Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

On the Development of a Proton Conducting Solid Polymer Electrolyte Using Poly(ethylene oxide)

Sudeshna Patra,[1] Anand B. Puthirath, [1] Thazhe Veettil Vineesh, [1] Sreekanth Narayanaru, [1] Bhaskar Soman, [1]

Shruti Suriyakumar, [2] A. Manuel Stephan, [2]and Tharangattu N. Narayanan[1]*

*Corresponding author: tnn@tifrh.res.inor tn_narayanan@yahoo.com

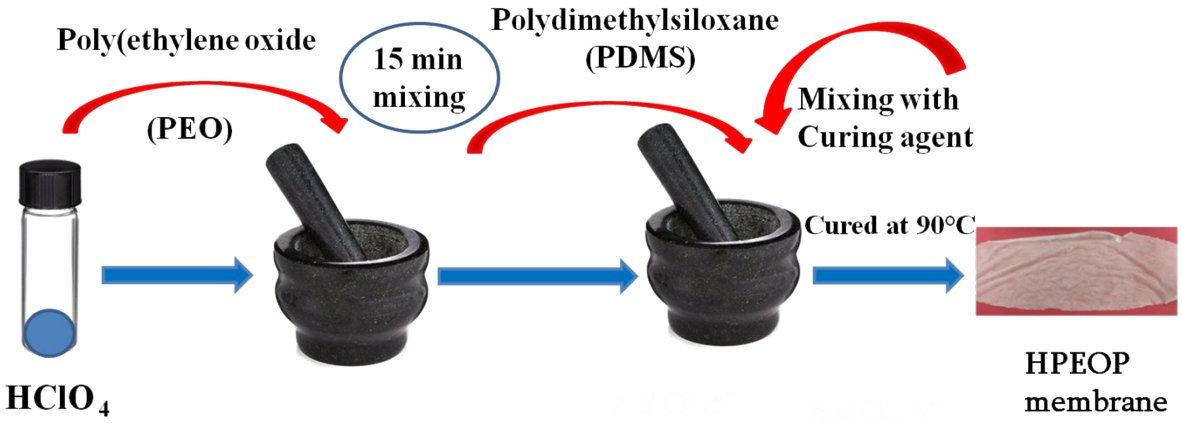


Figure S1: synthesis sequence for the development of solid state proton conducting polymer electrolyte

PDMS Cross-linking process:

The Sylgard 184 Silicone Elastomer from Dow Corning is supplied as two part liquid component kit (1:1 ratio of base and curing agent)

The Base (part A) contains the followings:

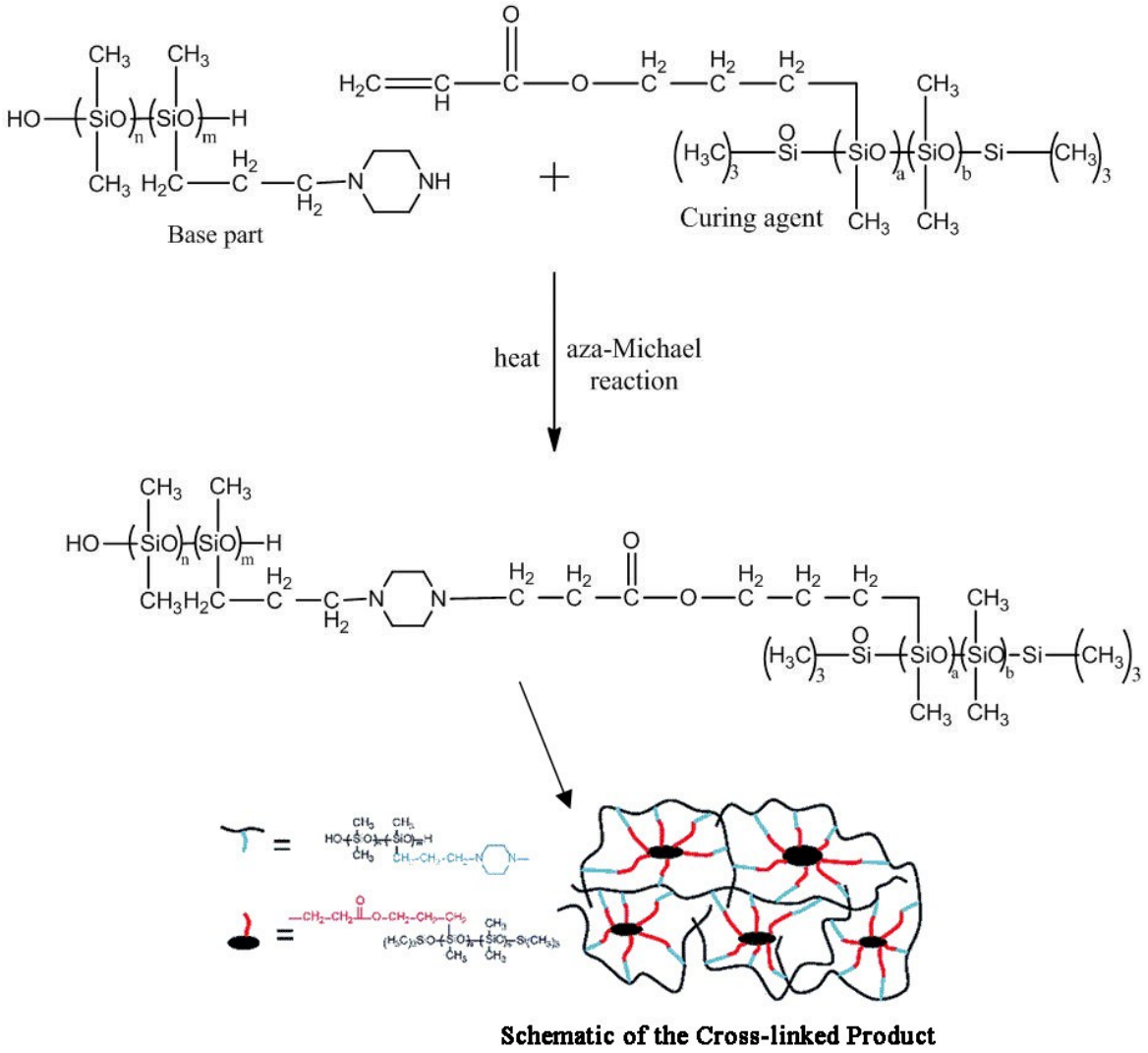
1. Dimethyl siloxane, dimethylivinyl terminated
2. Dimethylvinylated & trimethylated silica
3. Tetra (trimethoxysiloxy) silane
4. Ethyl benzene

The Curing Agent (part B) contains the followings:

1. Dimethyl methylhydrogen siloxane
2. Dimethyl siloxane, dimethylvinyl terminated

3. Dimethylvinylated and trimethylated silica
4. Tetramethyl tetravinyl cyclotetra siloxane
5. Ethyl benzene

The cross linking is happening due to an aza-michael addition reaction. The reaction is an aza-Michael reaction which is an addition reaction between a nucleophile (Michael donor) and an electron deficient alkene molecule (Michael acceptor).[1] The mechanism can be explained as follows:[2]



Schematic of the Cross-linked Product

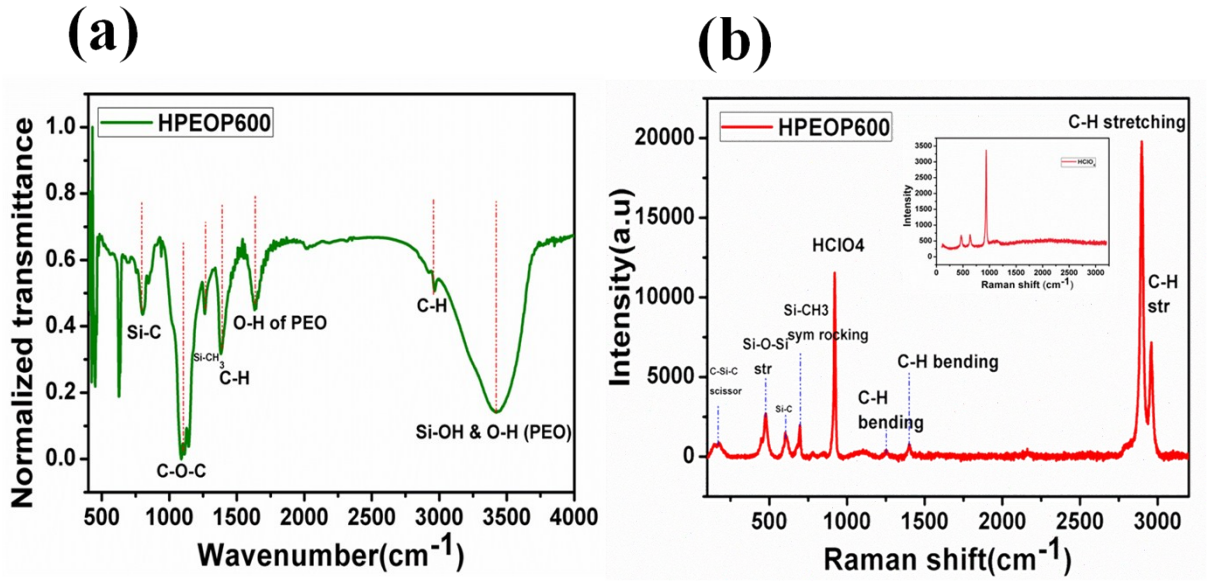


Figure S2: (a)Infrared & (b)Raman spectra of HPEOP600 sample. Inset is showing Raman spectra of Perchloric acid (HClO4).

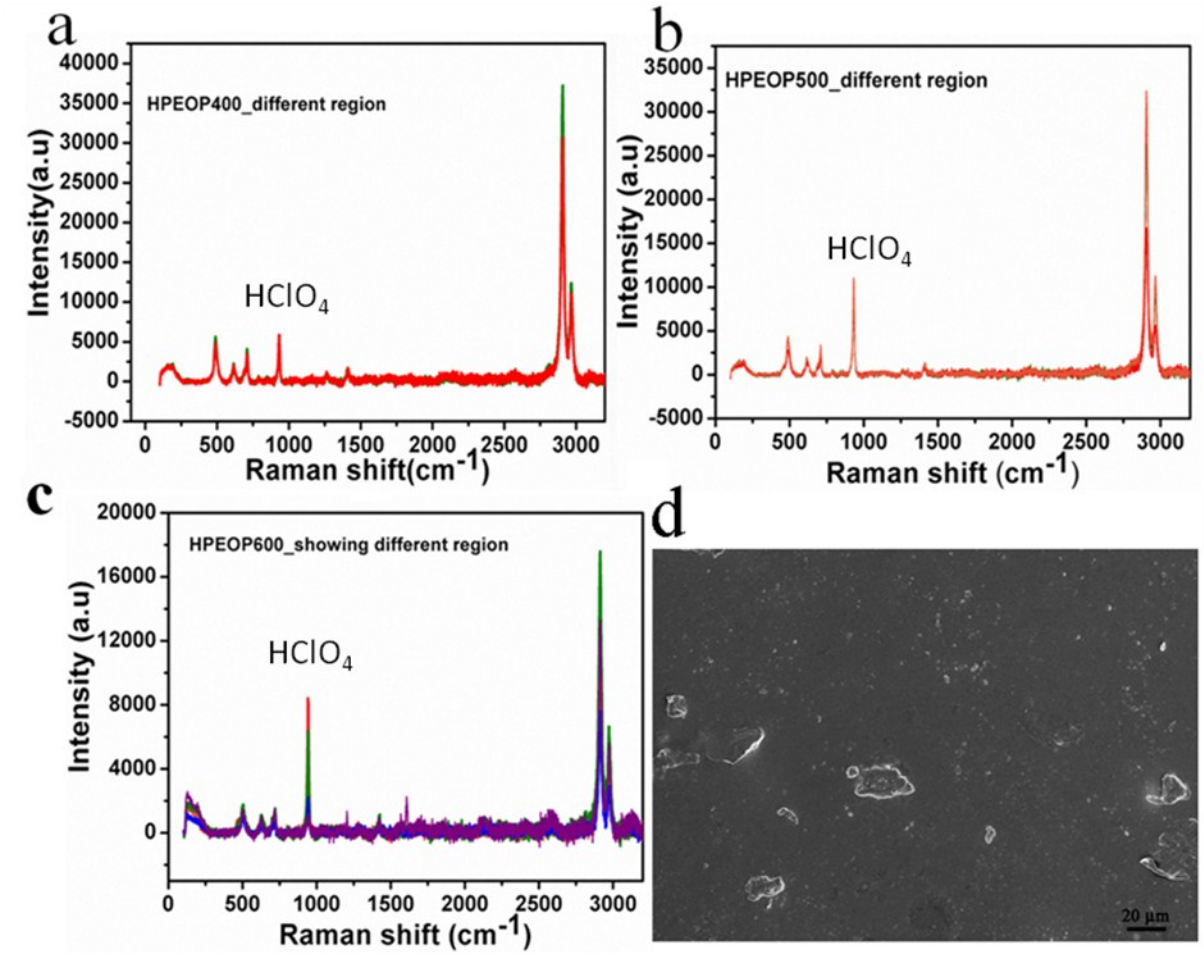


Figure S3: (a-c) Raman spectra of different HPEOP sample showing different region of the samples, (d) SEM image of PEOP (PEO-PDMS).

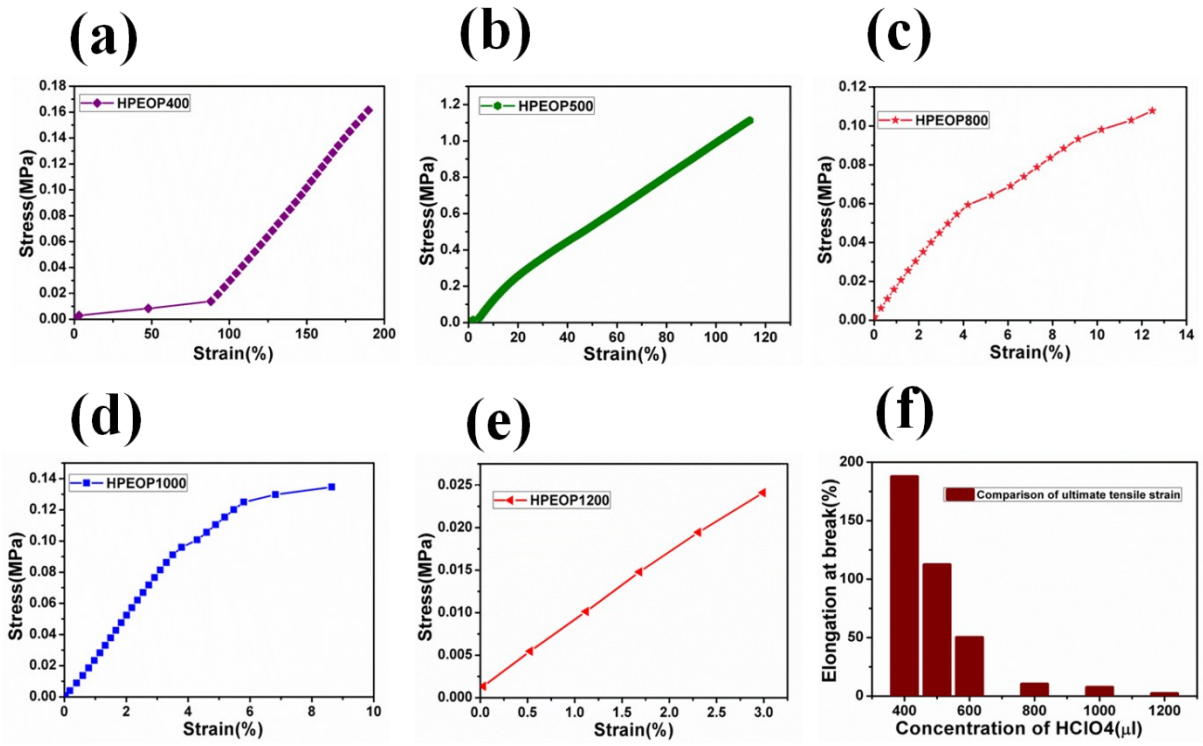


Figure S4: Stress-strain curves of different HPEOP sample in control force mode (a-e). (f) is showing comparison of elongation at break for different sample.

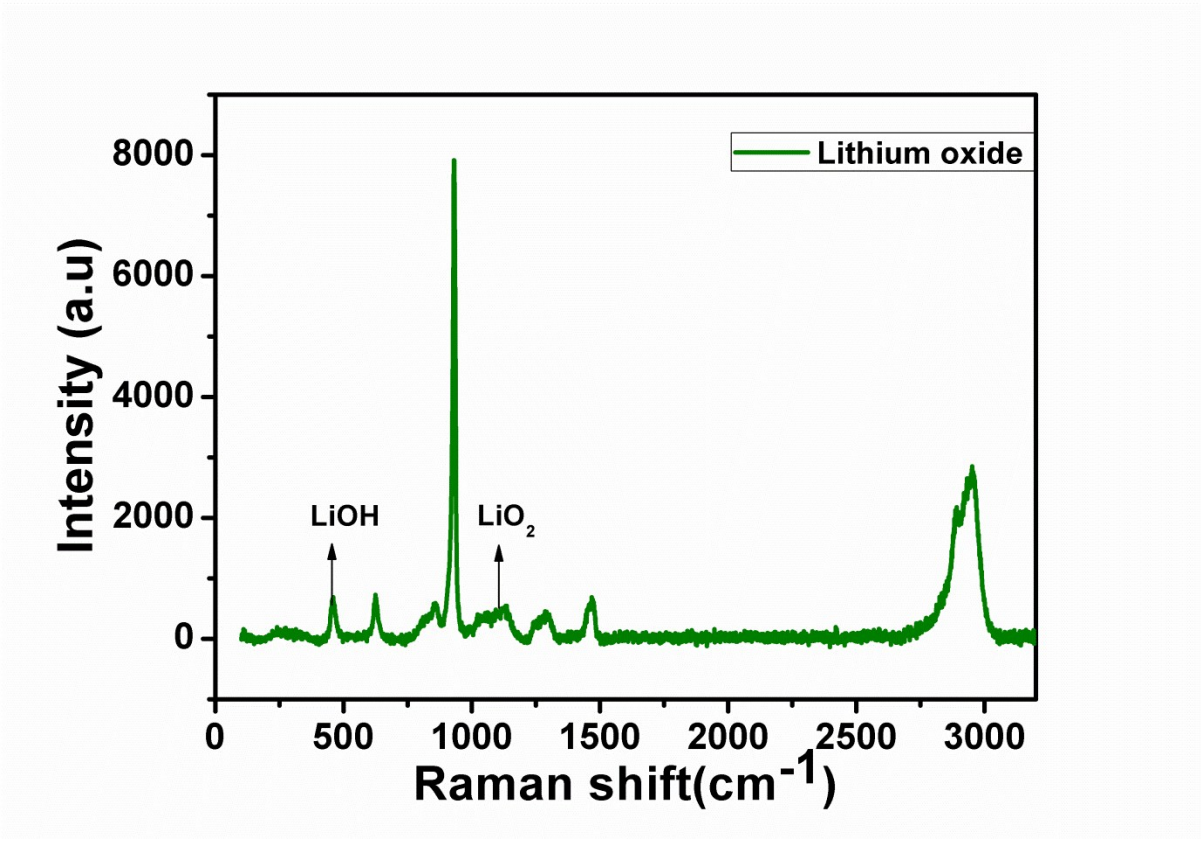


Figure S5: Raman spectra of black deposits on the surface of swagelok cell (steel) indicating the formation of lithium oxide

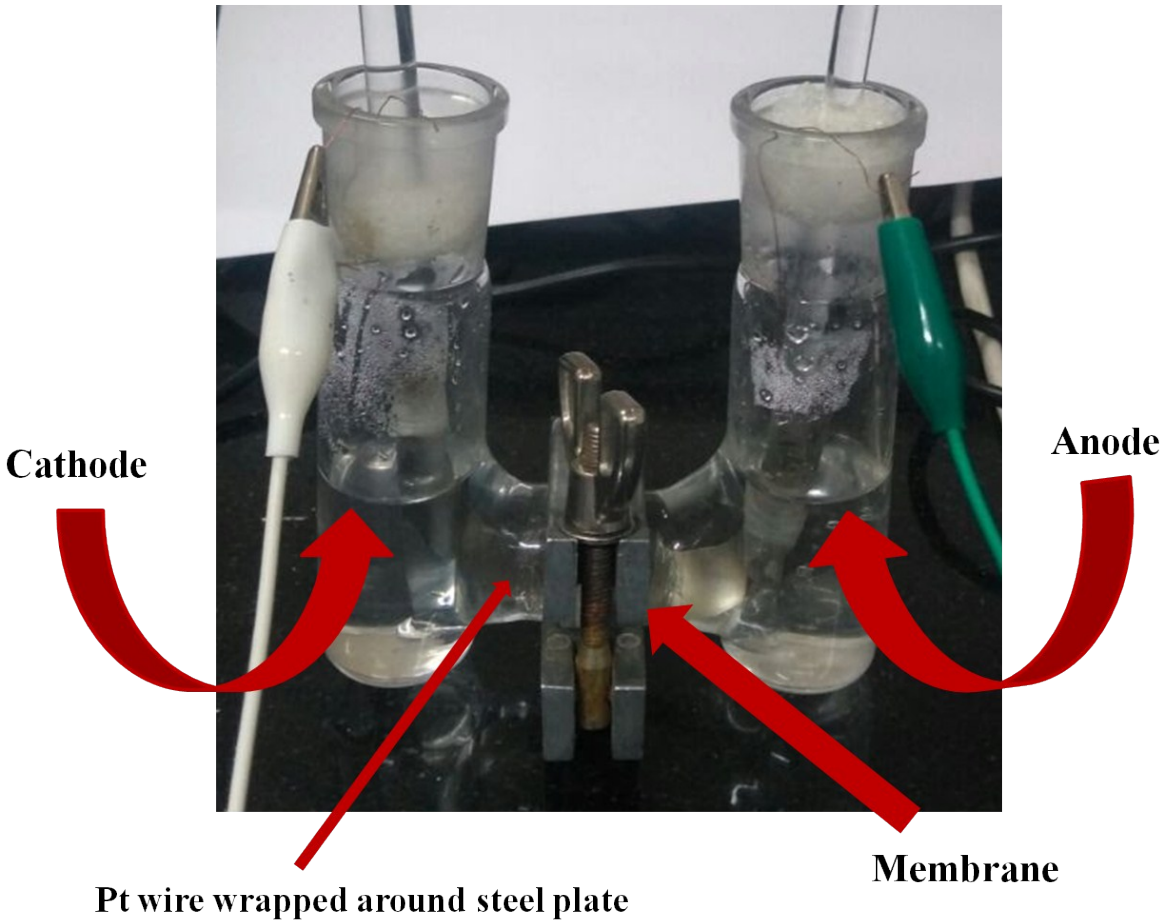


Figure S6: The home-made electrolysis set-up used throughout the chronoamperometry experiment.

Calculation of electrochemical active surface area:

The surface of an electrode should be neat and clean to avoid any parasite reactions. In order to quantify the intrinsic catalytic activity of the electrode electrochemically active surface must be determined. Here we have calculated the active surface area of the pt electrode (pt wire) used in the water electrolysis setup. The technique used here is a cyclic voltammetry.

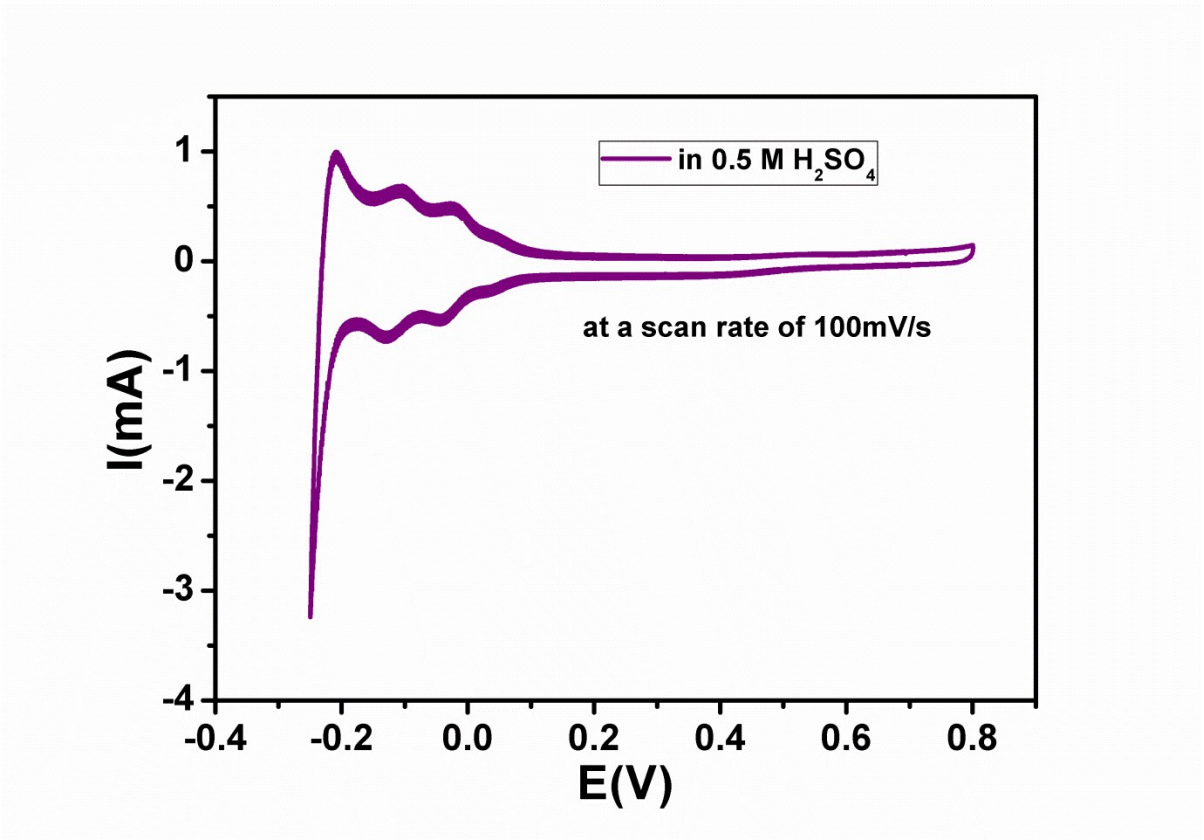


Figure S7: Voltammetric curve obtained by cyclic voltammetry (100th cycle) for platinum electrode in H_2SO_4 solution

Protons from the sulphuric acid are adsorbed at the surface of the electrode during the reduction of platinum while these atoms of hydrogen are desorbed during the oxidation process.

$$Had \longrightarrow H^+ + e^-$$

The total number of electrons liberated during oxidation gives the measure of the number of desorbed hydrogen atoms and consequently the number of adsorption sites present on the electrode can be calculated. The total charge corresponding to the hydrogen desorption is associated with the integral of the curve for a certain interval of potential. The total charge of desorption can be expressed as follows.

$$Q = 1/Vb + \int_{E1}^{E2} I.dE$$

Where V_b is the scan rate. The whole equation should be divided by 210 $\mu C.cm^{-2}$ which is the electrical charge associated with monolayer adsorption of hydrogen.

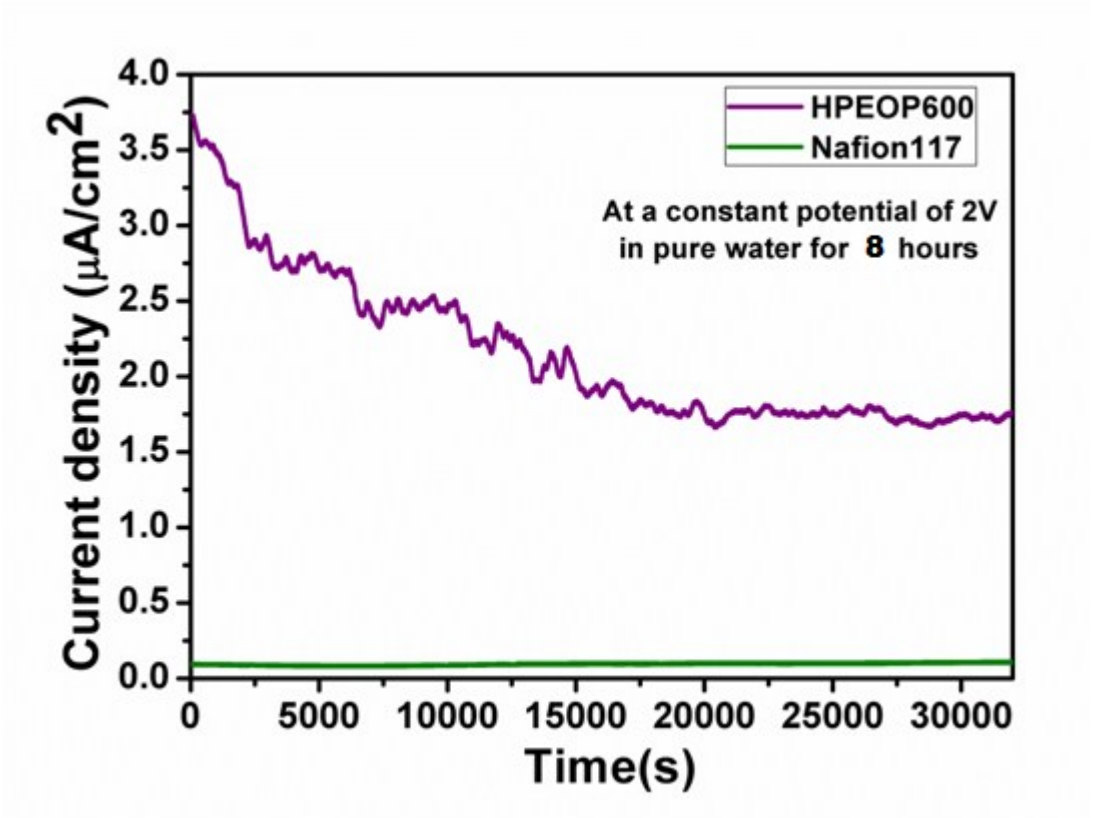


Figure S8: Chronoamperometry study of Nafion 117 & HPEOP600 in pure water for 8 hours.

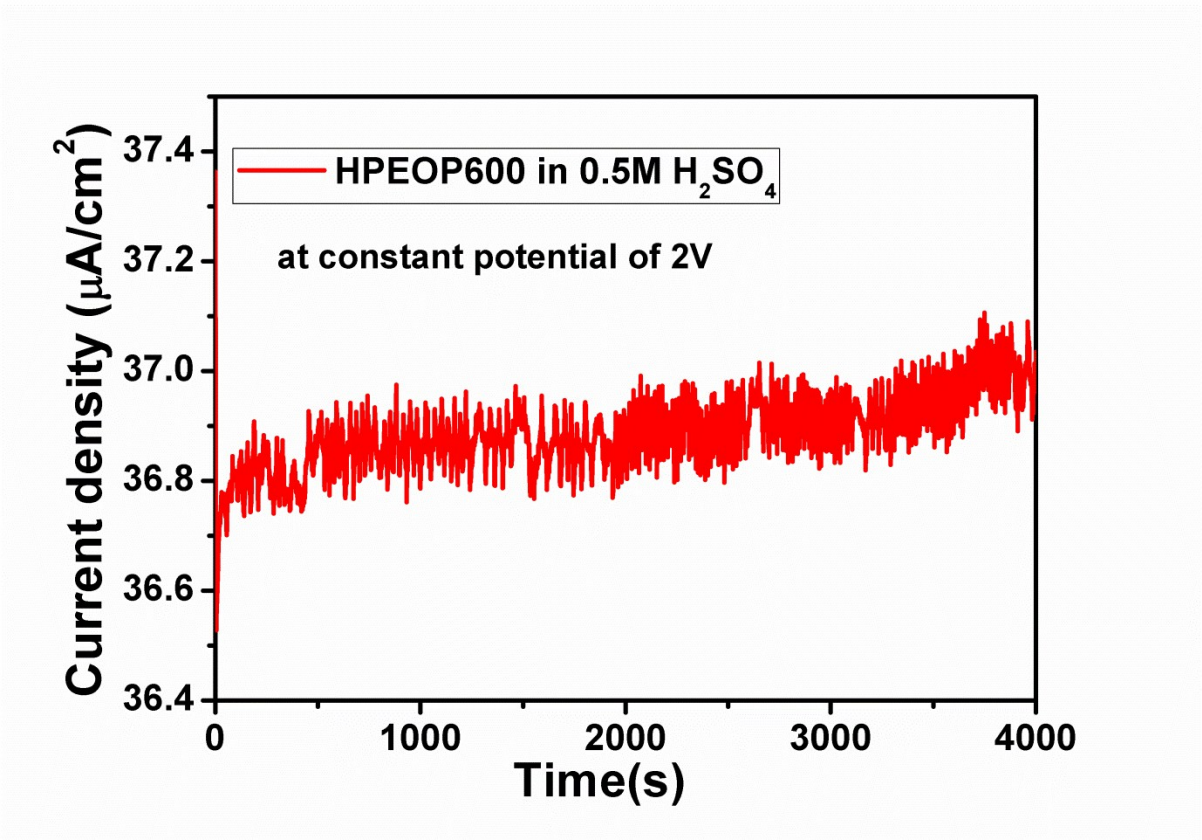


Figure S9: Chronoamperometry study of HPEOP600 in 0.5M H_2SO_4.

Table S1: Ultimate tensile stress & elongation at break for all the samples

Membrane	Tensile stress, σ (MPa)	Elongation at break(%)
HPEOP400	0.24±0.11	187.72±2.75
HPEOP500	0.86±0.35	112.42±1.62
HPEOP600	0.62±0.01	50.07±1.75
HPEOP800	0.09±0.02	10.25±1.93
HPEOP1000	0.09±0.05	7.44±1.70
HPEOP1200	0.023±0.006	2.19±0.75

Table S2: Cost analysis of laboratory grade HPEOP600 sample

Material	Company	Amount	Cost(INR)
Poly(ethylene oxide)	Sigma Aldrich	100mg	73.10
Polydimethylsiloxane	Dow - Corning	1mL	4.82
Cross linker	Dow - Corning	100µL	0.62
Perchloric acid	Sigma Aldrich	600µL	7
Total	225 cm^2		85.54

References:

1. A. Genest, D. Portinha, E. Fleury and F. Ganachaud, *Prog.Polym. Sci.* 2017, **72**, 61.

2. L. Feng, L. Zhou and S. Feng, *RSC Adv.* 2016, **6**, 111648.