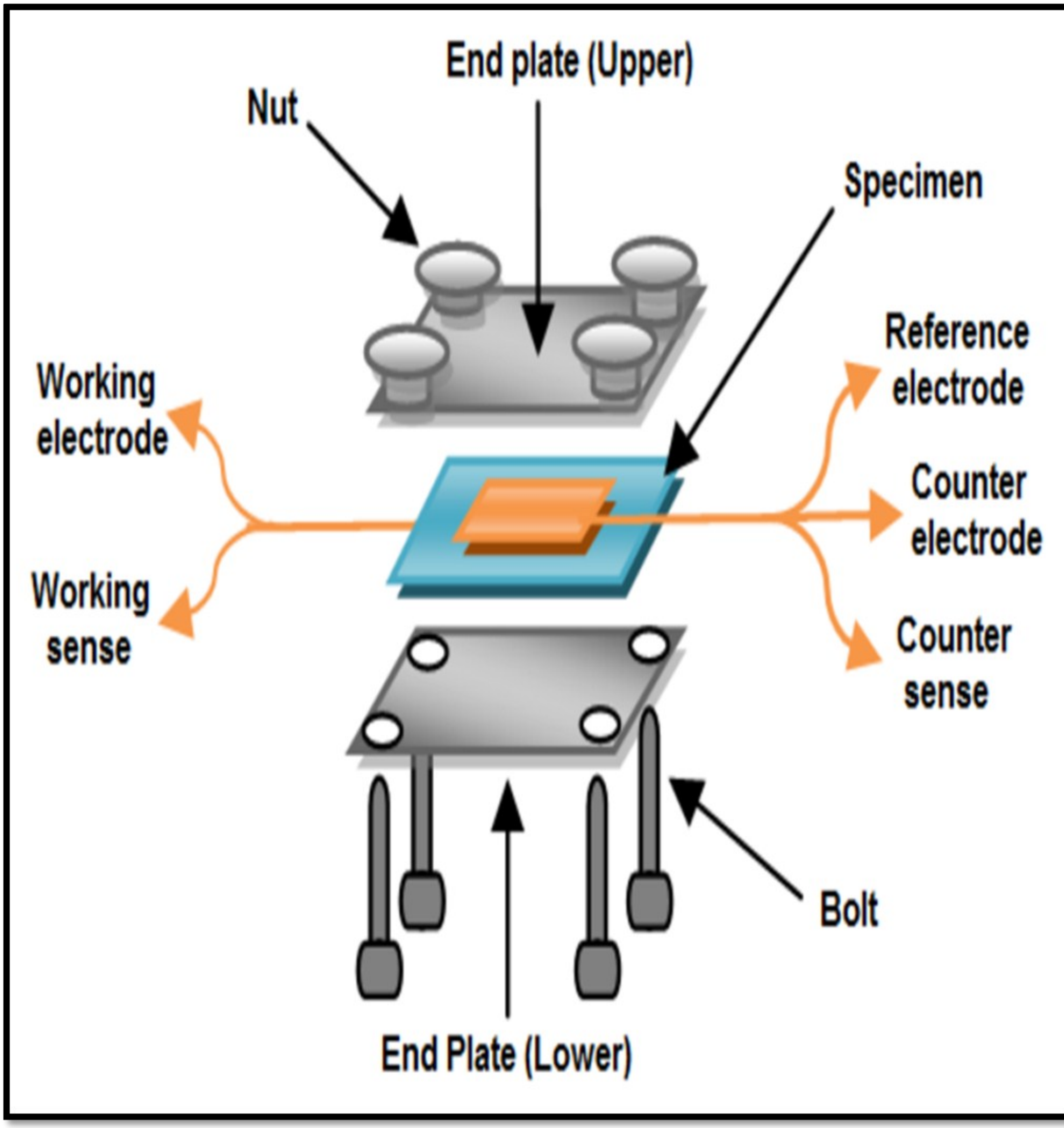


Table 1(T1): Differential Scanning Calorimetry (DSC) analysis of membranes.

Sample Name	Melt onset Temp (°C)	Melt peak Temp (°C)	Enthalpy(J/g) [ΔH_f]	% Crystallinity
Pure LDPE	97.84	112.11	155.834	53.166
SPE-7	97.66	112.41	105.13	35.87
SPE-15	97.54	112.77	83.217	28.4
SPE-30	96.20	111.31	66.26	22.6
SPE-45	104.30	112.13	96.98	33.6
SPE-1 hr	105.1	112.45	143.47	48

Table 2 (T2): A comparative study of MFCs in terms of power generation using different membranes

MFC Type	Electrodes	Used Membranes	Maximum Power density	References
Dual chamber	Composite electrodes (Stainless steel and Graphite)	Nafion 112	1.5 mWm^{-2}	1
Air cathode MFC	Carbon papers	Nafion 117	239.4 mWm^{-2}	2
Air cathode MFC	Carbon papers	SPEEK/PES	70 mWm^{-2}	3
Dual chamber	Graphite Plates	Fe3O4/PES nanocomposite	20 mWm^{-2}	4
Dual chamber	Graphite Rods	Sulfonated polyethylene/poly(styrene-co-divinyl benzene)	44.1 mWm^{-2}	5
Air cathode MFC	Carbon cloths	Sulfonated polyethylene (as MEA)	86.7 ± 5 mWm^{-2}	Present study

References:

1. Godwin JM, Evitts RW, Kennell GF. Microbial fuel cell with a polypyrrole/poly(methylene blue) composite electrode. Reports in electrochemistry 2012; 2:3.

2. Lu N, Zhou SG, Zhuang L, Zhang JT, Ni JR. Electricity generation from starch processing waste-water using microbial fuel cell technology. Biochem Eng J 2009; 43:246–51.

3. Lim, S. S.; Daud, W. R. W.; Md Jahim, J.; Ghasemi, M.; Chong, P. S.; Ismail, M. Sulfonated Poly(ether Ether Ketone)/poly(ether Sulfone) Composite Membranes as an Alternative Proton Exchange Membrane in Microbial Fuel Cells. *International Journal of Hydrogen Energy* 2012, *37*, 11409–11424.

4. Rahimnejad, M.; Ghasemi, M.; Najafpour, G. D.; Ismail, M.; Mohammad, A. W.; Ghoreyshi, A. A.; Hassan, S. H. A. Synthesis, Characterization and Application Studies of Self-made Fe3O4/PES Nanocomposite Membranes in Microbial Fuel Cell. *Electrochimica Acta* **2012,** *85*, 700–706.

5. Grzebyk, M.; Poźniak, G. Microbial Fuel Cells (MFCs) with Interpolymer Cation Exchange Membranes. *Separation and Purification Technology* **2005**, *41*, 321–32.

Table 3(T3): Cost comparison of membranes

Membranes	Costs (USD)
Nafion	~1.8-2.3$/cm^2
AEMs(e.g., AMI 7001)	~1.2-1.6$/cm^2
CEMs(e.g., CMI 7000)	~0.6-1.2$/cm^2
Sulfonated LDPE membranes	~0.1-0.3$/100cm^2

Figure S5: Membrane electrode assembly (MEA) in single chambered MFCs

Abbreviation/symbol	**Description**

batch	Batch/fed-batch mode operation/process
continuous	Continuous flow mode process
t_{total}	Total experimetal duration
t_{max}	Day of maximum performance
A_{an}	Projected surface area of the anode
A_{cat}	Projected surface area of the cathode
A_{mem}	Projected surface area of the membrane
ESA	Electrode surface area (projected)
V	Total reactor volume
V_{an}	Total anolyte volume
V_{cat}	Total catholyte volume
C	Substrate/product conentration
C_{in}/COD_{in}	Influent substrate/COD concentration
C_{out}/COD_{out}	Effluent substarte/COD concentration
ΔC Or ΔCOD	Substrate concentration change (Initial-final)
M	molar mass of the compound
Ag/AgCl	Silver/Silver chloride reference electrode
SHE	Standard hydrogen electrode (reference electrode)
E_{an}	Anode potential
E_{cat}	Cathode potential
E_{cell}	Cell voltage
OCP	Open circuit potnetial
I	Maximum current for batch process
$I_{steady\ state}$	Steady state current for continuous process
R_{int}	Internal resitance
R_{ext}	External resistance
j_{ESA}	Electrode surface based current density
j_{Vol}	Volumetric current density (w.r.t. $V_{an}/V_{cat}/V$)
P	Power
ε_C	Coulombic efficiency
∫I*dt	Charge - Integration of current and time
F	Faraday´s constant
b_{es}	Difference in degree of reduction between substrate and product
$VFR_{influent}$	Volummetric influent flow rate to the anode/cathode chamber
HRT	Hydraulic retention time of anolyte/catholyte for continuous process
Ms/Mp	Moles of substrate used/product produced
$\Delta n_{product/substarte}$	Moles of product produced/substarte used

Q_{total}	Theoretical charge
$Q_{product(S)}$	Charge recovered in the product(s)
ε_E	Energetic efficiency
$\Delta Gf_{product}$	Energy content of product
$\Delta Gf_{substrate}$	Energy content of substrate
ΔH	Heat of combustion of the compound
∫Ecell*I*dt	Power produced over time t
P_{vol}	Volumetric production rate (for product(s))
P_{ESA}	Electrode surface based production rate (for product(s))
Ep1	Energy content product 1
Ep2	Energy content product 2

Potential (in mV) of the routinely used reference electrodes *vs* SHE (at 25 °C)				
RE type	**E (mV)_Experimental**	**E (mV) *vs* SHE**	**E (V) *vs* SHE**	
Ag/AgCl (0.1 M KCl)	0	288	0.288	
Ag/AgCl (3.5 M KCl)	0	205	0.205	
Ag/AgCl (sat. KCl)	**0**	**199**	**0.199**	Used in the experiment
Ag/AgCl (3 M NaCl)	0	209	0.209	
Ag/AgCl (sat. NaCl)	0	197	0.197	
Ag/AgCl (seawater)	0	250	0.25	
SCE (0.1 M KCl)	0	336	0.336	
SCE (1 M KCl)	0	280	0.28	
SCE (3.5 M KCl)	0	250	0.25	
SCE (sat. KCl)	0	244	0.244	
SCE (sat. NaCl)	0	236	0.236	

Microbial fuel cells (MFCs)

Green represents the system values

Red and **Blue** marked are not applicable here

Nature of process	**Mixed substrate to electricity**		**COD value: 1800±240 mg l−1 (total nitrogen: 114±27 mg l−1, PO4–P: 33±6 mg l−1, MgSO4:48 mg l−1).**

Parameter	**Units**	**Formula**	**Data and calculations**
	SYSTEM CHARACTERISTICS		
Projected surface area of the anode *(A_{an})*	m^2		0.0006
Projected surface area of the cathode *(A_{cat})*	m^2		0.0006
Projected surface area of the membrane *(A_{mem})*	m^2		0.0025
Name of target product			Electricity
Total reactor volume *(V)*	m^3		0.00015
Total anolyte volume *(V_{an})* for batch	m^3		0.00015
Total anolyte volume *(V_{an})* for batch	L		0.15
Total catholyte volume *(V_{cat})* for batch	m^3		NIL
Feed/flow rate (anolyte)	L/d		0.1
Hydraulic retention time (*HRT* of anolyte) for continuous	d	V_{an}/feed rate; for example for anolyte	1.5
Average distance between anode	m		0

and cathode

MEASURED PARAMETERS

Anode potential *(E_{an})*	V vs reference	Ag/AgCl	-0.3	
Cathode potential *(E_{cat})*	V vs reference	Ag/AgCl	1	
Cell voltage *(E_{cell})*	V vs reference	Ag/AgCl	0.24	
Open circuit potnetial *(OCP)*	V *vs* reference	Ag/AgCl		
Maximum oxidation current *(I)* for batch	A	as recorded	0.000213	Note: For calculaitng charge (Q), consider EITHER average current over the total batch cycle (t_{total}) OR area under the current curve i.e., Integration of I x t relationship for t_{total}
Steady state current *($I_{steady\ state}$)* for continuous	A	as recorded	0.0036	Note: For calculaitng charge (Q), consider EITHER average current over the total batch cycle (t_{total}) OR area under the current curve i.e., Integration of I x t relationship for t_{total}
Total experimental duration/days of current generation *(t_{total})*	days		7	
Internal resitance *(R_{int})*	Ω		1	
External resistance *(R_{ext})*	Ω		1	
Influent COD *(COD_{in})/Initial substrate conentration (C_{in})*	g/L		1.8	
Effluent COD *(COD_{out})/Final substrate cocentrationn (C_{out})*	g/L		0.21	

Wastewater treatment efficiecny/COD removal	%	$((COD_{in}-COD_{out})/COD_{in})*100$	88.3333333 3	
Organic loading rate	g_{COD}/L.d	$(COD_{in}$*feed rate)/Anolyte volume	1.2	

CALCULATED PARAMETERS

Anode potential (E_{an})	V vs SHE	as calculated from tab sheet	-0.1	Note: where the system is operated with "working electrode" counter electrode potential is only valid when measured with second reference electrode
Cathode potential (E_{cat})	V vs SHE	as calculated from tab sheet	1.2	
Cell voltage (E_{cell})	V vs SHE	as calculated from tab sheet	1.6	
Open circuit potential *(OCP)*	V vs SHE	as calculated from tab sheet		
Surface based current density (j_{ESA}; w.r.t. A_{an}) for batch	A/m^2	I/A_{an}	0.355	
Volumetric current density (J_{Vol} w.r.t. V_{an}) for batch	A/m^3	I/V_{an}	1.42	
Volumetric current density (J_{vol} w.r.t. V; toal reactor volume) for batch	A/m^3	I/V	1.42	
Surface based current density (j_{ESA}; w.r.t. A_{an}) for continuous	A/m^2	$I_{steady\ state}/A_{an}$	6	
Volumetric current density (J_{vol} w.r.t. V_{an}) for continuous	A/m^3	$I_{steady\ state}/V_{an}$	24	
Volumetric current density (J_{vol} w.r.t. V; toal reactor volume) for continuous	A/m^3	$I_{steady\ state}/V$	24	

Power *(P)* for batch/continuous	W	E_{cell}*I or $I_{staedy\ state}$	0.00005112
Power density (w.r.t. A_{an}) for batch/continous	W/m^2	P/A_{an}	0.0852
Power density (w.r.t. A_{cat}) for batch/continous	W/m^2	P/A_{cat}	0.0852
Volummetric power density (w.r.t. *V; total reactor volume*) for batch/continuos	W/m^3	P/V	0.3408