

Supporting Information

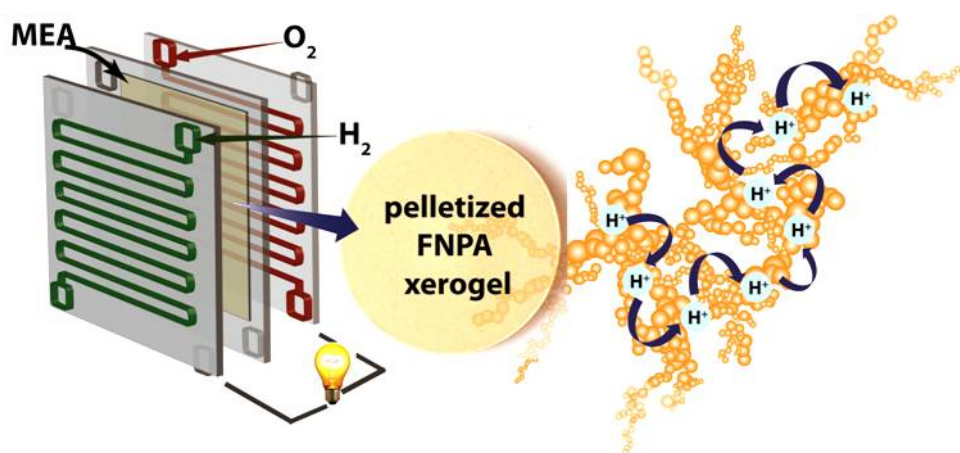
Fe (III) Phytate Metallogel as a Prototype Anhydrous, Intermediate Temperature Proton Conductor

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Section 1: Experimental methods and measurements

1.1. General synthesis:

The chemicals, ferric (III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and phytic acid solution (50 wt% (w/w) in H_2O) used for the present study were purchased from Sigma Aldrich Chemicals. N, N-dimethyl formamide (DMF) was purchased from Rankem Chemicals. All the starting materials were used without any further purification.

The synthesis of FNPA metallo gel involves mixing of DMF solution of Fe^{3+} and phytic acid in different volumetric ratios. Of all, 2:1(v/v) was observed to gelate faster. The metallo gel was allowed to age for another 12 h in order to strengthen the gel fibres.

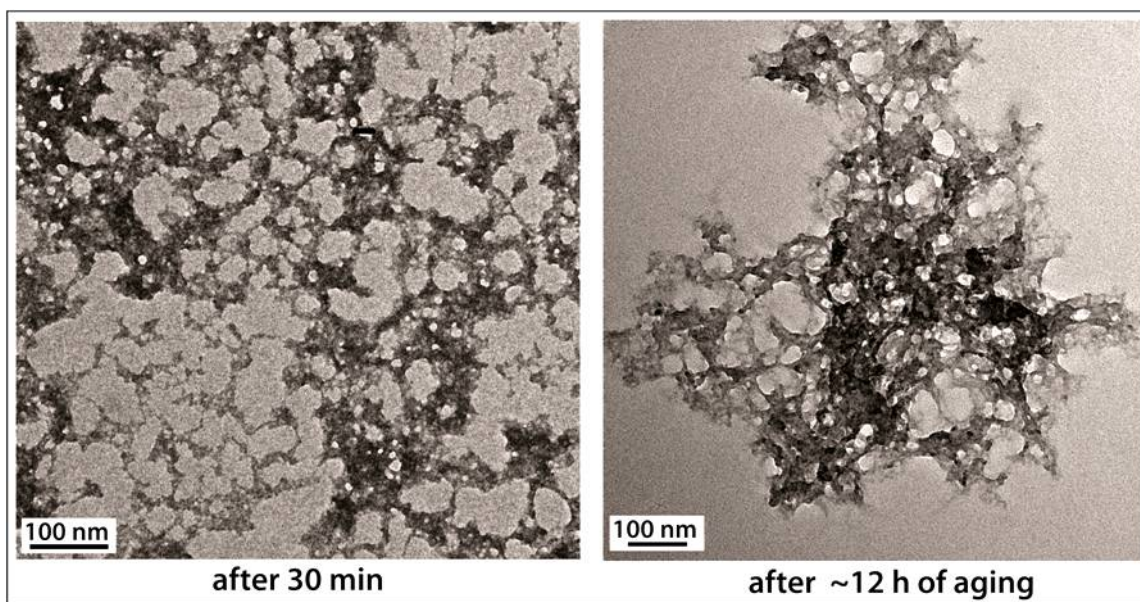


Figure S1. HRTEM images of FNPA metallo gel after 30min and ~12h of mixing Fe^{3+} and phytic acid solutions in DMF in 2:1 volumetric ratio.

1.2. Rheology, TGA, FTIR and PXRD Experiments:

The rheology experiments were carried out using a TA-ARES rheometer equipped with force rebalance transducer. Couette geometry with cup and bob diameter of 27, 25 mms and height 38 mm was used for the rheology measurements. The Thermo Gravimetric Analysis (TGA) experiments were carried out in nitrogen atmosphere from 25–800 °C using a SDT Q600 TG-DTA analyzer at heating rate of 10 °C min⁻¹. The Fourier Transform Infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer equipped with universal ZnSe ATR (attenuated total reflection) accessory or using a Diamond ATR (Golden Gate) in the 400-4000 cm⁻¹ region.

Section2: Characterization of FNPA-metallogel and xerogel

2.1. Rheology Studies: Frequency and strain dependent studies of Fe-metallogels

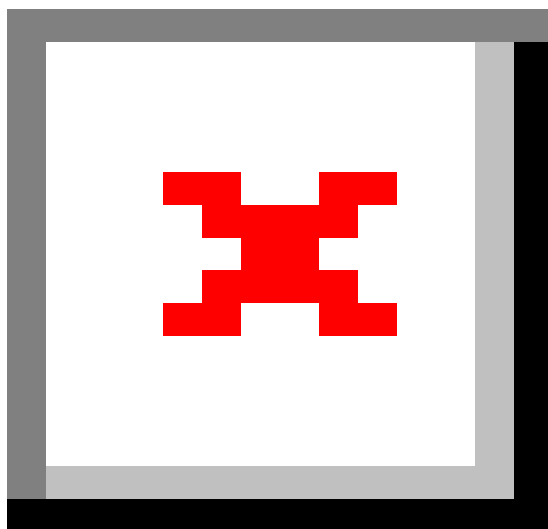


Figure S2. a) Strain dependent b) Frequency dependent studies of FNPA metallogel (2:1 v/v) synthesized at 90°C, c) Strain dependent d) Frequency dependent studies of FNPA metallogel (2:1 and 3:1 v/v) synthesized at RT after 6 days.

2.2. Pore-Size distribution

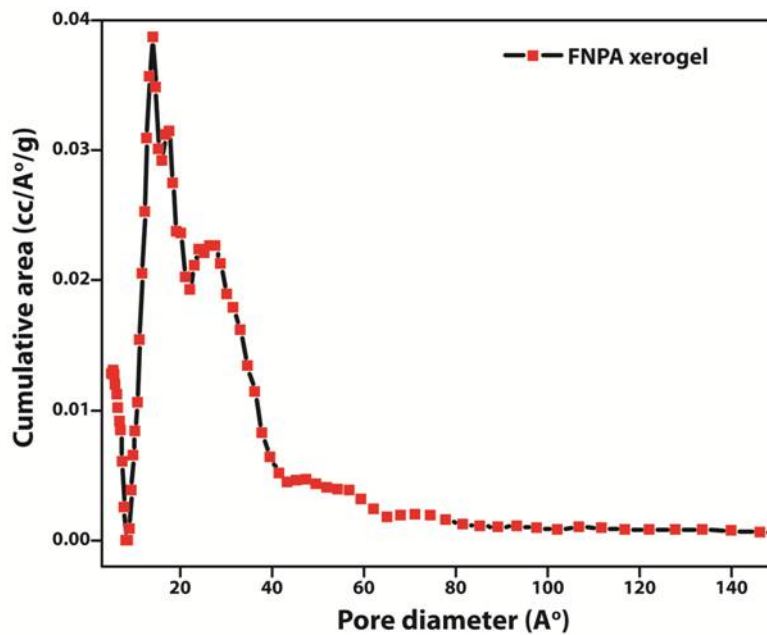


Figure S3. (a) Pore size distribution of FNPA xerogel (2:1) synthesized at 90°C.

2.3. HRTEM studies

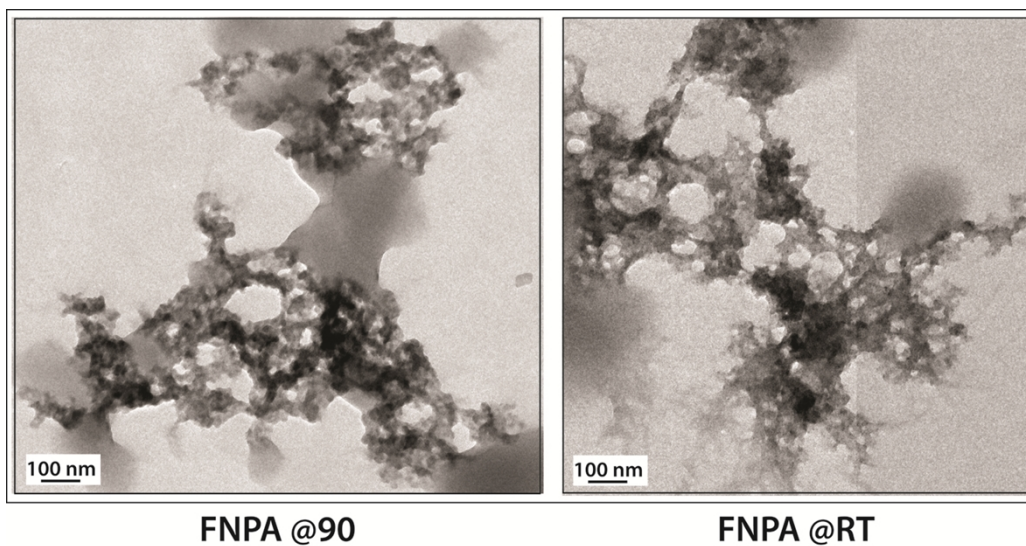


Figure S4. (a) HRTEM of FNPA metallogel synthesized at (b) 90°C, (c) RT after 6 days.

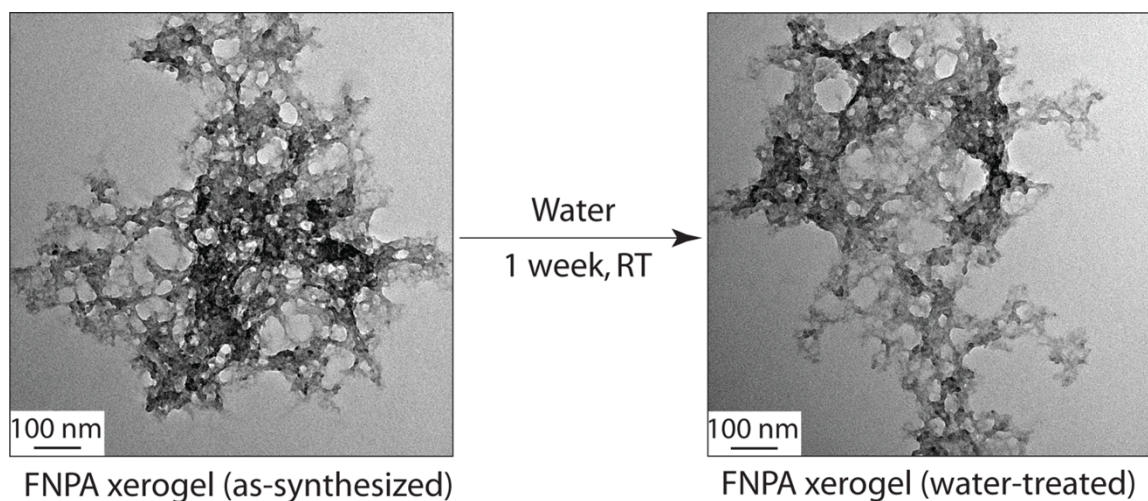


Figure S5. HRTEM image of FNPA xerogel after water treatment (DI water) for 1 week at room temperature.

2.4. PXRD and Thermogravimetric analysis of FNPA-Xerogel

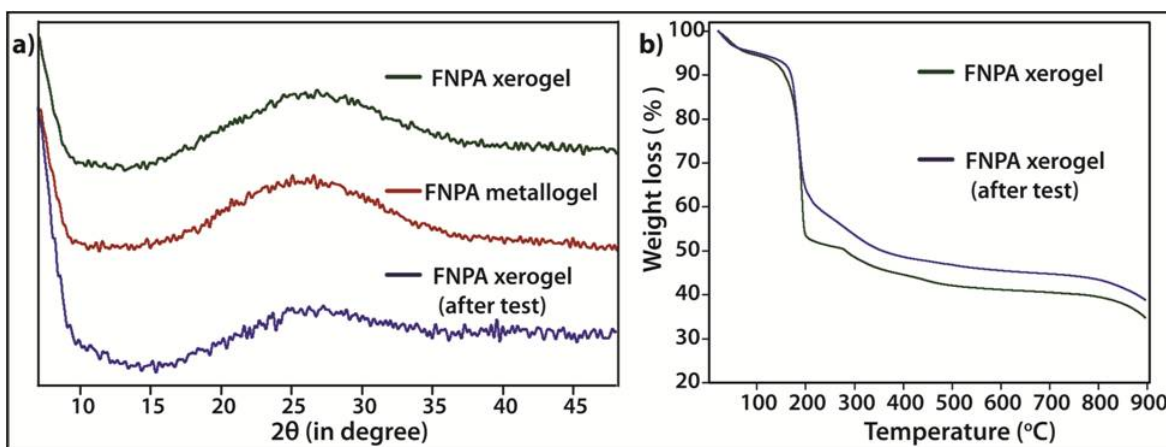


Figure S6. a) PXRD pattern of FNPA metallogel and xerogel indicating the material's highly amorphous nature. b) TGA plots of FNPA-xerogel before and after proton conductivity measurements.

In order to quantitatively determine the effect of temperature on the weight loss of the material, isothermal TGA analyses of FNPA xerogel was performed at three different temperatures (130 $^\circ\text{C}$, 150 $^\circ\text{C}$ and 160 $^\circ\text{C}$) for 4 h each. A comparative study (Figure S7) of the thermograms suggests weight loss of ~ 14 wt % at 130 $^\circ\text{C}$, due to the evaporation of solvent (DMF and water). The framework degradation sets in only after 150 $^\circ\text{C}$ resulting in a massive

weight loss of ~40%, which could thus be found to be the prime reason behind the drop in proton conductivity. [Weight loss at 150 °C = ~40%; Weight loss at 160 °C = ~45%].

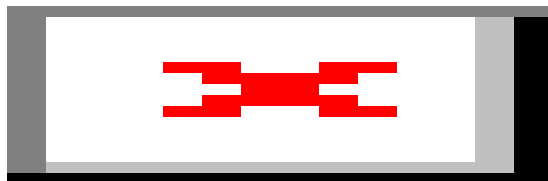


Figure S7. TGA profile of FNPA xerogel a); Zoomed view of the TGA profile up to 200 °C b) and isothermal TGA thermograms of FNPA xerogel at three different temperatures (130 °C, 150 °C and 160 °C) c). Quantification of weight loss incurred at each step.

2.5. IR spectra of FNPA xerogel

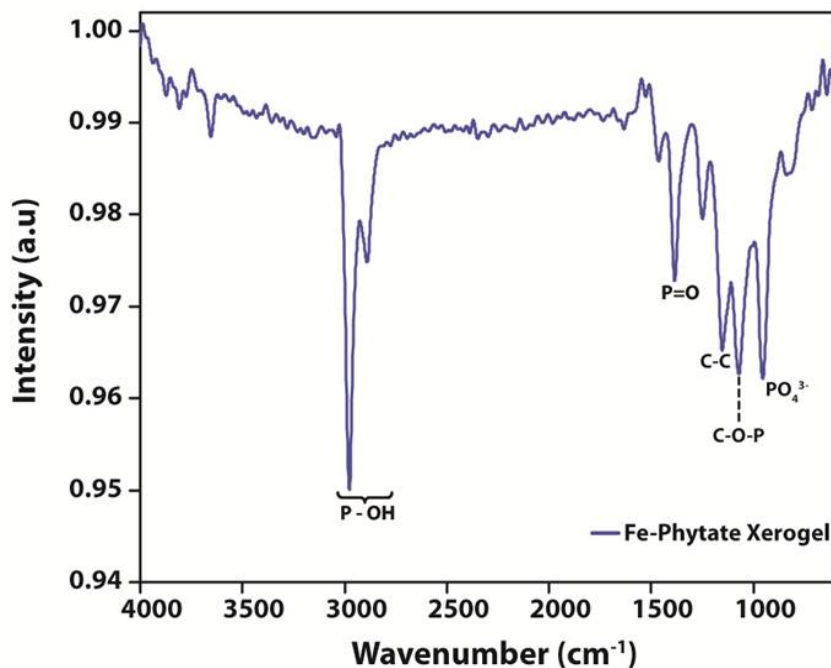


Figure S8. IR spectra of FNPA xerogel

2.6. Study of

(i) Factors affecting the diameter of the metallogel nanospheres

The concentration of the gelator is known to be one of the factors determining the mechanical property of the gelator. Likewise, in the present experiment, it was observed that an increment in gelator concentration proportionally thickens/strengthens the gelator fibres. A concentration dependent HRTEM study of the FNPA metallogel indicated that that the diameter of the nanospheres (and the diameter of the gelator fibre as well) is directly related to the concentration of the gelator. (Please see the table given below)

<u>Concentration</u> (Fe:Phytate = 2:1)	<u>Diameter of the nanospheres</u>
9.3 wt% (2X)	100-120 nm
4.65 wt% (X)	40-80 nm
1.16 wt% (0.25 X)	10-20 nm

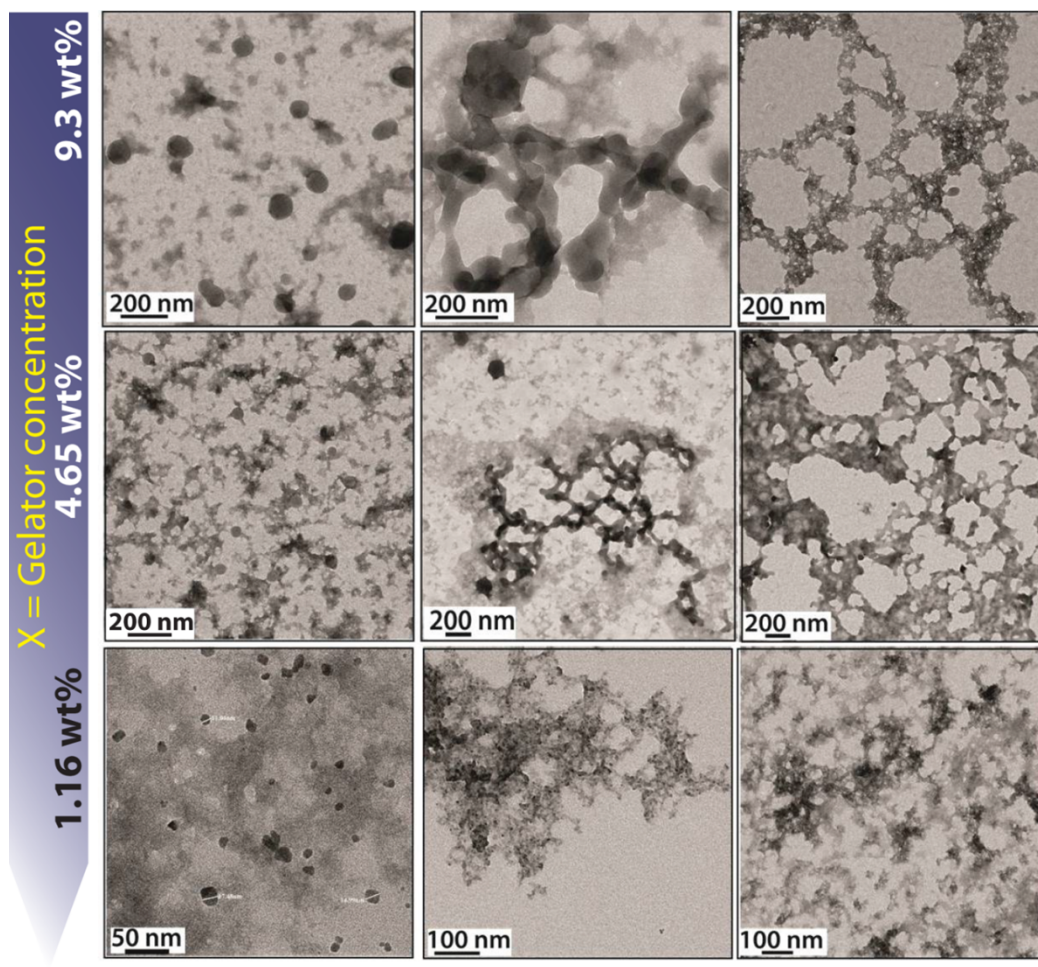


Figure S9: Concentration-dependent HRTEM analysis of FNPA gel ($X=4.65$ wt %)

(ii) Effect of solvent:

We have tried several polar as well as non-polar solvents for gelation. Results of those trials have been tabulated below:

Table 1: Solvents tried for gelation

S.No.	Solvent	Phase	Gelation time	Gel-phase color	Kamlet-Taft solvent parameters		
					α	β	π^*
1	H ₂ O	G	-	-	1.17	0.47	1.09
2	DMF	G	1 hr	White	0.00	0.69	0.88
3	DEF	G	1 hr	Yellow	-	-	-
4	DMAC	P	-	-	0.00	0.76	0.88
5	NMP	P	-	-	-	-	-
6	Acetone	P	-	-	0.08	0.43	0.71
7	THF	P	-	-	0.00	0.55	0.58
8	CH ₃ CN	P	-	-	0.19	0.40	0.75
9	MeOH	S	-	-	0.98	0.66	0.60
10	EtOH	S	-	-	0.86	0.75	0.54
11	<i>i</i> -PrOH	S	-	-	0.76	0.84	0.48
12	<i>n</i> -Hexane	I	-	-	0.00	0.00	-0.04
13	Et ₂ O	I	-	-	0.00	0.47	0.27
14	EtOAc	I	-	-	0.00	0.45	0.55
15	CH ₂ Cl ₂	I	-	-	0.13	0.10	0.82
16	CHCl ₃	I	-	-	0.20	0.10	0.58
17	Benzene	I	-	-	0.00	0.10	0.59
18	Toluene	I	-	-	0.19	0.40	0.75
19	DMF/H ₂ O	S	-	-	-	-	-

[Solvent abbreviations: DMF = *N*, *N'*-dimethylformamide; DEF = *N*, *N'*-diethylformamide; DMAC = *N*, *N'*-dimethylacetamide; NMP = 1-methyl-2-pyrrolidone; THF = Tetrahydrofuran. Abbreviations: S = solution; G = stable gel; I = insoluble; P = precipitates.]

2.7. MALDI-TOF MS of FNPA metalloel

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) was performed for FNPA gel using dithranol as matrix. The sample concentration was ca.1.0 μM in DMF. Concentration of the matrix solution (in THF) was made to 1mg/mL and added to the sample solution in 1:1 ratio. The resulting solution was deposited on a stainless steel sample holder and dried under vacuum. The sample was then scanned with N_2 laser (intensity = 4500) at a scan rate of 150 shots per spectrum. The samples were analyzed under optimized conditions in positive reflectance mode. A prominent peak at $m/z = 781.9367$ was observed which corresponds to $2\text{Fe}^{3+} + 1$ Phytic acid $+ 8\text{H}^+$.

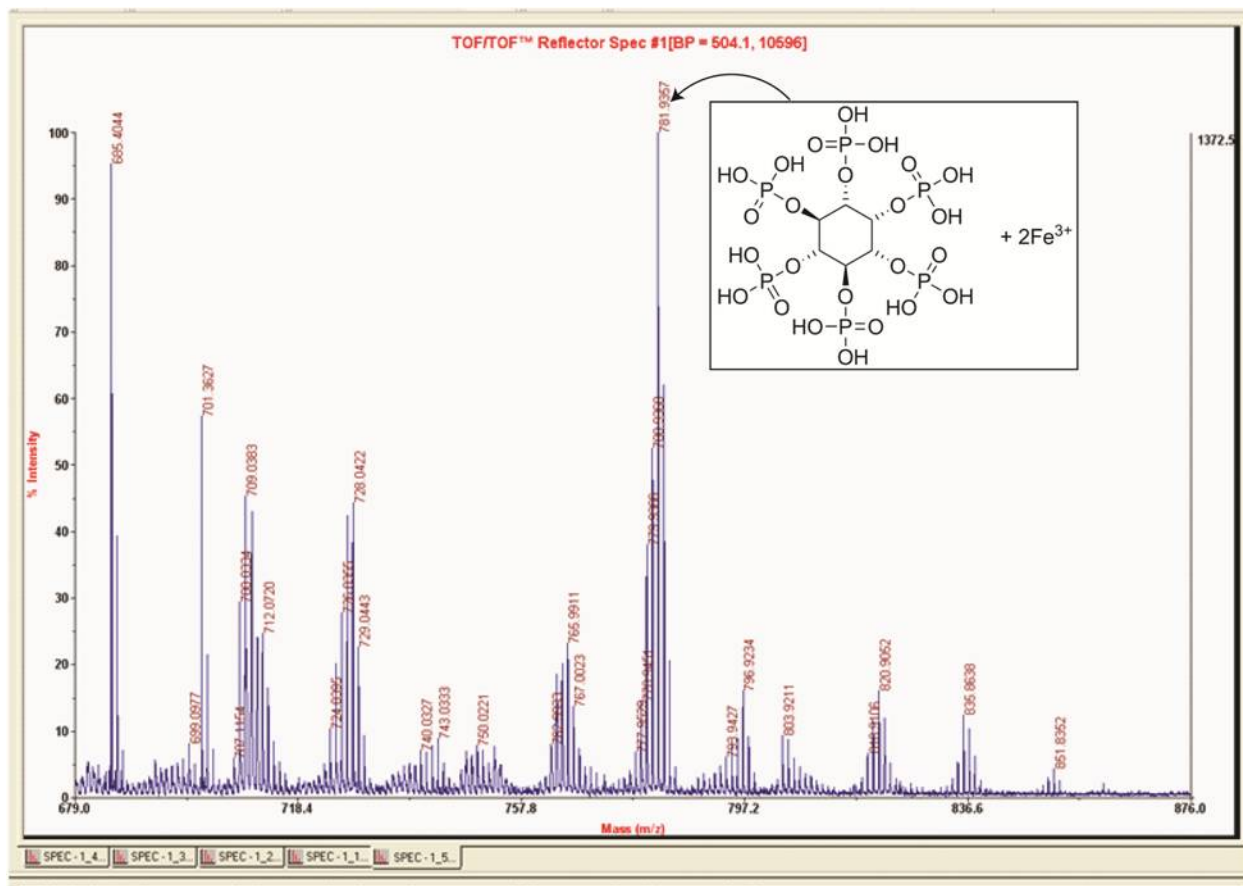
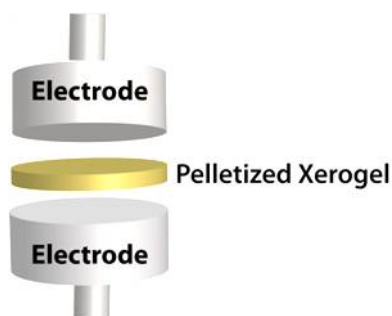


Figure S10. MALDI-TOF MS spectra of FNPA metalloel indicating presence of prominent peak at m/z value ~ 781 .

Section 3: Proton Conduction experimental details of FNPA xerogel

3.1. Determination of Proton conductivity using Stainless Steel (SS) electrodes



Alternating current (AC) impedance measurements were performed to study the proton conducting ability of the metallogel *via* quasi-four probe method. ca. 200mg of FNPA xerogel, obtained on slow drying of FNPA metallogel at 70-80°C, was pressed using a standard die (13 mm diameter) into pellets of 0.25-0.35 cm thickness (Absolute, Mitutoyo Co. Ltd., Japan with accuracy 0.01 mm) and then evacuated at 80°C under vacuum. The pellet was manually pressed between two stainless steel blocking electrodes. The electrode assembly was then placed inside a temperature controllable incubator (SH-241, ESPEC Co. Ltd., Japan) connected to *BioLogic* VPM3 electrochemical work station. The set up was flushed with dry N₂ before the measurement to ensure complete dryness. The pellet was the heated slowly from RT to 130°C. The membrane resistance was calculated by fitting the Nyquist plots obtained at each temperature.

The proton conductivity of the pelletized xerogel was determined using the following relation;

$$\sigma = l/(R.A)$$

where σ = proton conductivity (S.cm⁻¹),

l = pellet thickness (cm),

R = resistance of the pellet (Ω) and

A = area of the pellet (cm²).

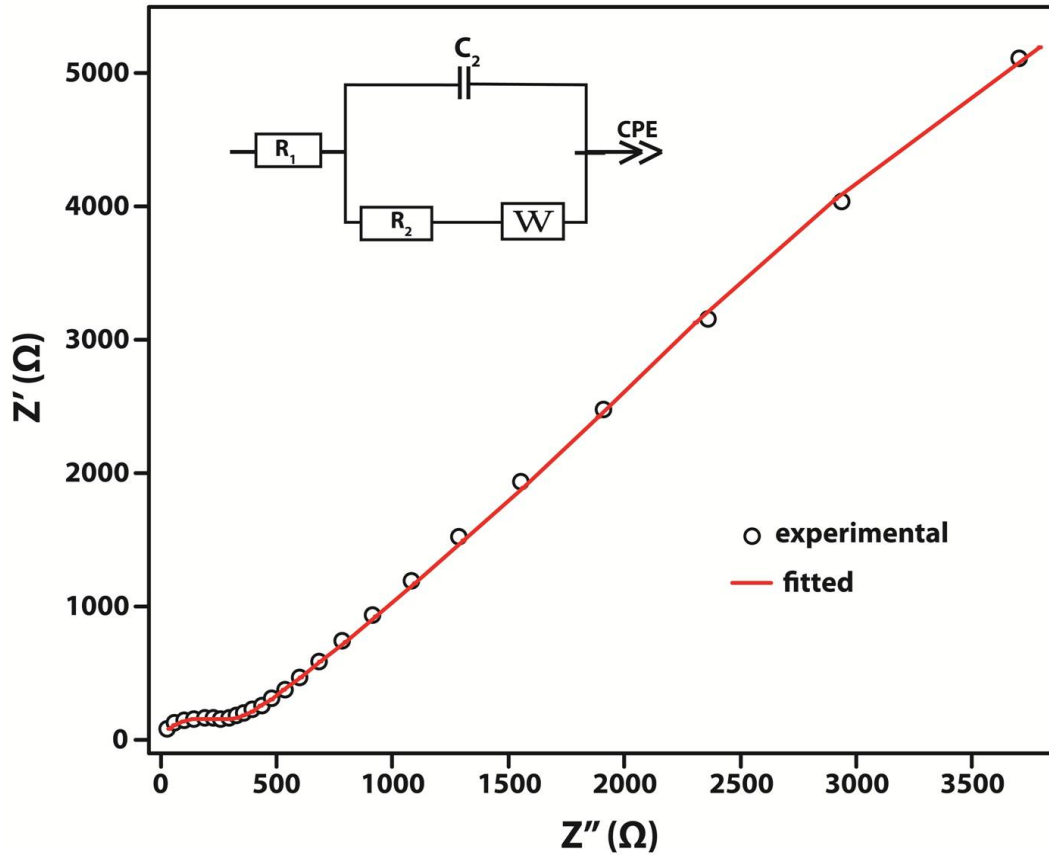


Figure S11. Equivalent circuit determined for the Nyquist plot obtained at 130°C with circuit model used for data fitting (inset).

wherein,

R_1 = Membrane electrolyte resistance,

C_2 = double layer capacitance,

R_2 = charge transfer resistance at electrode-electrolyte interface,

W = Warburg Diffusion impedance,

CPE = Constant Phase Element.

3.2. Fabrication of Membrane Electrode Assembly (MEA) using pelletized FNPA xerogel

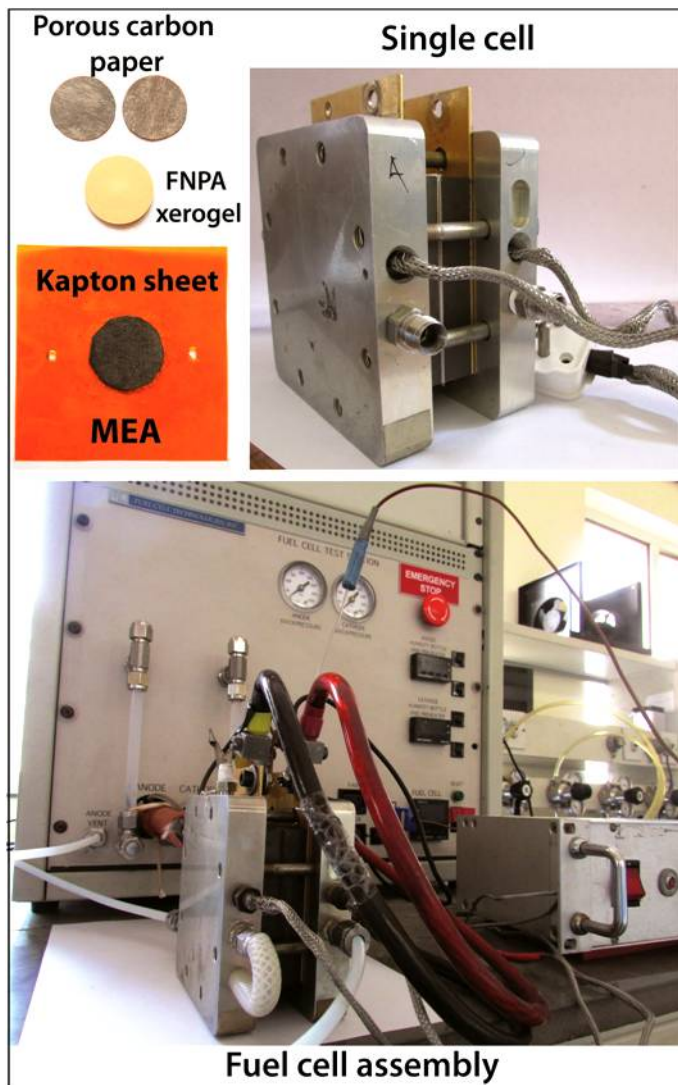


Figure S12. Optical photograph of the fuel cell assembly using fabricated MEA with pelletized FNPA xerogel as solid electrolyte.

Standard PEFMC protocol was used for the MEA fabrication. Initially, FNPA xerogel powder was pelletized using 2.5 mm diameter die. ca.800 mg xerogel powder was used for making each pellet. The electrodes were prepared by spraying the Pt catalyst ink onto the porous carbon paper (35CC-SGL with 15% PTFE content). The pellet was then placed in between the two platinized carbon electrodes [each containing Pt catalyst (Johnson Matthey) + Vulcan carbon support (VX 72) + Nafion binder (20%)] with Kapton as gasket and cold pressed by applying 1000 KgN

pressure for 2 min. The MEA was then arranged onto graphite plates using FRT gasket for single cell assembly (active area = 4cm², Fuel cell Tech).

The single cell test fixture used for fuel cell polarization study consists of following components:

- *Aluminium end-plates*
- *Graphite mono polar plates provided with integrated O-ring gasket and serpentine gas flow field*
- *Cathode loading: 1 mg/cm²; N/C: 0.4; electrode thickness: 320 μm*
- *Anode loading: 1 mg/cm²; N/C: 0.4; electrode thickness: 324 μm*
- *Gas flow: 0.5 slpm for anode as well as cathode.*
- *Operating temperature: RT-120 °C*
- *Membrane pellet thickness: 1615 μm*
- *Uncompressed MEA thickness: 2259 μm*
- *Compressed MEA thickness: 1848 μm*
- *% of the compression : 18 %*
- *Thickness of Gasket used : 714 μm*

3.3. Electromotive force studies (EMF) of fabricated Membrane Electrode Assembly (MEA)

For EMF measurements, the cell was fed with pure dry hydrogen (99.999%) at anode and pure dry O₂ (99.9%) at cathode. The EMF study showed a starting Open Circuit Voltage (OCV) of 0.807 V at 30°C. On further increasing the temperature, the OCV shoot upto 1.02 V ± 0.02 at 120°C and remained constant thereafter. The OCV was observed to remain stable for the next 5 h, which clearly reveals the denser nature of the pellet. On further rising the temperature to 130°C, the OCV immediately dropped to 0.85 V and thereafter the study was terminated. The sudden decrease in the OCV could be attributed to the cross flow of the reactant gases across the pellet membrane.

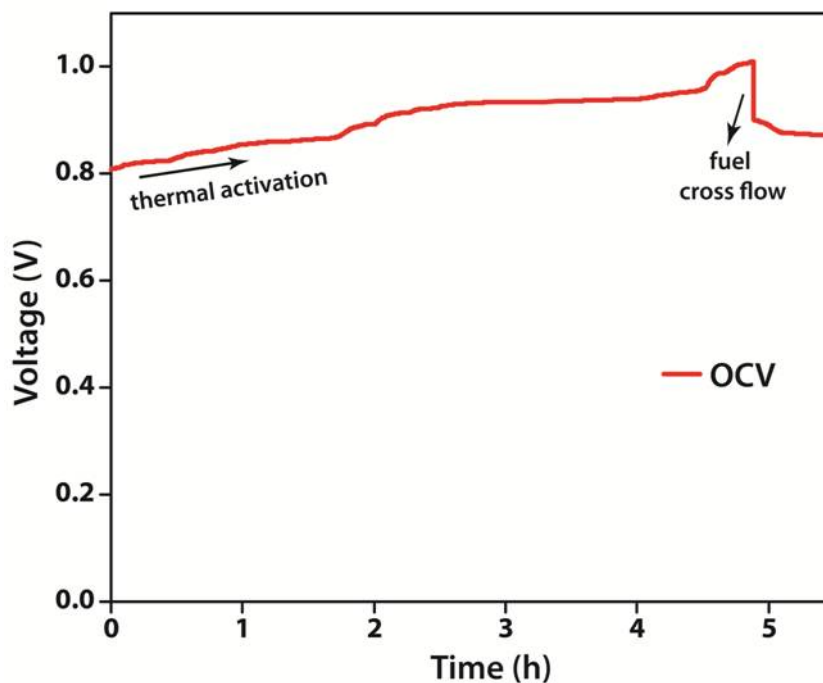


Figure S13. Lifetime measurement of OCV obtained using the fabricated MEA at 120°C.

3.4. *In situ* Impedance study on the fabricated Membrane Electrode Assembly (MEA)

The *in situ* impedance measurements was carried out *via* two electrode configuration using *BioLogic* VPM3 electrochemical work station in the frequency range of 1MHz–100Hz and 10 mV input voltage amplitude, with O₂ passing cathode used as working electrode and H₂ passing anode as counter and reference electrodes. The results were studied using Nyquist plots obtained at each temperature (from RT to 120°C). The plots were then fit using a PEFC fuel cell equivalent circuit and the membrane resistance was calculated determined by the intercept made on the real axis at the high frequency regime in the complex impedance plane.

Following equivalent circuit was used for fitting the experimental data:

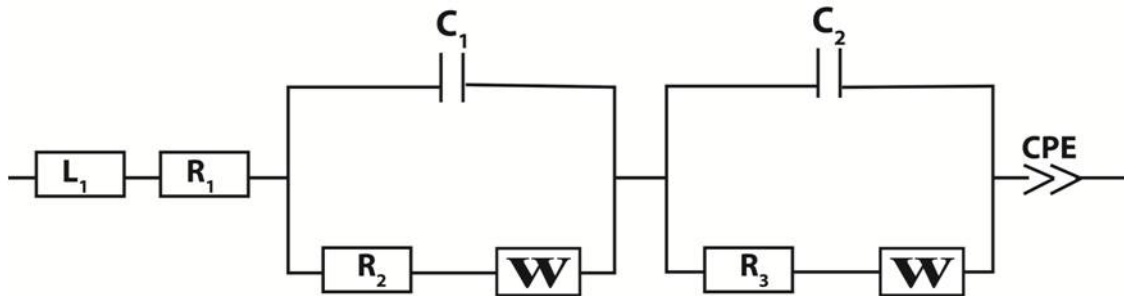


Figure S14. Equivalent circuit used for fitting the Nyquist plots obtained from MEA impedance analysis.

wherein,

- L₁** = Inductance
- R₁** = Membrane electrolyte resistance,
- C₁, C₂** = double layer capacitance at anode and cathode respectively,
- R₂, R₃** = charge transfer resistance at anode-electrolyte and cathode - electrolyte interface respectively,
- W** = Warburg Diffusion impedance,
- CPE** = Constant Phase Element.

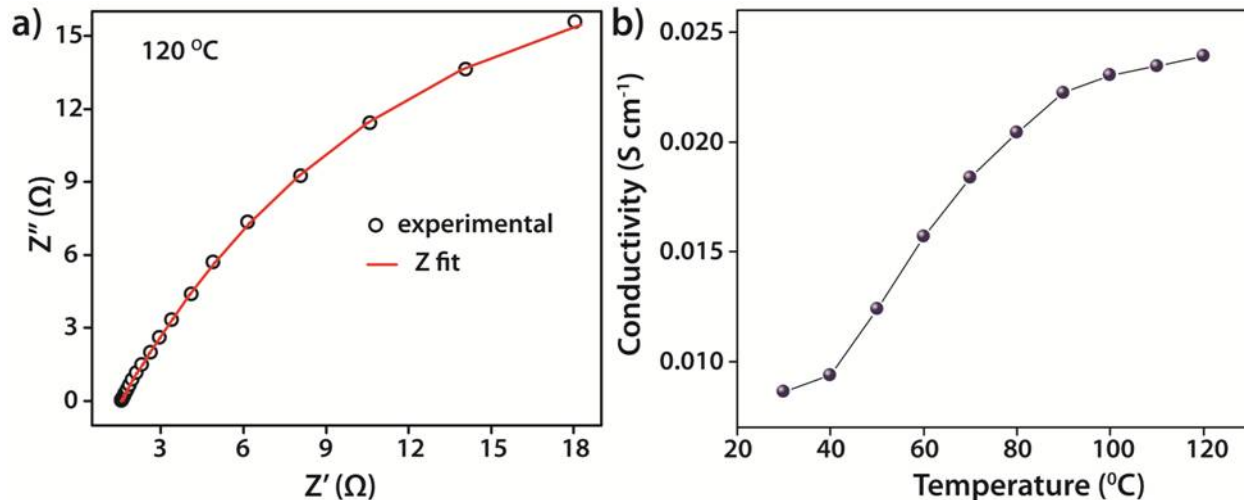


Figure S15. a) Nyquist plot obtained at 120°C using MEA; b) variation of MEA membrane conductivity with temperature..

3.5. Calculation of Activation Energy (E_a) involved in proton conduction

Activation energy was determined using the slope of the straight line obtained using following equation,

$$\sigma_T = \sigma_0 \exp(-E_a/k_B T)$$

wherein, σ -proton conductivity (S/cm), σ_0 -preexponential factor, k_B -Boltzmann constant, T -temperature (K).

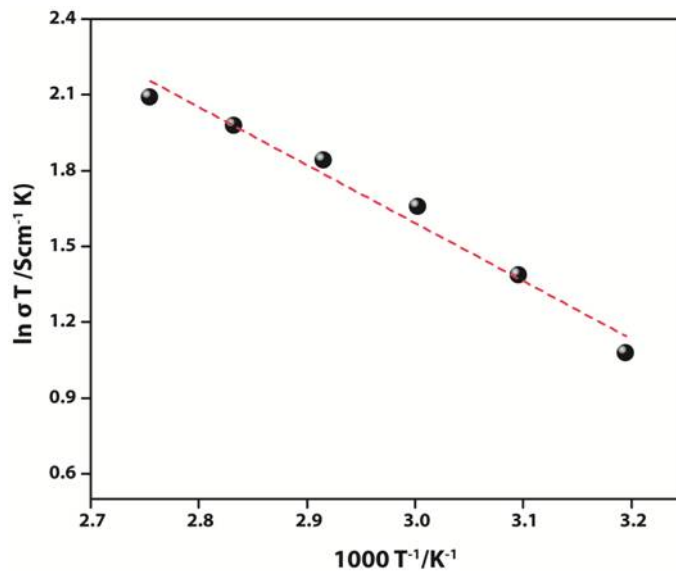


Figure S16. Arrhenius-type plot obtained at different temperatures

3.6. Direct Current (D.C) linear polarization studies

On stabilization, linear polarization studies were performed starting from OCV in 5 mV steps (holding time at each step was 1 sec) until the potential decreased to 0.3V.

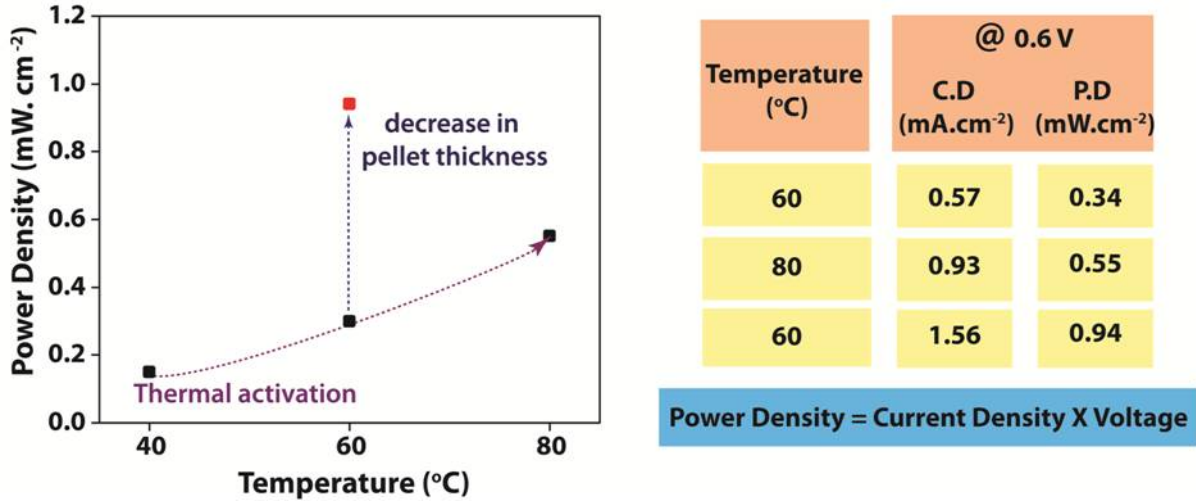


Figure S17. Plot of power density as a function of temperature indicating the influence of pellet thickness (thicknesses of the two pellets used are 1615 μm and 735 μm).