



High Temperature Ceramic Proton Exchange Membranes for Direct methanol Fuel Cells

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Why high temperature?

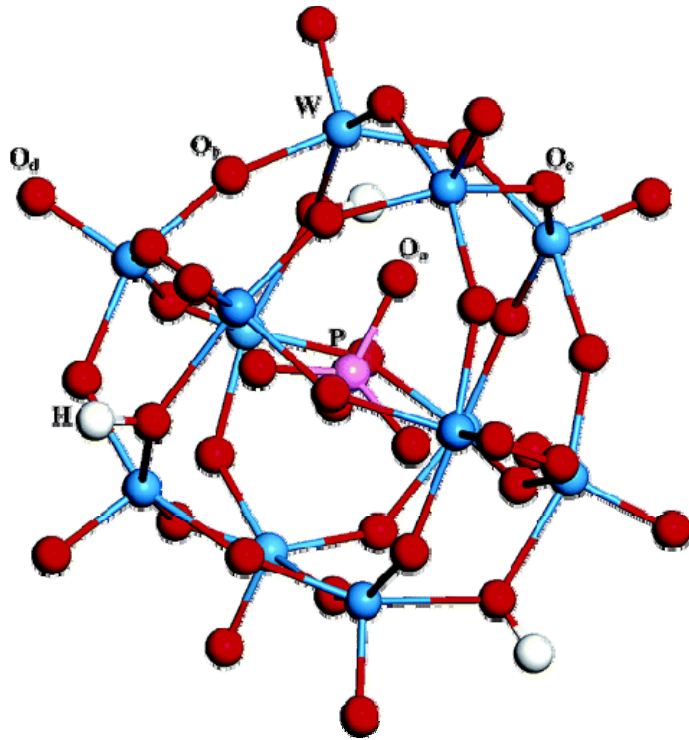
Limitations of the PEMFCs operated at temperature $\leq 100^{\circ}\text{C}$

- Significant poisoning of Pt-based catalysts by CO – an intermediate of oxidation reaction of common fuels such as methanol, formic acid and ethanol and a major product of reforming reaction of natural gas
- Significant methanol crossover through conventional polymeric membranes
- Ethanol cannot be used as fuel in PEMFCs @ temperatures $< \sim 100^{\circ}\text{C}$ - No effective catalysts can break C-C bonds in ethanol
- High loading of platinum precious metal based catalysts due to the sluggish reaction kinetics for the methanol oxidation and oxygen reduction
- High purity hydrogen

Current R&D on HT proton exchange membranes

- PEM fuel cells based on Nafion membrane operating temperature **$\sim 50^{\circ}\text{C}$** .
- Hybrid membranes (Nafion/silica, Nafion/zirconia, etc) operating temperature: **$\sim 80^{\circ}\text{C}$**
- Polybenzimidazoles (PBI)/phosphoric acid: **$\sim 130^{\circ}\text{C}-160^{\circ}\text{C}$**
- Solid acid proton conductor based on CsH_2PO_4 shows promising conductivity of 0.022 S/cm at 240°C but the proton conductivity depends on the phase transformation around $125-150^{\circ}\text{C}$ - ***limited operation window (humidification & temperatures) and system instability.***
- Reports of conductivities on various inorganic composite silica systems such as $\text{CsHSO}_4\text{-SiO}_2$, $\text{P}_2\text{O}_5\text{-SiO}_2$, $\text{P}_2\text{O}_5\text{-TiO}_2\text{-SiO}_2$, $\text{P}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$. However, the cell performance is very low, 30-40 mW/cm² at 30°C . Very few reports of cell performance at elevated high temperatures.

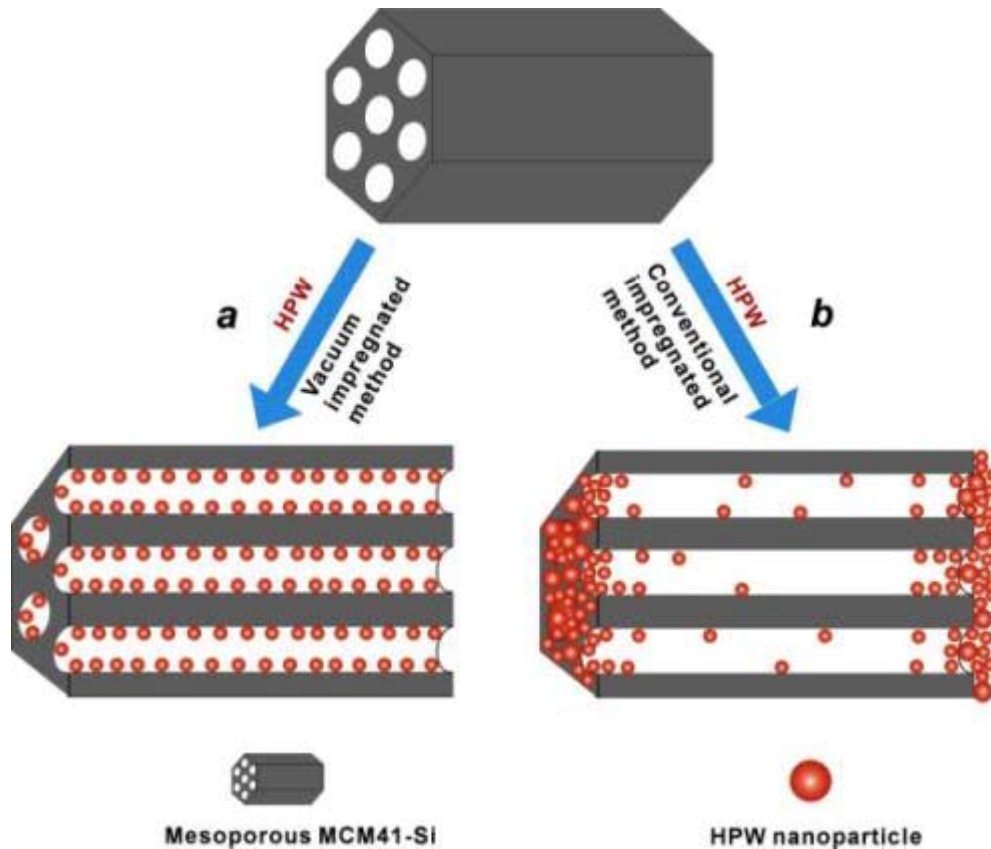
Proton conducting heteropoly acid (HPA)



Heteropoly acid, or HPA
 $H_3MX_{12}O_{40}$ (M = P, Si; X = W, Mo)

- HPAs are known superionic conductors in their hydrated states. $H_3PW_{12}O_{40}$ or HPW is the strongest acid with highest proton conductivity.
- In fully hydrated Keggin structure, the channels around the anions can contain up to 29 H_2O
- Conductivity at RT: 0.17-0.18 S/cm
- HPW alone cannot be used as high temperature PEM. Its conductivity decreases significantly with temp, $<10^{-8}$ S/cm at 160°C under anhydrous conditions

Formation of HPW/MCM-41 mesoporous silica composites



* $\text{H}_3\text{PW}_{12}\text{O}_{40}$ dissolves in water, forming $\text{PW}_{12}\text{O}_{40}^{3-}$ ions

* SiOH in the presence of acidic HPW becomes SiOH_2^+ .

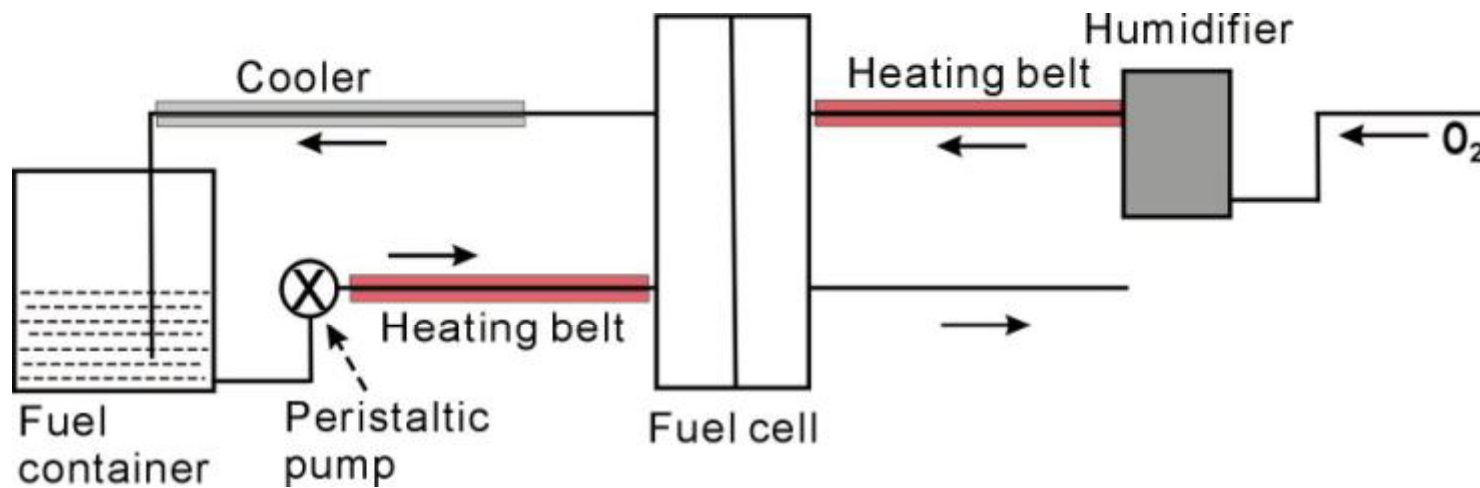
1. Synthesis of mesoporous silica, MCM-41;
2. Impregnation of HPW, forming HPW/MCM-41.

A two step process.

Experimental

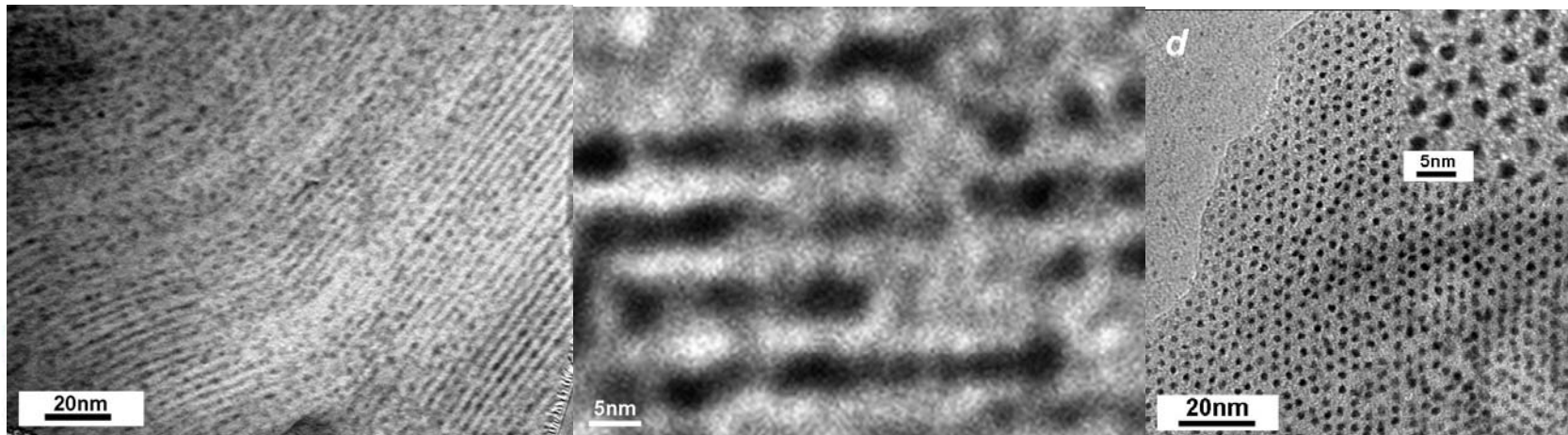
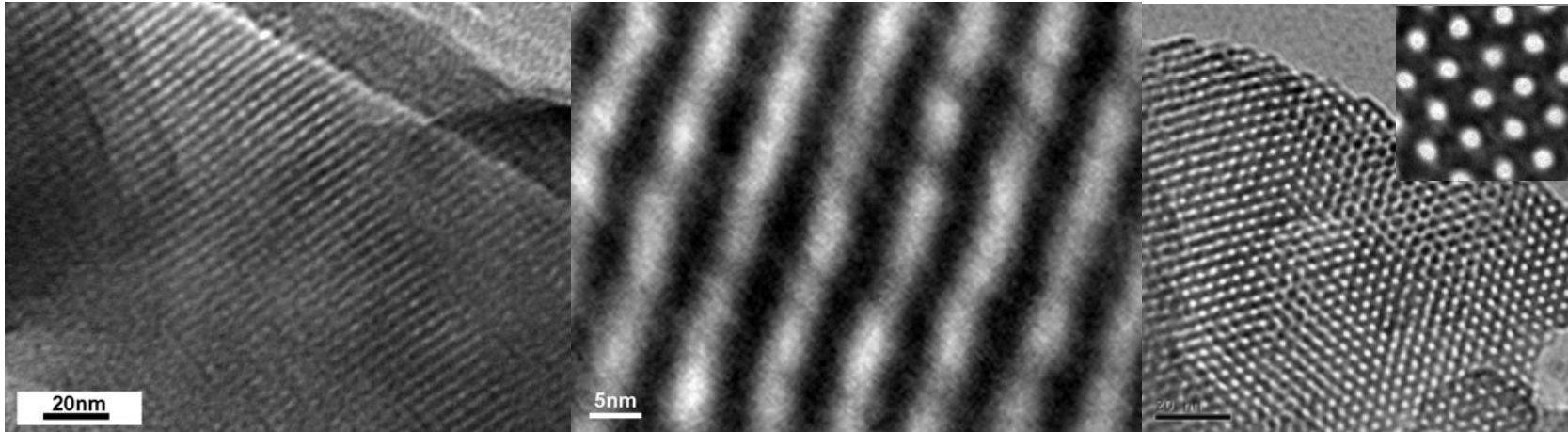
- Synthesis of MCM-41 mesoporous silica
 - cetyl trimethyl ammonium bromide (6.g) was dissolved in DI-water (48 mL). NH_3 was added to the solution and heated to 30°C , then add 25g tetraethylorthosilicate, followed by hydrothermal treatment at 90°C for 48 h. The powder was filtered, washed, dried, and then calcined at 550°C for 6 h under N_2 , another 6 h under air.
- HPW/MCM-41 composite PEM cells
 - HPW was introduced to MCM-41 by vacuum-assisted impregnation methods (VIM).
 - HPW/MCM-41 composites were hot-pressed at 250°C with polyimide as the binder, forming PEM discs.
 - MEA was made of 30wt%HPW/MCM-41 membrane and Pt/C (60wt% Pt/C, Johnson Matthey) catalysts anode and cathodes.

Test set-up for the HT-cells in methanol fuel



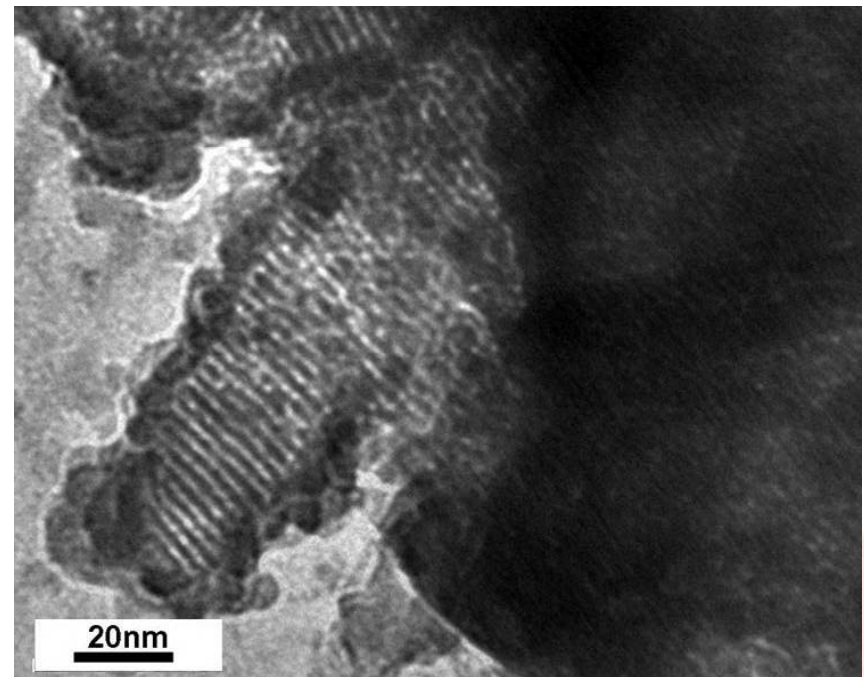
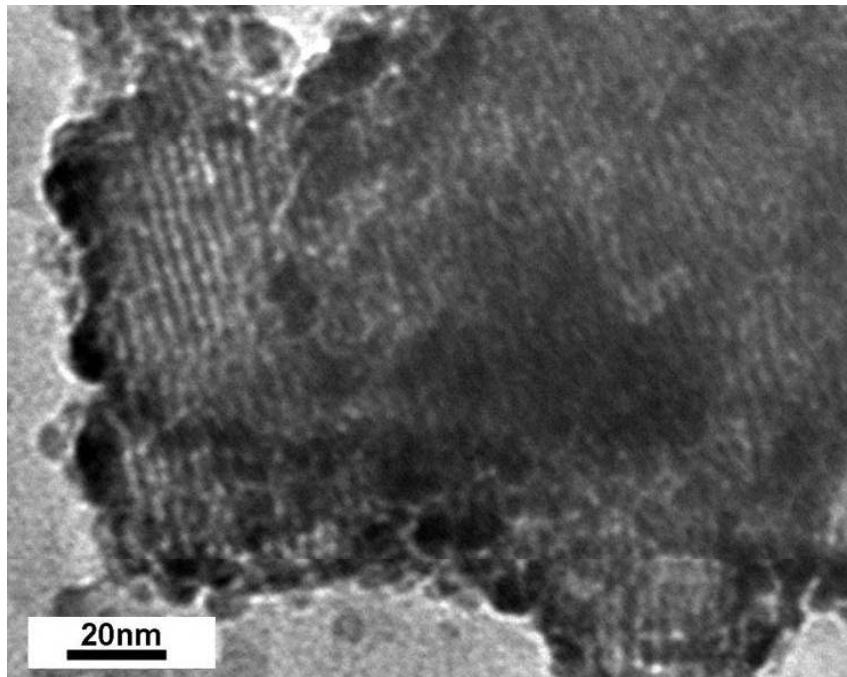
TEM of MCM-41 & HPW/MCM-41

MCM-41



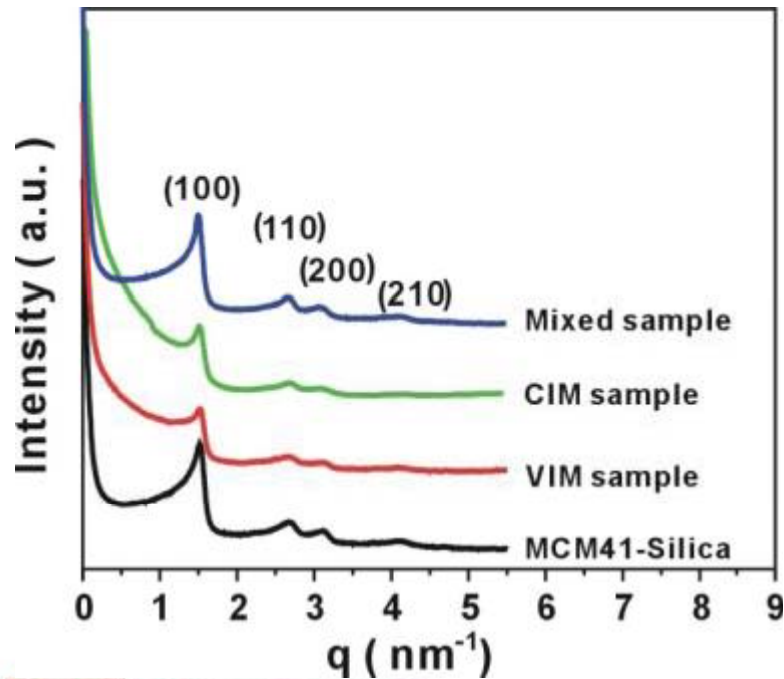
30wt%HPW/MCM-41 by vacuum-assisted impregnation

TEM of HPW/MCM-41 by conventional impregnation

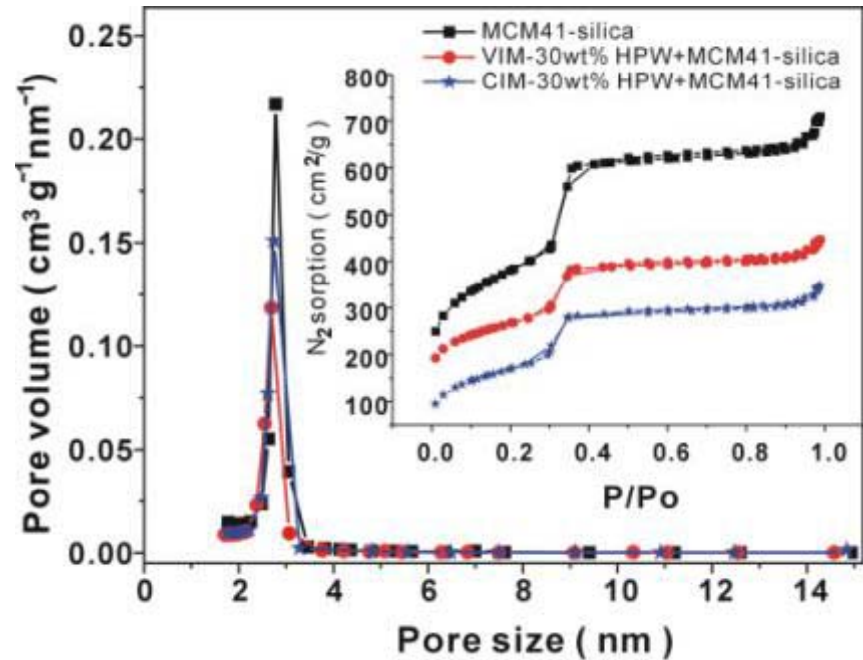


SAXS & pore size

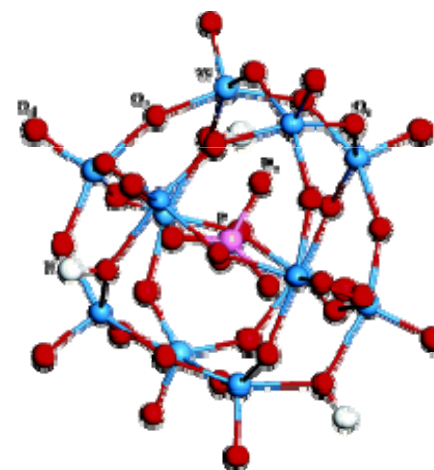
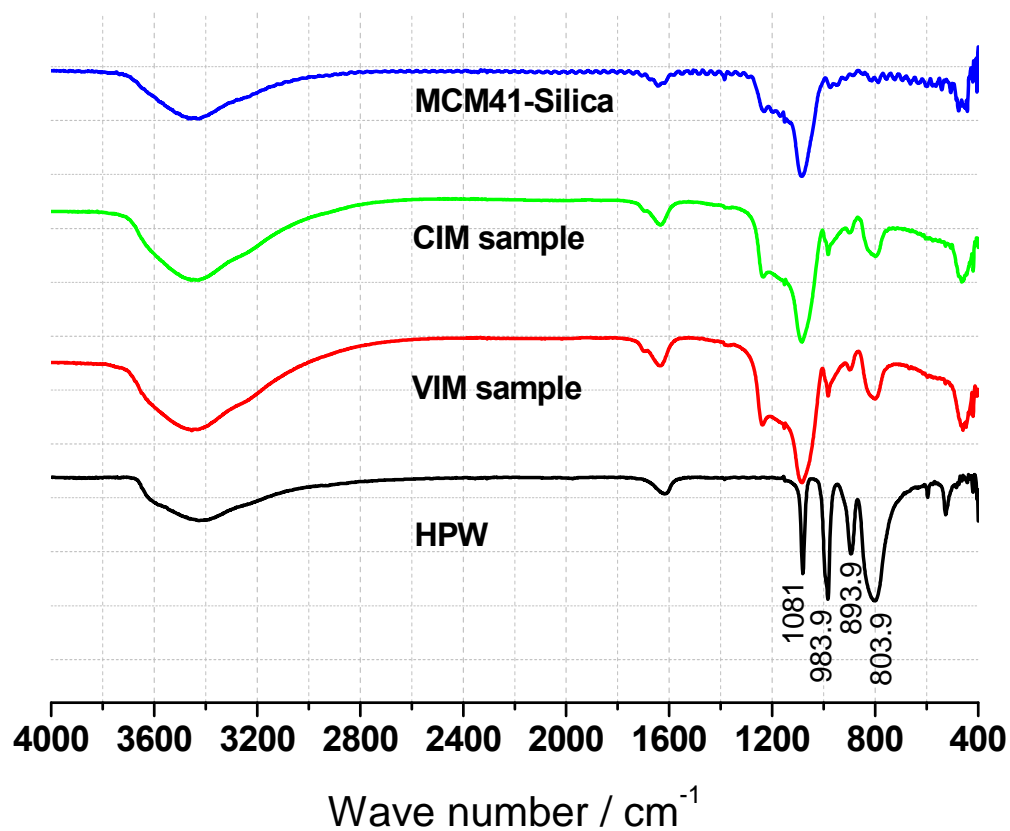
Small angle XRD



Adsorption/desorption isotherms



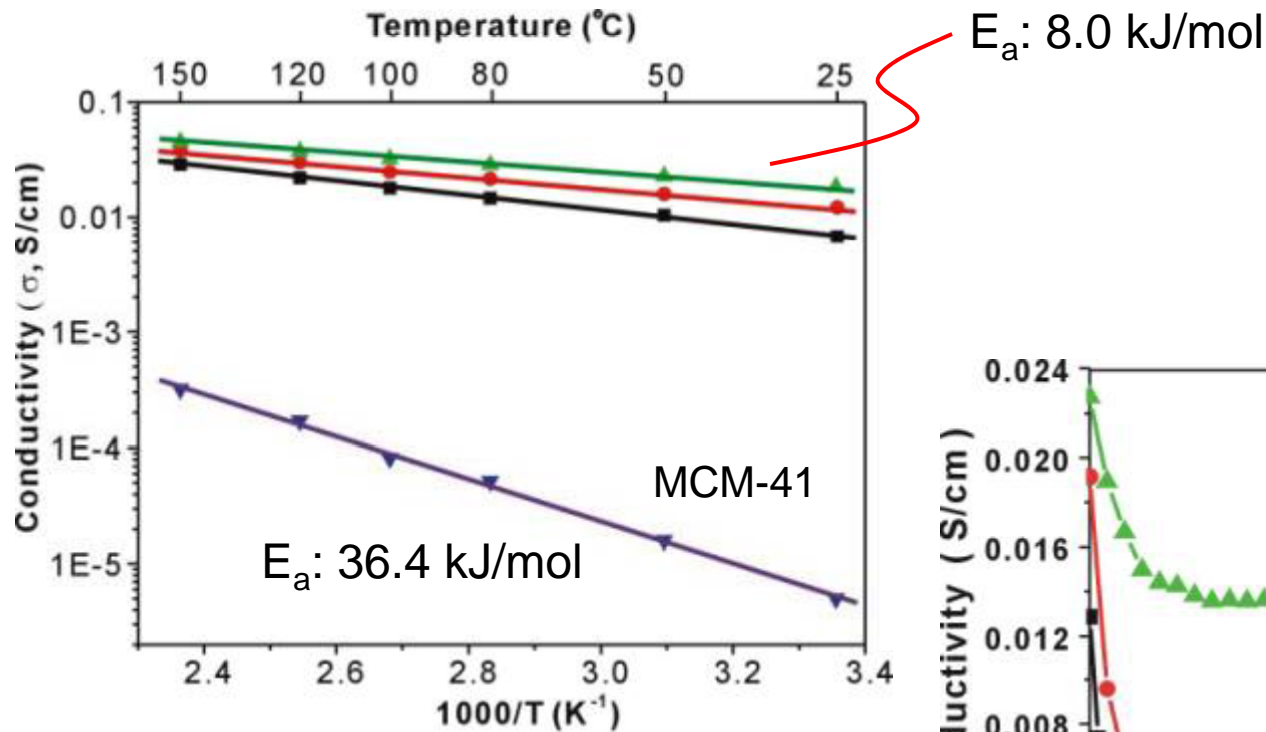
FT-IR of HPW/MCM-41



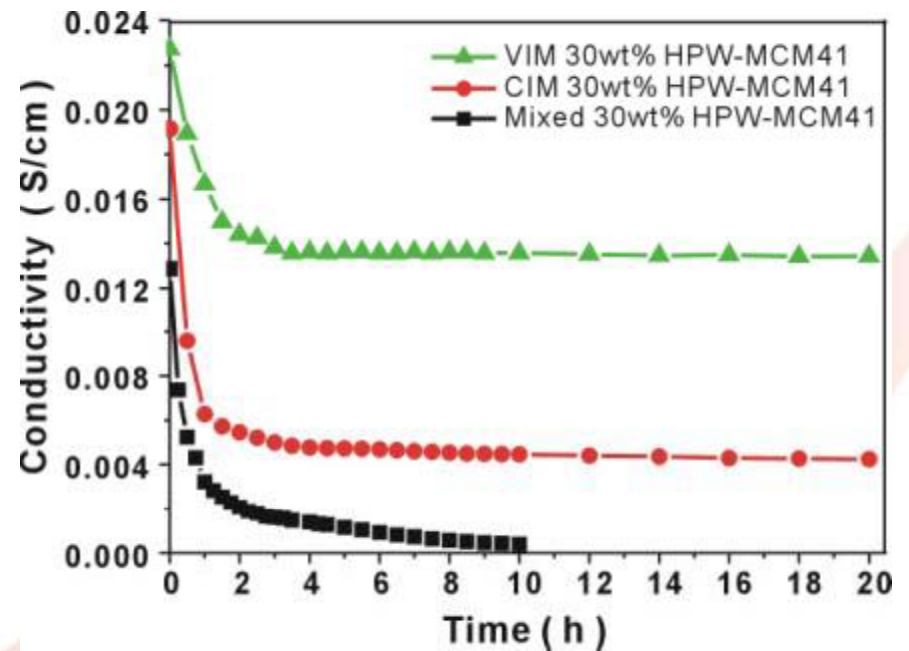
	P-O _a	W-O _d	W-O _b -W	W-O _c -W
HPW	1081.0	983.9	893.9	803.9
CIM	1079.7	982.2	900.4	798.8
VIM	1084.7	982.4	898.9	799.9

Conductivity & stability

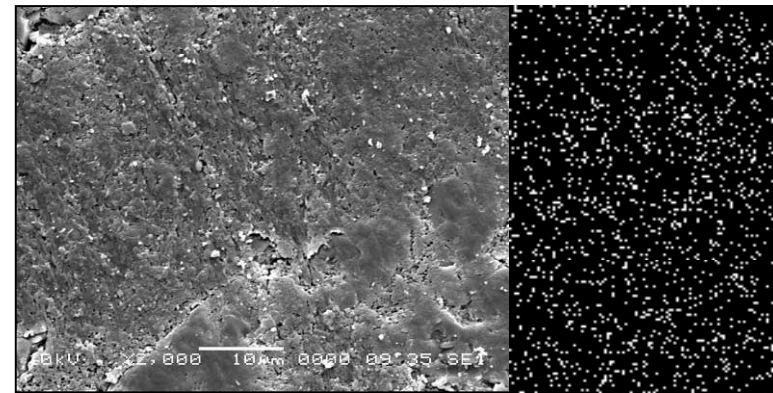
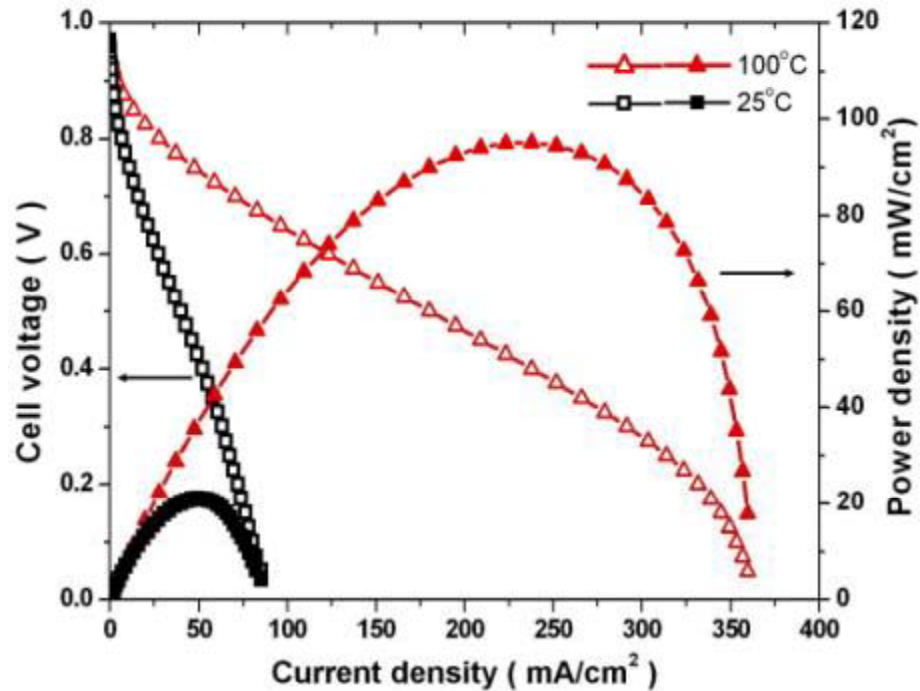
Conductivity



Stability



Performance in H₂/O₂

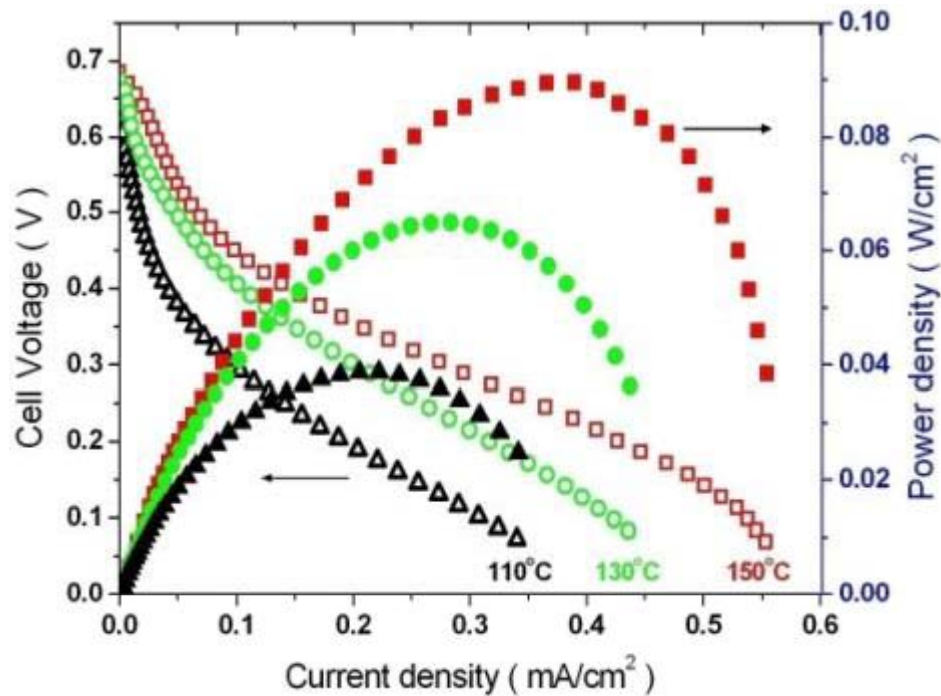


100%RH, Anode: Pt/C (Pt: 0.5 mg/cm²);
cathode: Pt/C (Pt: 0.5 mg/cm²).



30wt% HPW/MCM-41
membrane: ~1 mm thick.

Performance in methanol/O₂



- 30wt%HPW/MCM-41 meso-silica electrolyte membrane; ~1 mm thick;
- Temp/RH: 110°C/2.2%RH, 130°C/1.1%RH and 150°C/0.67%RH;
- O₂ flow rate: 300ml min⁻¹; back pressure: 1.5atm;
- Methanol solution (2.0 M) flow rate: 1ml/min;
- Cathode Pt loading: 1mg/cm² 50wt%Pt/C; Anode Pt loading: 4mg/cm² 50wt%PtRu/C.

Conclusions

- **Successful synthesis and demonstration of a high temperature proton exchange membrane fuel cell based on vacuum-assisted impregnated HPW/MCM-41 mesoporous silica**
 - Proton conductivity: 0.015 S/cm @ 25°C & 0.04 S/cm @ 150°C (100%RH)
 - Good proton conductivity stability
 - Power density; 95 mW/cm² @ 100°C in H₂/O₂, 0.5 mg/cm² Pt for anode & cathode
- **Demonstrated feasibility of HT-PEMFCs based on HPW/MCM-41 mesoporous silica for DMFCs**
 - 90 mW/cm² @ 150°C and 0.675RH (oxygen) in methanol fuel.
- **Challenges: catalysts and long-term stability of HT-PEMFCs for methanol fuels**

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