Modeling of Electrochemical Cells:
Proton Exchange Membrane Fuel Cells
HYD7007 – 01

Lecture 08. Composite Membranes

Dept. of Chemical & Biomolecular Engineering
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Lecture Outline

- Motivation
- Silica
  - Structure of Nanoparticles
  - Performance Enhancements in Fuel Cells
- Titania
  - Structure of Nanoparticles
  - Performance Enhancements in Fuel Cells
- Platinum
  - Structure of Nanoparticles
  - Performance Enhancements in Fuel Cells

Motivation

An increase in the operating temperature of the PEM fuel cell would have the following advantages:

- increase the activity of the catalysts
- reduce catalyst poisoning
- lower the amount of catalyst required
- reduce the cost of the fuel cell

But higher operating temperatures would have the following disadvantages

- dry out the membrane
- diminish the connectivity of the aqueous domain
- lower the diffusivity and conductivity of charge within the membrane

One potential solution to this problem is to incorporate hydrophilic entities within the membrane that are better at retaining water at high temperature. These hydrophilic entities are typically metal or metal oxide nanoparticles. The resulting membranes are called composite membranes.

Structure of Nanoparticles

Silica: SiO$_2$
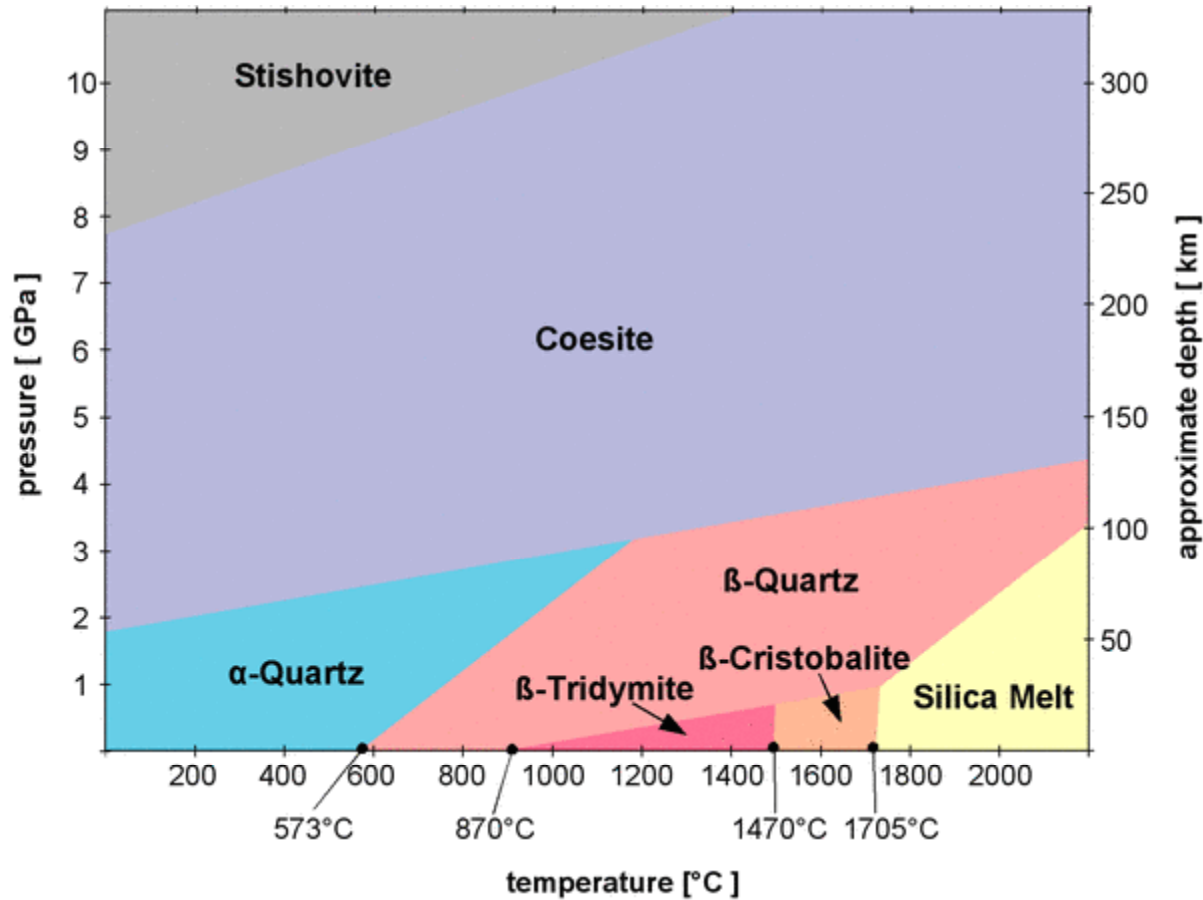
α-quartz (sand)

Bulk silica has many crystalline forms. At room temperature and pressure, a-quartz is the most stable.
If melted and quenched, amorphous silica or glass is formed.

quartz glass
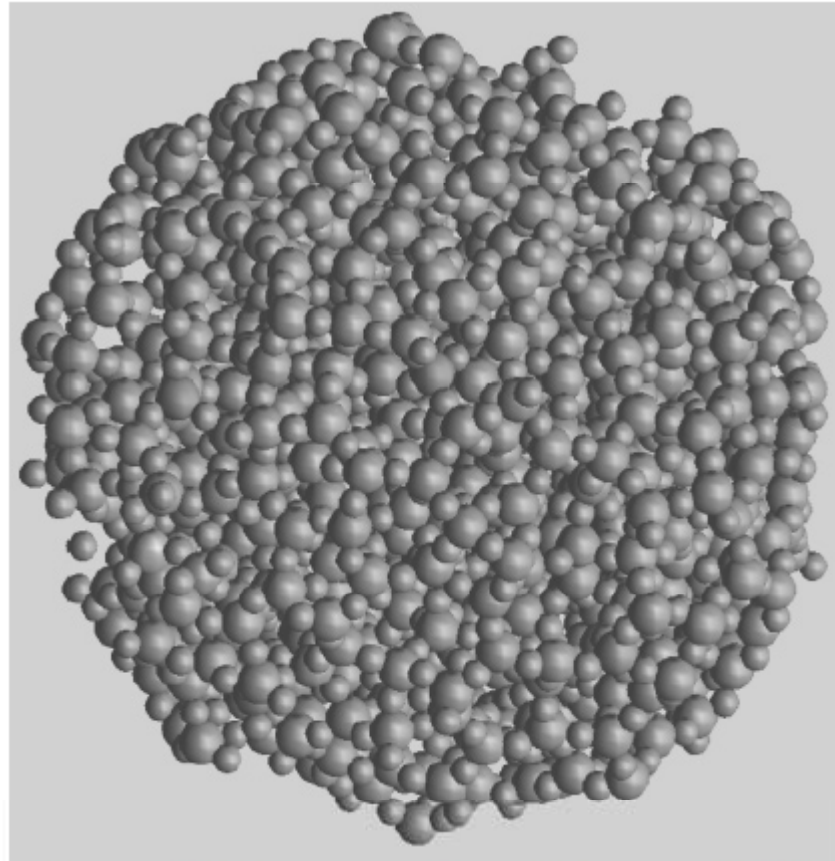
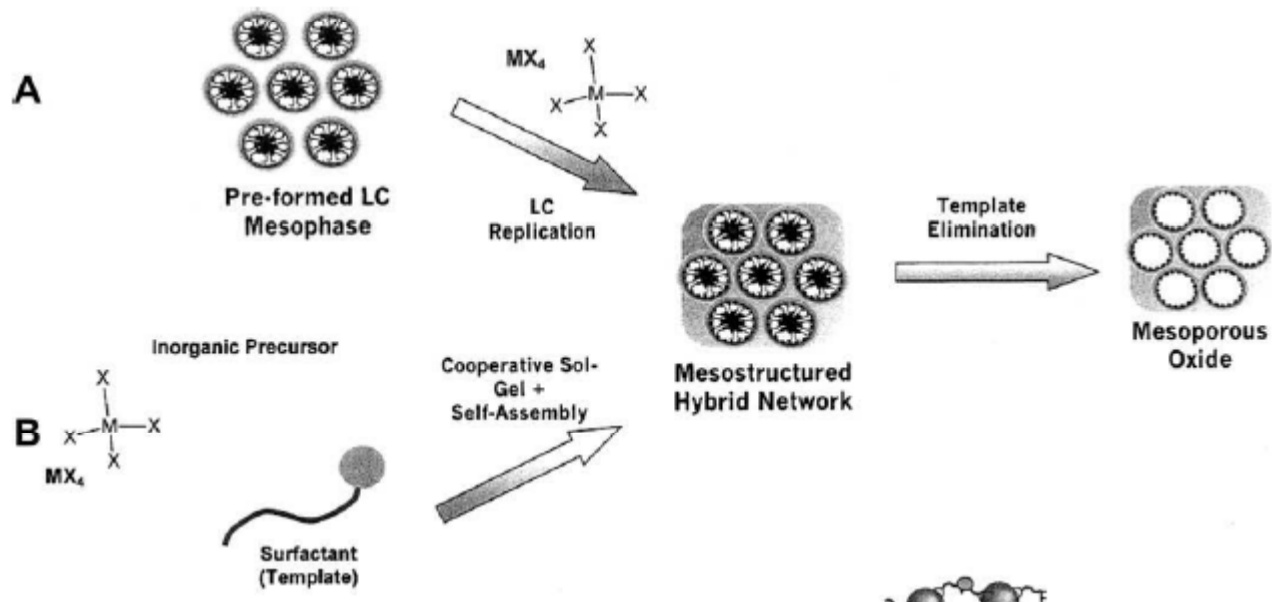http://www.quartzpage.de/gen_mod.html

Silica

Figure 4. Snapshot of amorphous 4 nm SiO_2 nanoparticle at $T = 350$ K. Small spheres denote oxygen atoms and large spheres denote silicon ones.

Silica nanoparticles also have a variety of forms. They can be amorphous (without long-range crystalline structure).

V.V. Hoang, J. Phys. Chem. B, 2007.

Silica

A

Pre-formed LC Mesophase — LC Replication — MX_4

Inorganic Precursor

B MX_4 — Surfactant (Template)

Cooperative Sol-Gel + Self-Assembly

Mesostructured Hybrid Network — Template Elimination — Mesoporous Oxide

Mesoporous silica (MCM materials) were first synthesized in the 1990s.
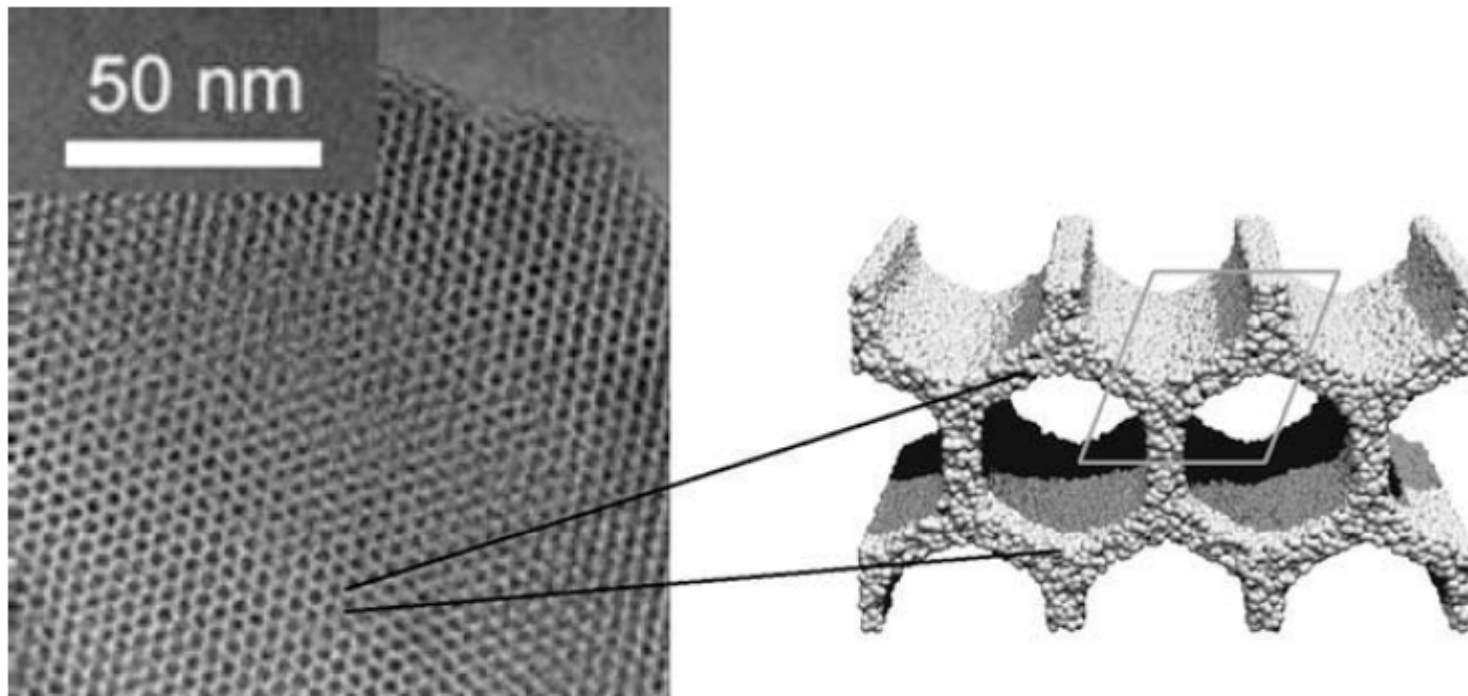They have large surface area and regular pore network.

Meynen, Microporous and Mesoporous Materials, 2009.

Silica

Fig. 4.3. TEM image of the honeycomb structure of MCM-41 and a schematic representation of the hexagonal shaped one-dimensional pores.

The silica is amorphous but is arranged in a regular array around pores.

Structure of Nanoparticles

Silica

One can obtain different morphologies depending upon the synthesis conditions.

MCM-48 has two non-intersecting pore networks.
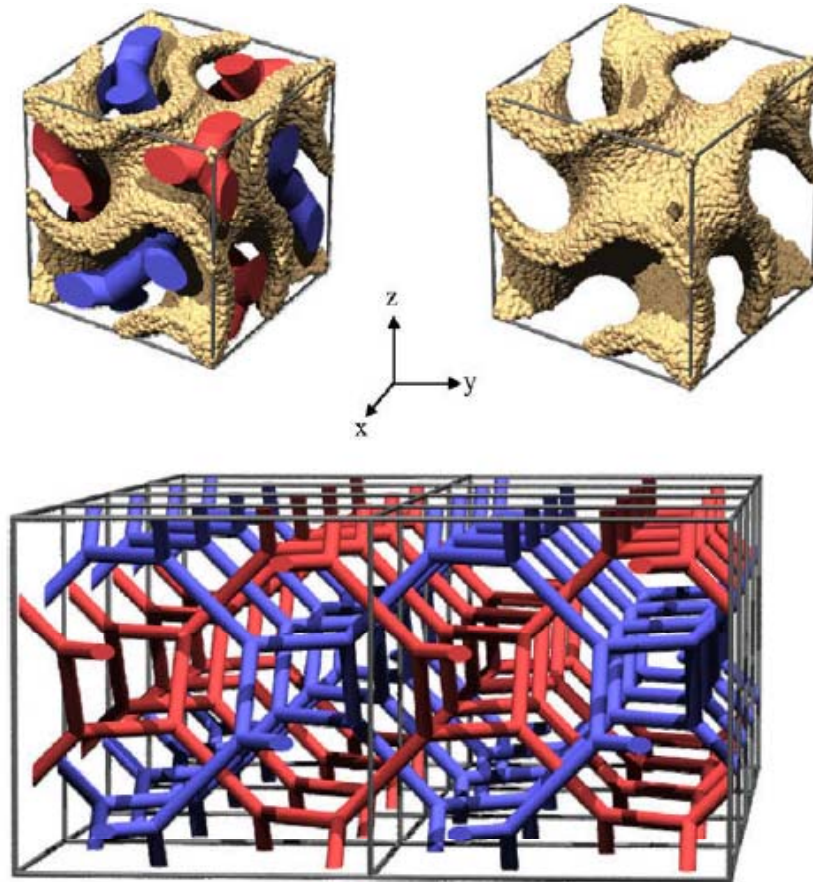
The silica is again amorphous.

Fig. 4.6. Cubic unit cell of MCM-48 with two independent micelle systems (red and blue rods) separated by the pore wall (upper right). Mathematical representation of a G gyroid minimal surface (upper left). Representation of 2 × 4 cubic unit cells without the pore walls. The rods represent two independent micelle systems (red and blue) moving towards the (100) direction (bottom). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Meynen, Microporous and Mesoporous Materials, 2009.

Structure of Nanoparticles

Silica

1 microns

- 45°

100 nm
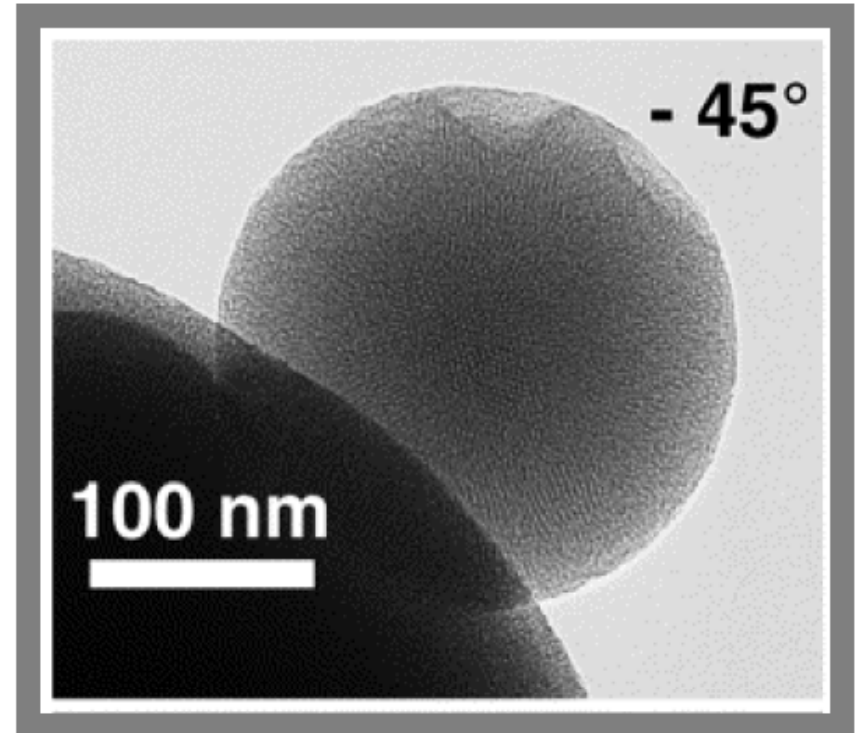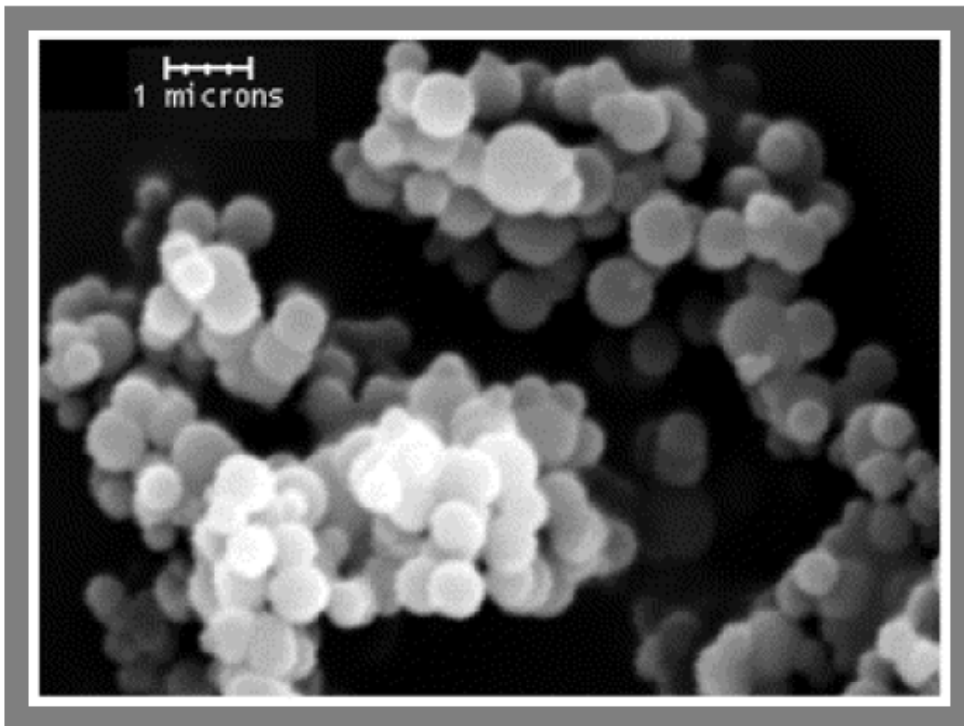
Mesoporous silica can be made into nanoparticles.
These particles are not solid. They are penetrated by a regular porous network.

Lebedev, Solid State Sciences, 2004.
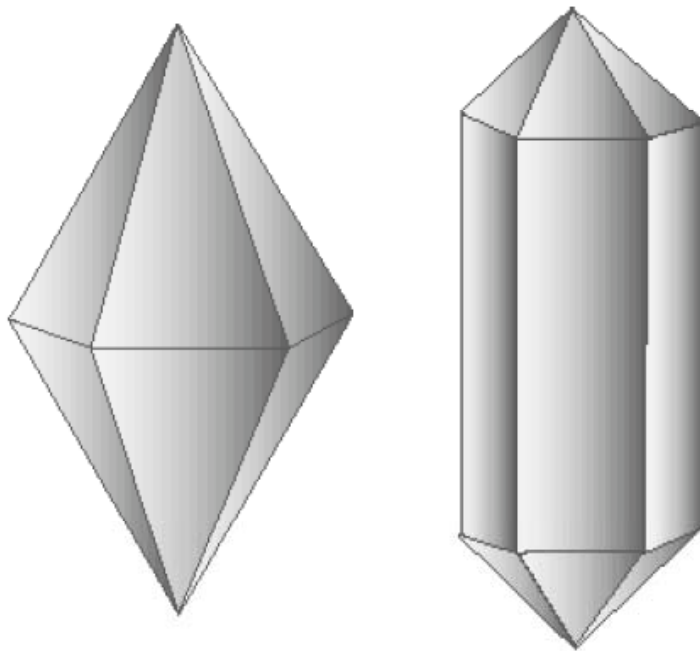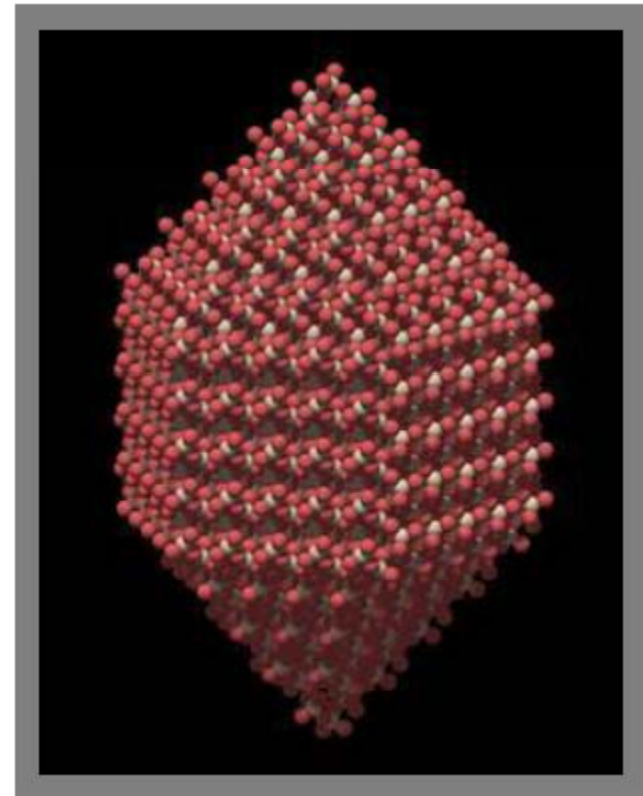
Structure of Nanoparticles

Silica

Figure 10. [23] Left: bipyramidal hexagon
Right: bipyramidal hexagonal prism

Presumably, one could also have crystalline silica nanoparticles but these have received much less attention than amorphous silica particles or mesoporous silica particles.

Lebedev, Solid State Sciences, 2004.

Fuel Cell Performance

Silica

Silica nanoparticles can be dispersed within Nafion membranes.
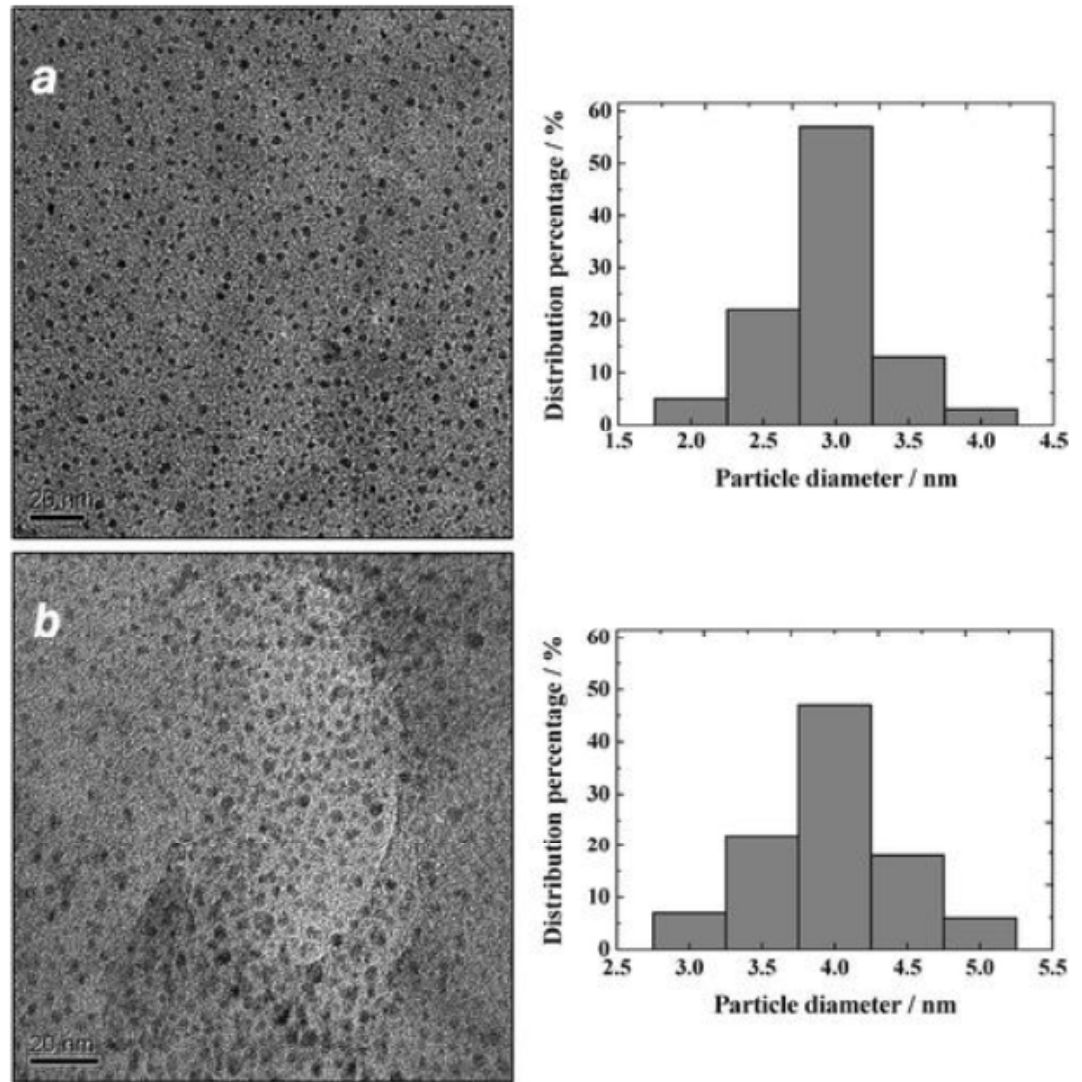
Figure 2. [9] TEM micrograph and histographs of a) 5 wt% Nafion-SiO$_2$ and b) 30 wt% Nafion-SiO$_2$ nanoparticles

Tang, J. Phys. Chem. C, 2008.

Fuel Cell Performance

Silica

Silica nanoparticles can be used to enhance conductivity at higher temperatures compared to pure membrane. The mesoporous silica perform better than particle silica.
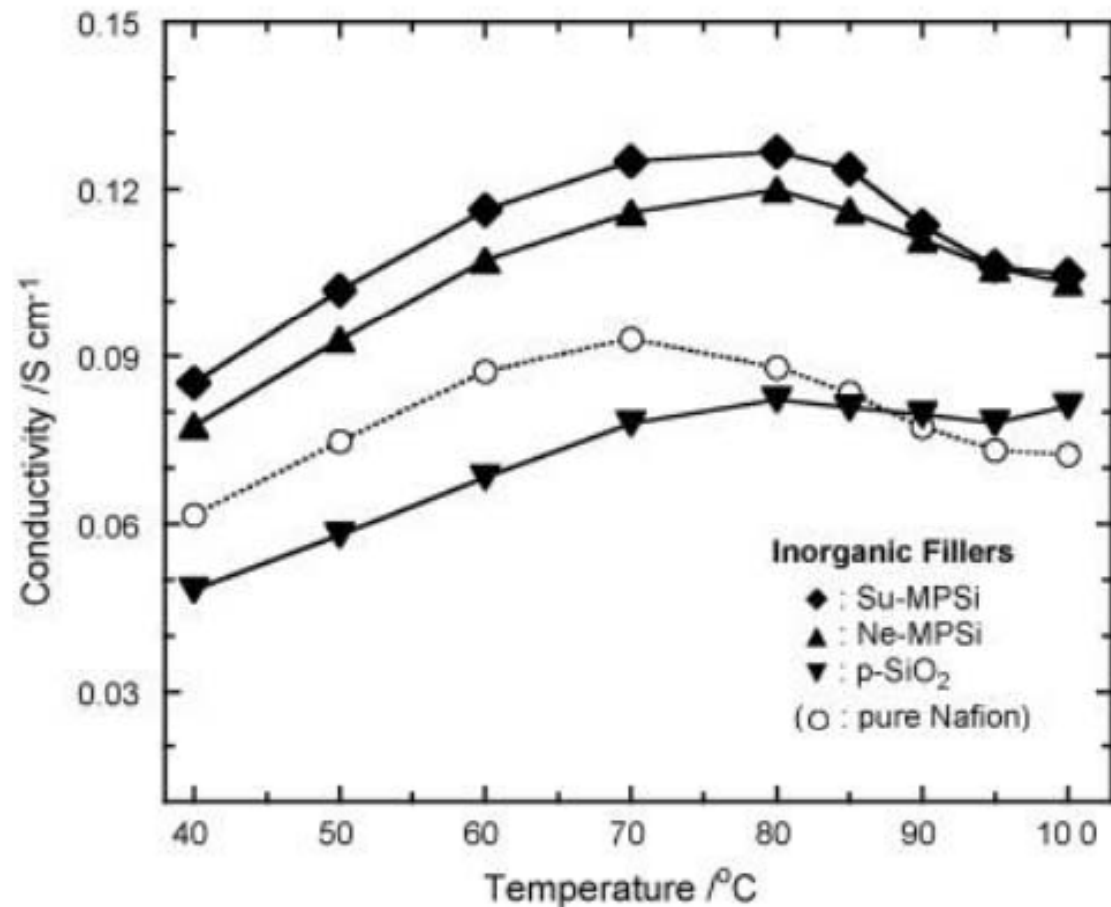All composites are at 5wt% here.

Figure 8. [15]Temperature dependence of proton conductivity for composites (5wt% ea.) at 95RH%

Tominaga, J. Power Sources, 2007.

Fuel Cell Performance

Silica

If you put too much nanoparticles into the membrane, then you lose conductivity, because the nanoparticles are not proton conductors.
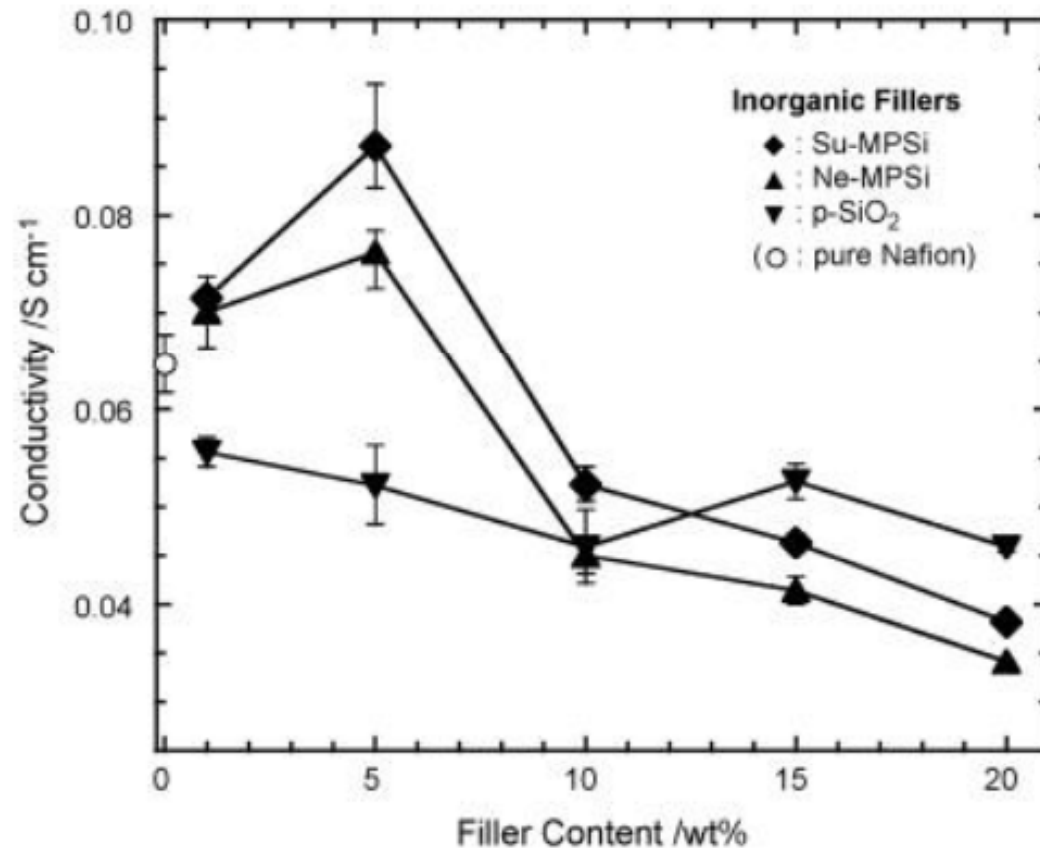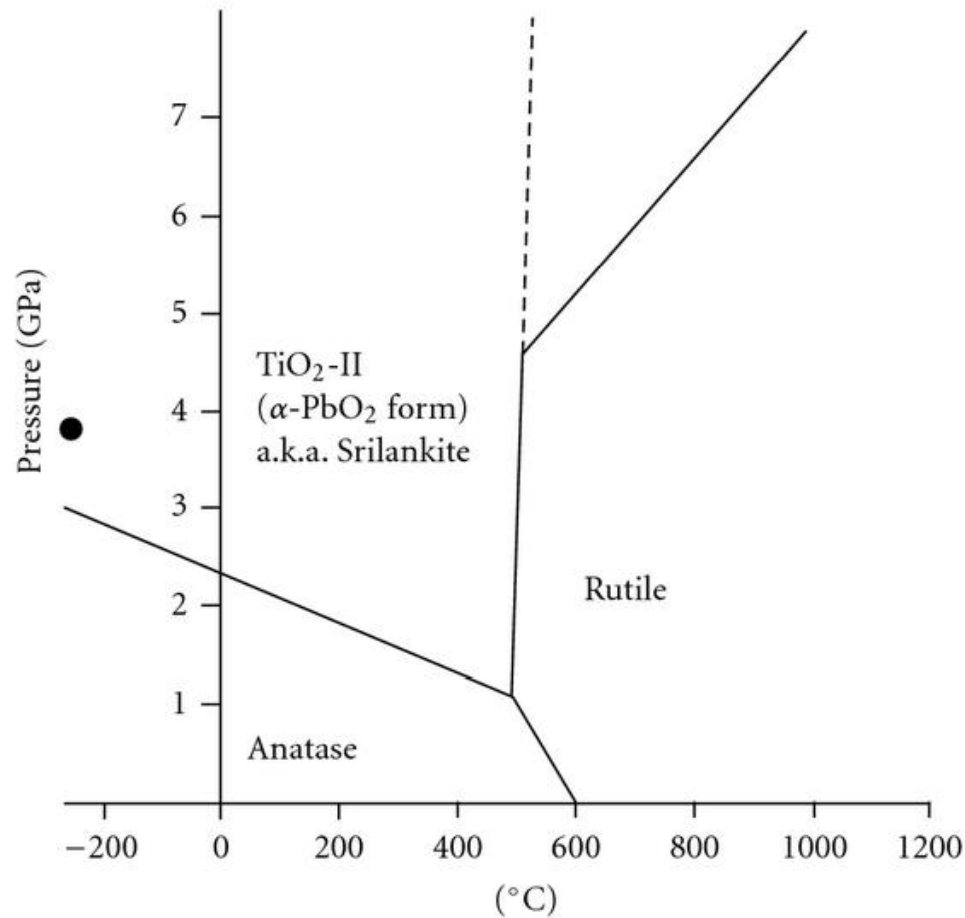

Figure 7. Relation between proton conductivity and filler content at 40°C and 95%RH. [15]

Tominaga, J. Power Sources, 2007.

Structure of Nanoparticles

Titania: (Titanium dioxide) TiO$_2$

Bulk titanium dioxide is crystalline.

Nie et al., Int. J. Photoenergy, 2009.

Structure of Nanoparticles

Titania: (Titanium dioxide) TiO_2
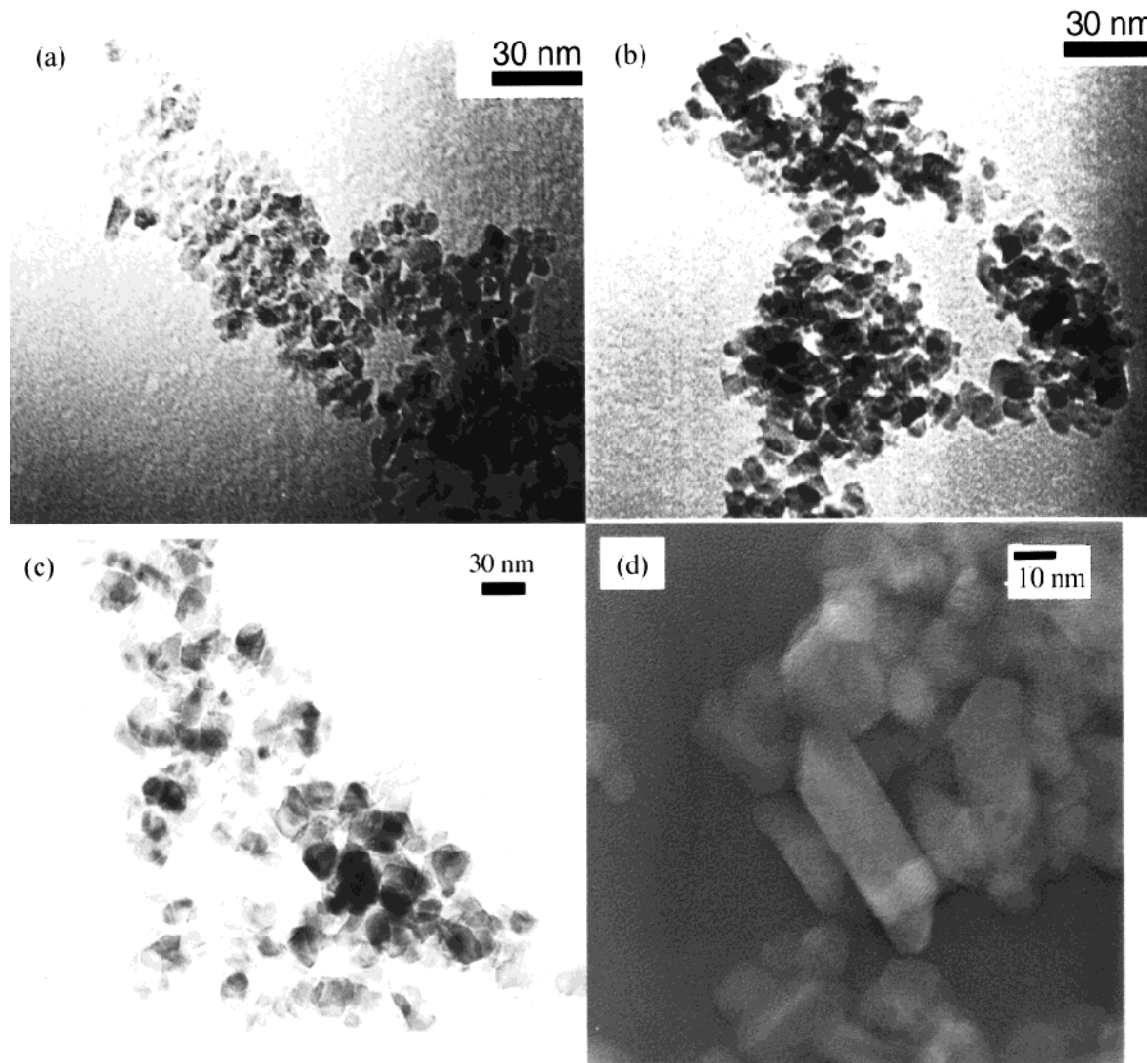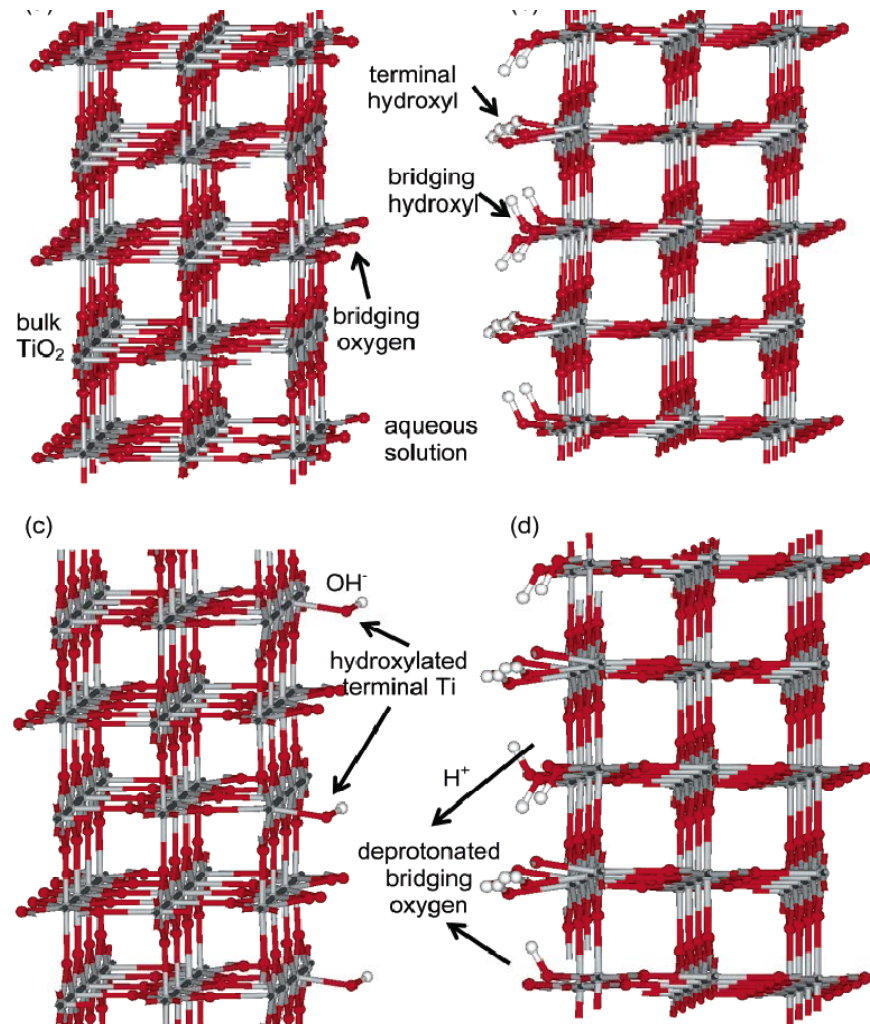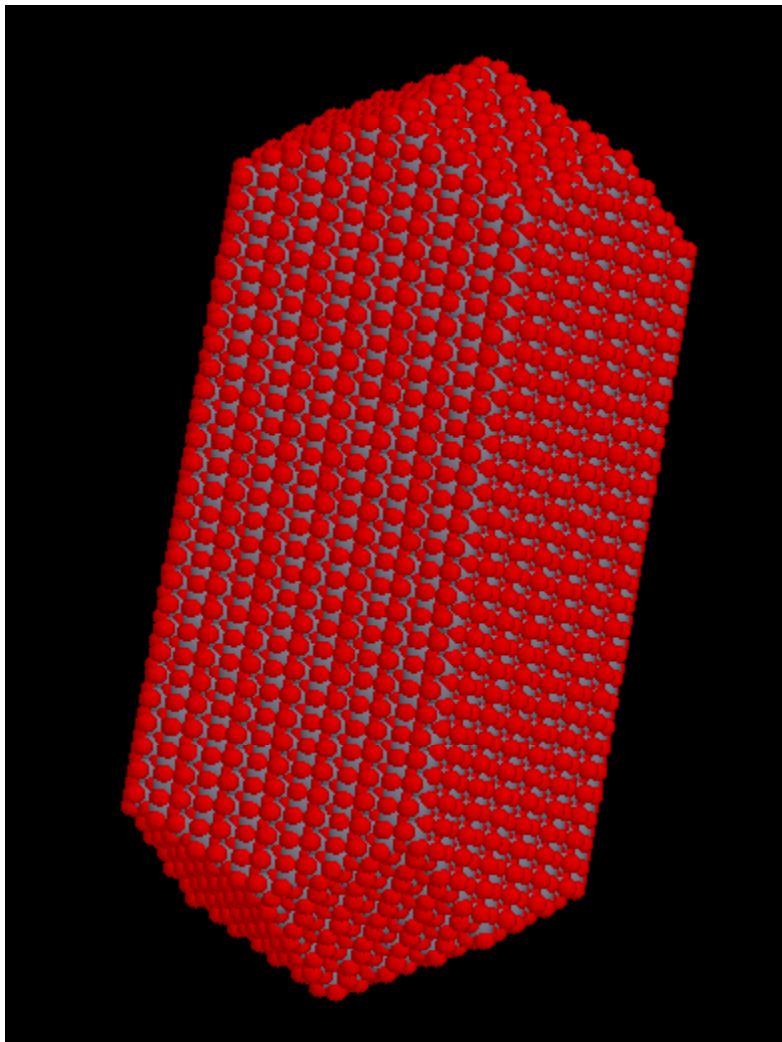

In contrast to silica, nanoparticles of titania are crystalline.   Wang and Ying, Chem. Mater., 1999.

Structure of Nanoparticles

Titania: (Titanium dioxide) TiO_2

terminal hydroxyl

bridging hydroxyl

bulk TiO_2

bridging oxygen

aqueous solution

(c)

OH$^-$

hydroxylated terminal Ti

(d)

H$^+$

deprotonated bridging oxygen

The surface of wet titania will provide protons.

Predota, J. Phys. Chem. B, 2004.
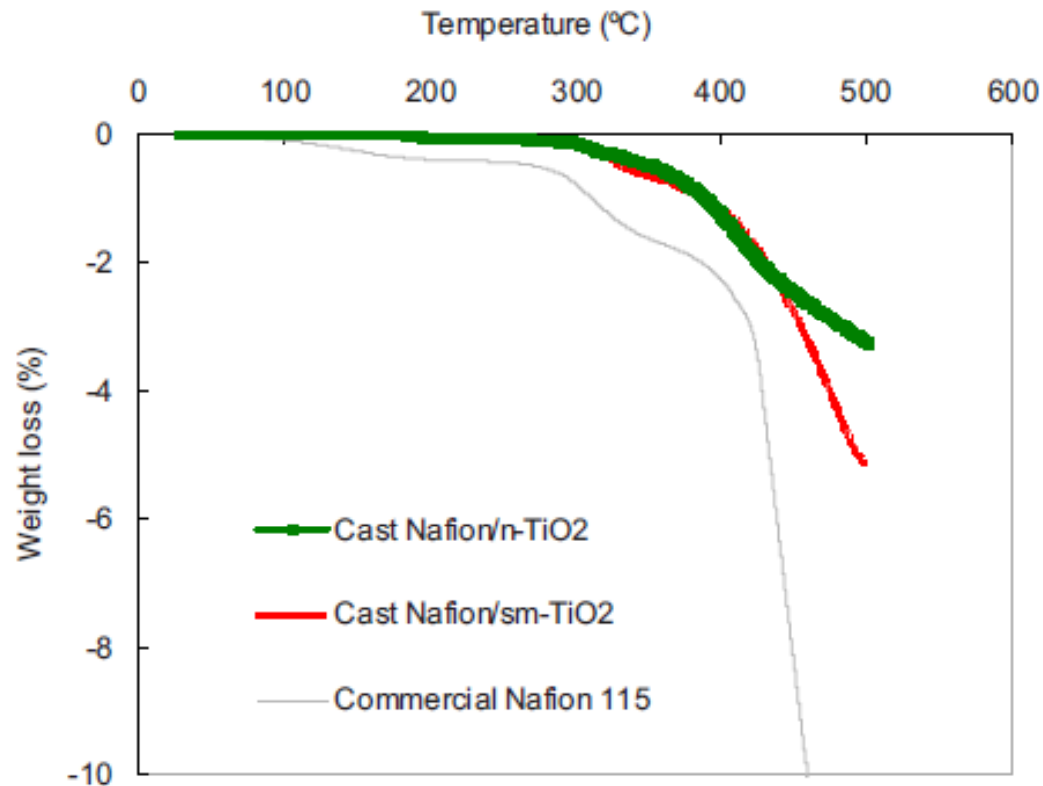
Fuel Cell Performance

Titania: (Titanium dioxide) TiO$_2$

Figure 7. (Color online) TGA of Nafion 115 and composite membranes containing TiO$_2$ in air at a scan rate of 5°C/min.

Water retention at higher temperatures is superior for composite membranes. n = nanoscale (n) and sm = sub-micron.

Abbaraju, J. Electrochem. Soc., 2008.

Fuel Cell Performance
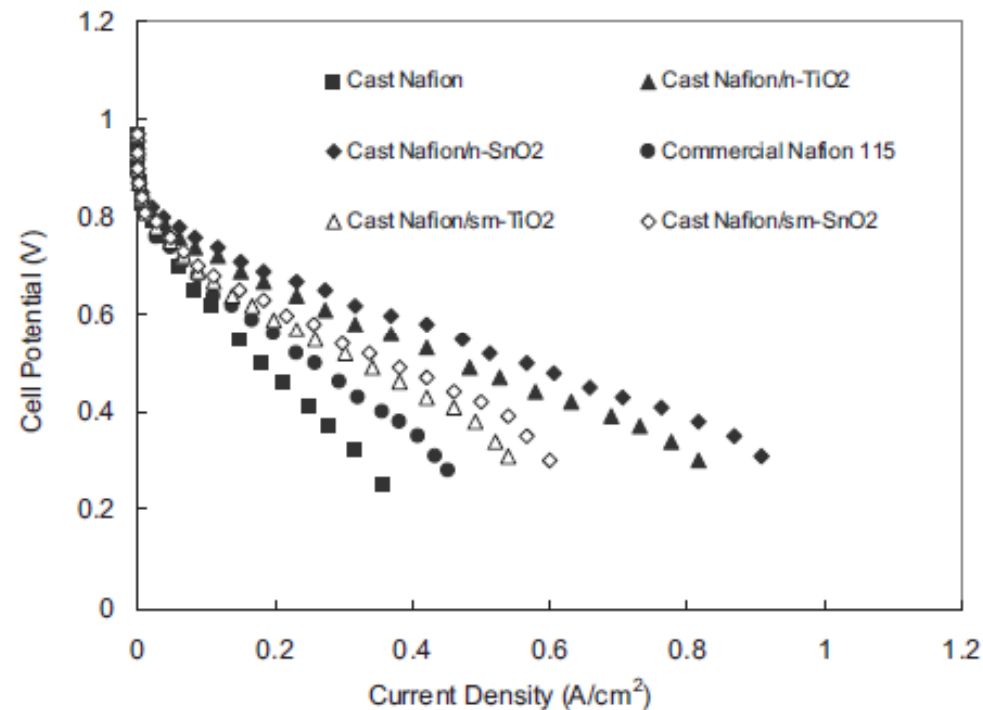
Titania: (Titanium dioxide) TiO$_2$

Figure 8. Performance of cells made with recast Nafion, recast Nafion + sm-TiO$_2$ of low surface area, recast Nafion + n-TiO$_2$ of high surface area, recast Nafion + sm-SnO$_2$ of low surface area, and recast Nafion + n-SnO$_2$ of high surface area at 31% RH. Commercial Nafion 115 membrane was also tested for comparison. Cells tested at 120°C with H$_2$ and O$_2$ pressures slightly above the ambient.

Water retention leads to better performance curves.

Abbaraju, J. Electrochem. Soc., 2008.
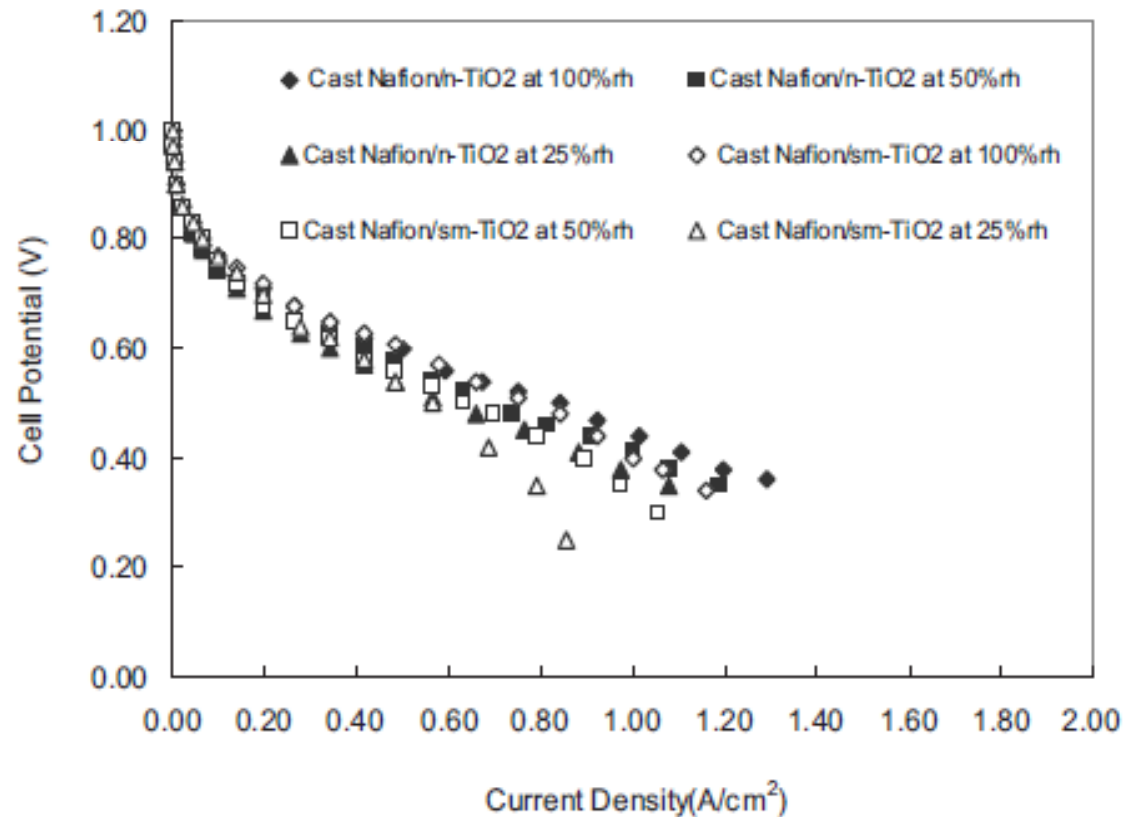
Titania: (Titanium dioxide) TiO$_2$

Figure 5. Performance of cells made with recast Nafion + sm-TiO$_2$ of low surface area and recast Nafion + n-TiO$_2$ of high surface area at various RHs. Cells tested at 80°C with H$_2$ and O$_2$ pressures slightly above the ambient.

Nanoscale (n) particles had better performance than larger sub-micron (sm) particles, especially at low humidity.

Abbaraju, J. Electrochem. Soc., 2008.

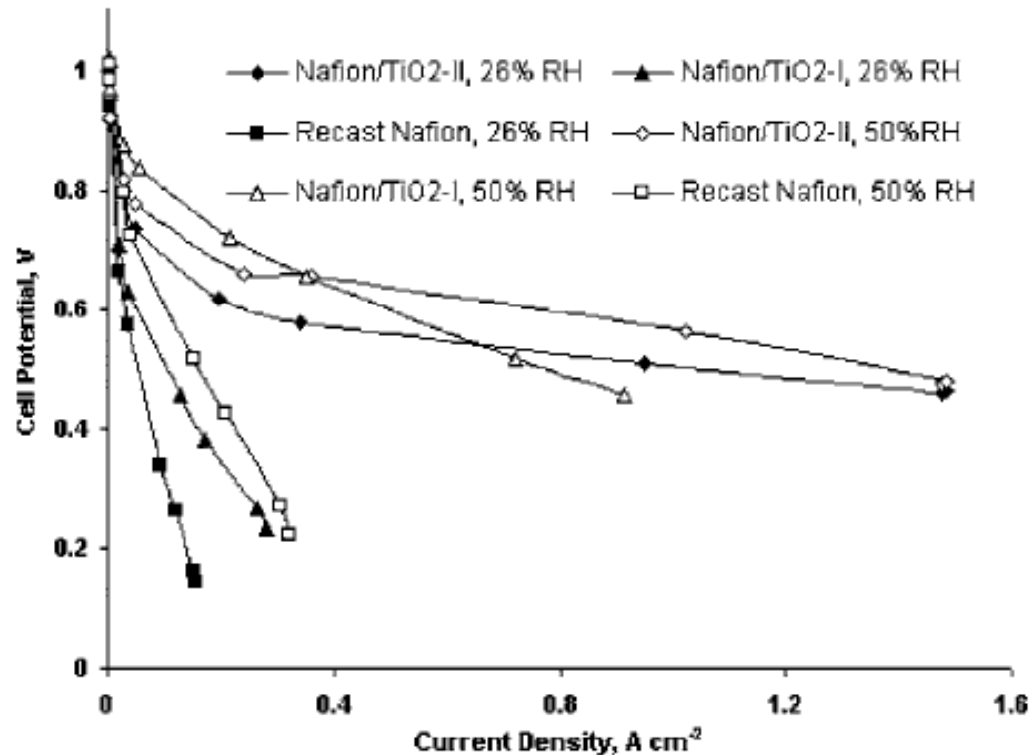# Fuel Cell Performance

Titania: (Titanium dioxide) TiO$_2$

Figure 8. Performance of H$_2$/O$_2$ PEM fuel cell operated with the recast Nafion and Nafion/10%TiO$_2$ composite membranes with TiO$_2$-I powder and TiO$_2$-II powder at 120°C, 3 bar, and various RH.

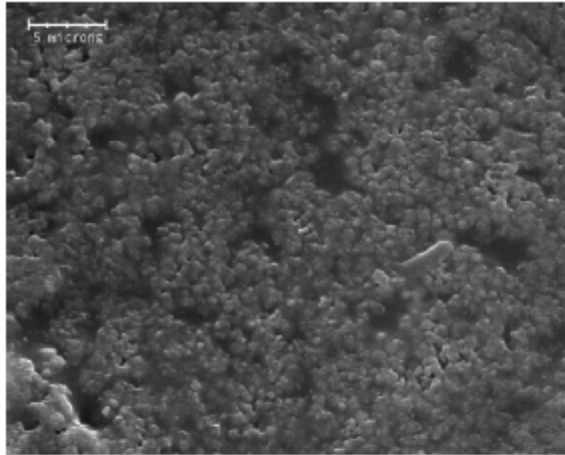How the nanoparticles are synthesized and integrated into the membrane can make a significant difference in performance.
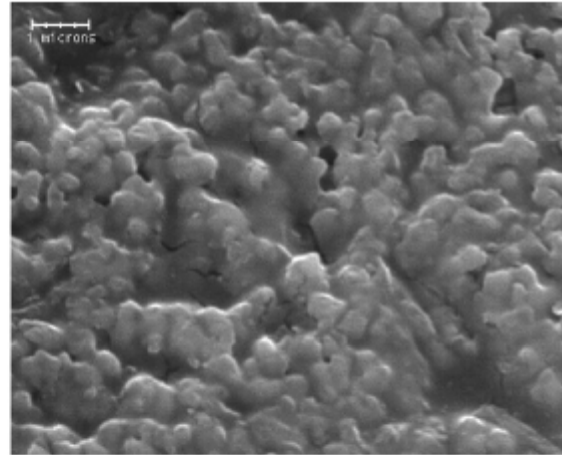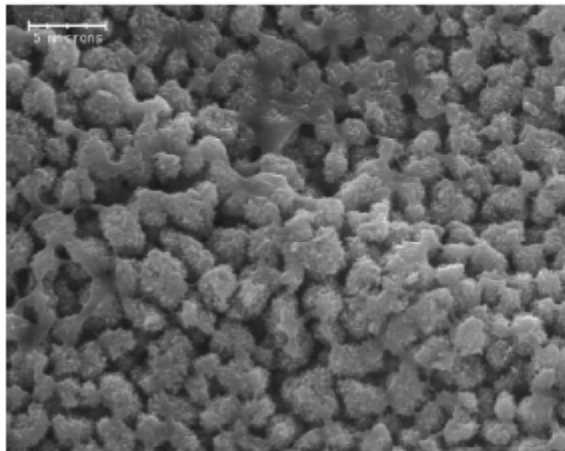
Chalkova, J. Electrochem. Soc., 2005.

Fuel Cell Performance

Titania: (Titanium dioxide) TiO_2

3500x
(a)

10000x
(c)

3500x
(b)

10000x
(d)

Figure 6. (a,c) SEM images of dull sides of the composite membranes morphology for Nafion/TiO$_2$-I and (b,d) Nafion/TiO$_2$-II at different magnification (a,c at 3500; b,d at 10 000).
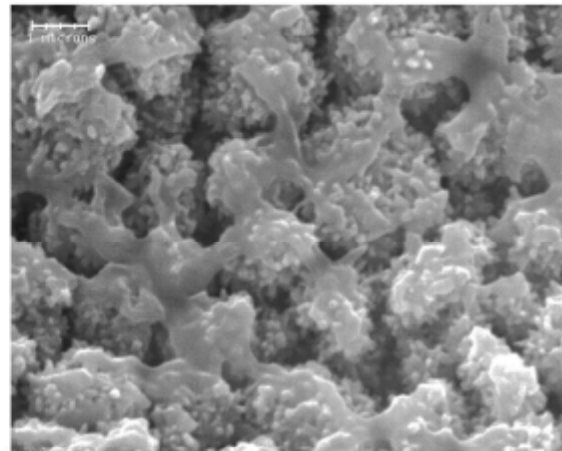
These two membranes gave the different performance shown on the previous slide.

Chalkova, J. Electrochem. Soc., 2005.

Platinum

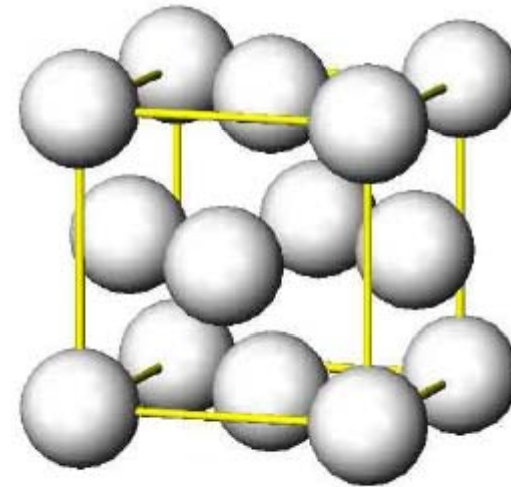Bulk platinum has an FCC structure.

Figura 2. *FCC unit cell*

Pt Nanoparticles

Qi, Huang, Wang, Yin and Li (J Nanopart Res, 2009) studied the nanoparticle size influence on the lattice parameters. Specifically they looked at spherical, cubic and cuboctahedral Pt nanoparticles with a number of atoms ranged from 79 to 2243, 108 to 2048 and 86 to 2436 respectively. They found that all the particles retained the fcc structure except for the cube with 108 atoms which was amorphous.
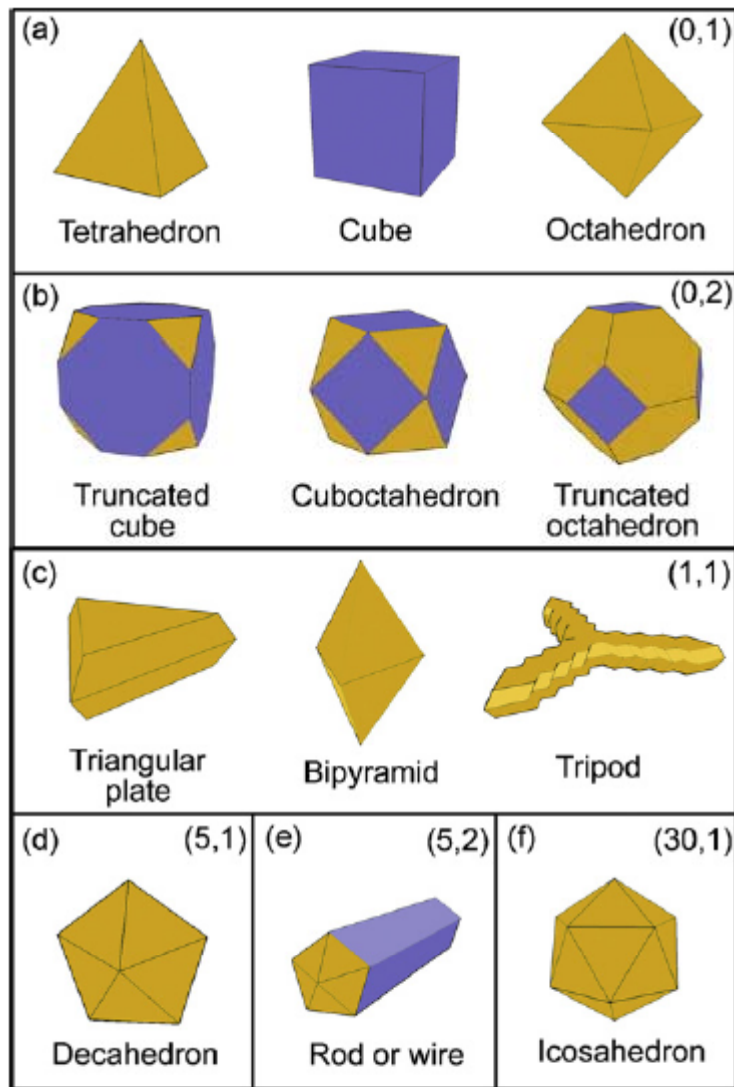
Structure of Nanoparticles

Platinum

Figure 2 Selective possible shapes of platinum nanoparticles (a and b) without defects and bounded by (a) one group and (b) two groups of facets; and (c–f) with different numbers of defects. The notation (m, n) represents the number of defects m, and different facets n, in crystals.

There are various geometries of Pt nanoparticles that can be synthesized today.

Peng, Nano Today, 2009.

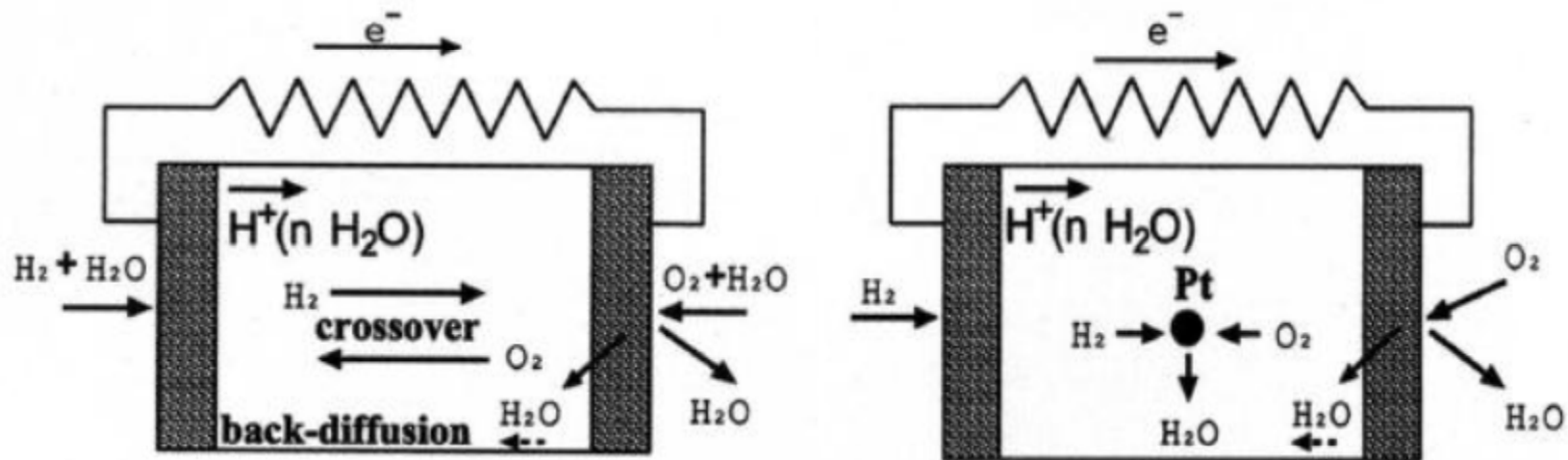# Fuel Cell Performance

Platinum

Figure 1. *Schematics of a conventional PEMFC with external humidification (left) of reactant gases and a self-humidifying Pt-PEMFC (right) [13]*

Platinum particles might not only work to retain moisture but also create water by reacting cross-over gases.

Watanabe, J. Electrochem. Soc., 1998.
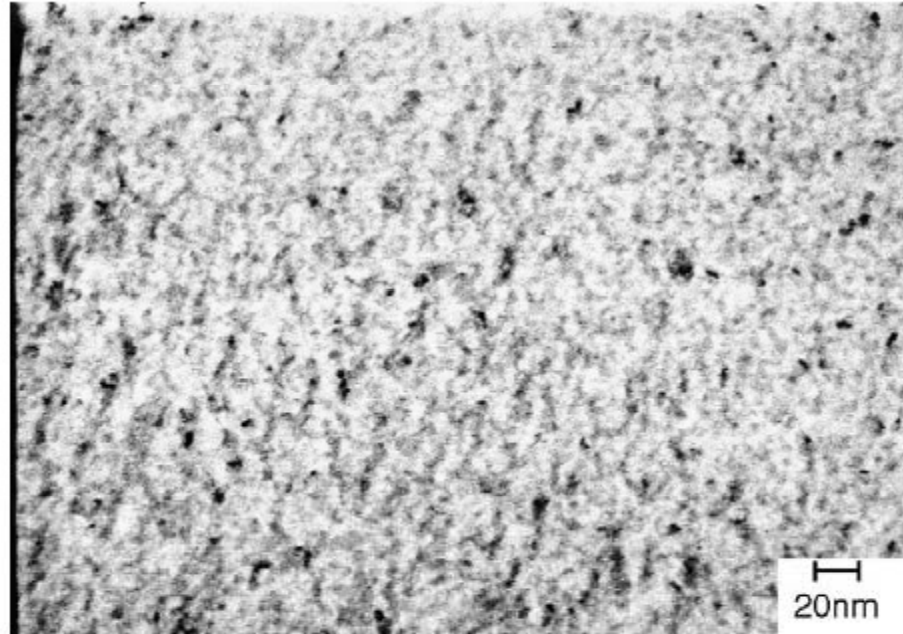
Fuel Cell Performance

Platinum

Fig. 5. STEM picture of Pt (0.1 mg/cm^2)-SiO$_2$ (4.5 wt%)-PEM prepared by 1-pentanol method. The sample was sliced by a microtome and put on a microgrid, followed by carbon deposition before the observation.

Pt or Pt/SiO$_2$ nanoparticles can be uniformly dispersed with Nafion.

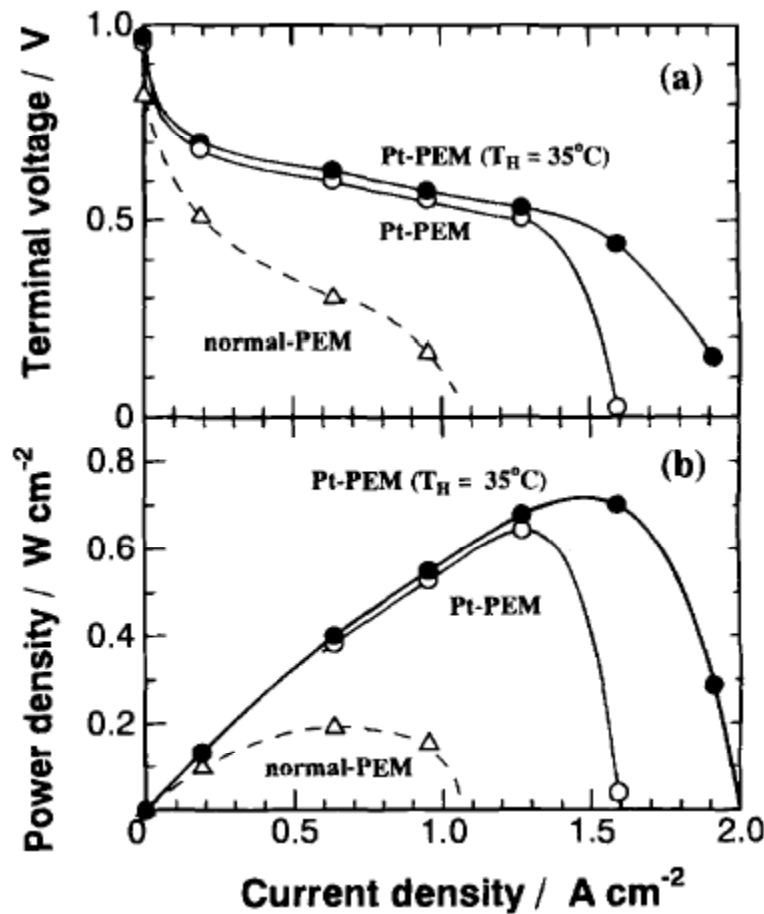Hagihara, Electrochimica Acta, 2005.

Fuel Cell Performance

Platinum

Fig. 3. (a) Current density–cell voltage curves for PEFCs with normal-PEM (△) and Pt-PEMs (○, ●) at 80°C and ambient pressure without external humidification (△, ○) and with slight humidification (●, T_H = 35°C, $P_{[H_2O]}$ = 0.056 atm). Utilization: H_2 70%, O_2 40%. (b) Current density-power density curves using the same symbols as (a).

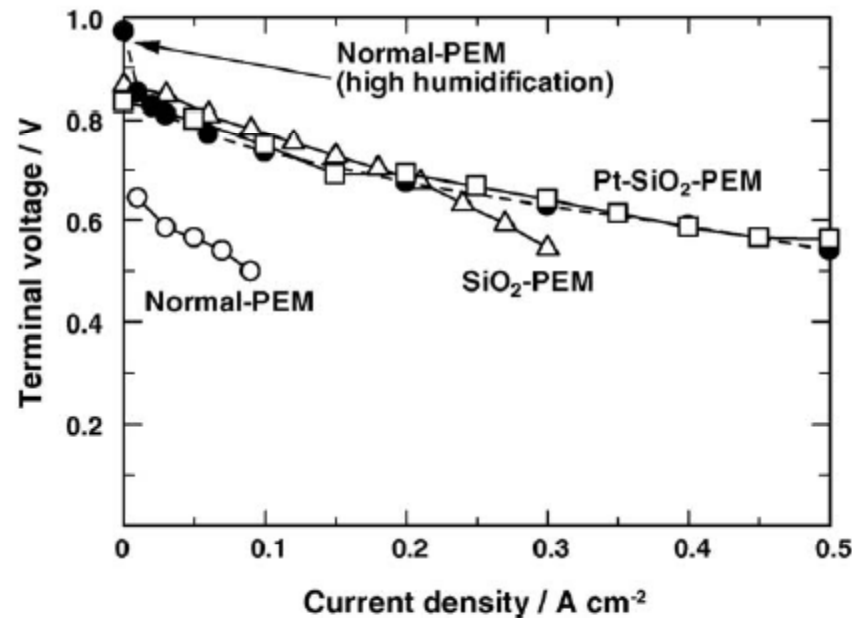The presence of Pt inside the PEM improved the performance of the fuel cell.

Watanabe, J. Electrochem. Soc., 1998.

Fuel Cell Performance

Platinum

Fig. 6. *I–V* curves of the standard cells using (□) Pt-SiO$_2$-PEM (Pt = 0.09 mg/cm^2, SiO$_2$ = 1.0 wt%), (△) SiO$_2$-PEM (SiO$_2$ = 7.9 wt%), and (○) normal-PEM operated at T_{cell} = 80 °C and ambient pressure with the reactant gases humidified at 30 °C. $U(H_2)$ = 70%, $U(O_2)$ = 40%. (●) The cell using normal-PEM under H$_2$ humidified at 80 °C and dry O$_2$.

The presence of Pt or Pt on SiO$_2$ inside the PEM allows for the use of unhumidified (dry) fuels.

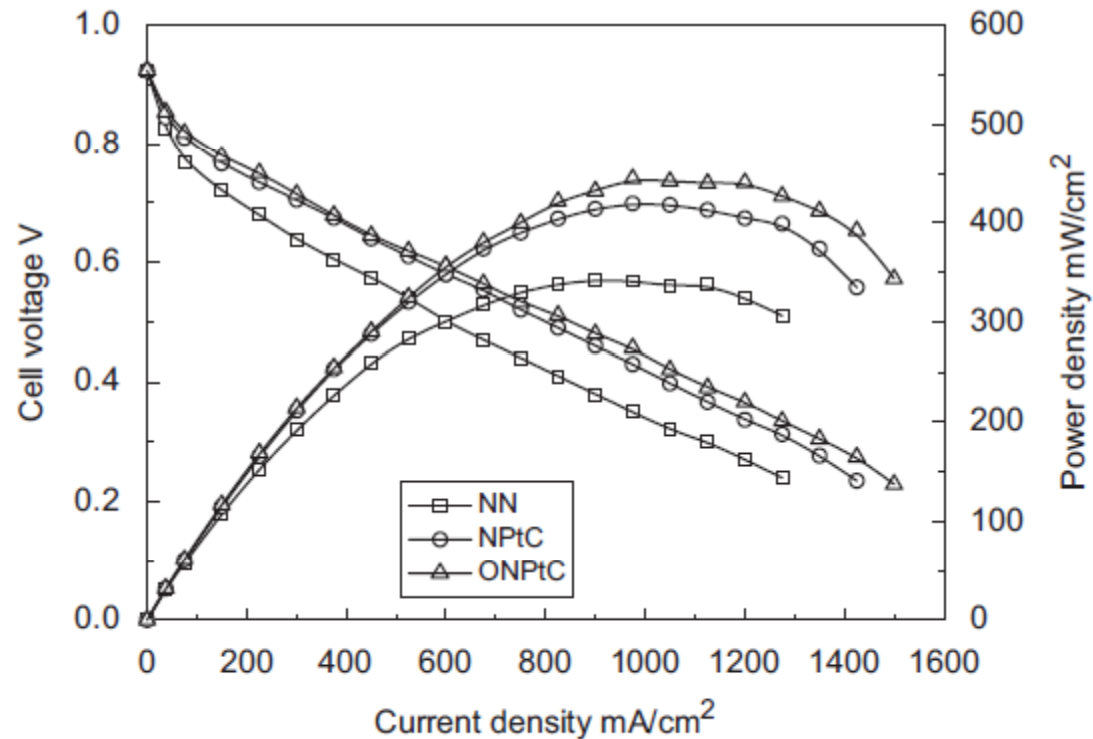Hagihara, Electrochimica Acta, 2005.

Fuel Cell Performance

Platinum

Fig. 7 – Polarization characteristics of the cells fabricated with the plain NN membrane and composite NPtC, ONPtC membrane, operated with dry H_2 and O_2 at 60 °C.

Ordered nanoparticle Pt on C particles performed better than non-order NPtC, which both performend better than pure Nafion (NN).

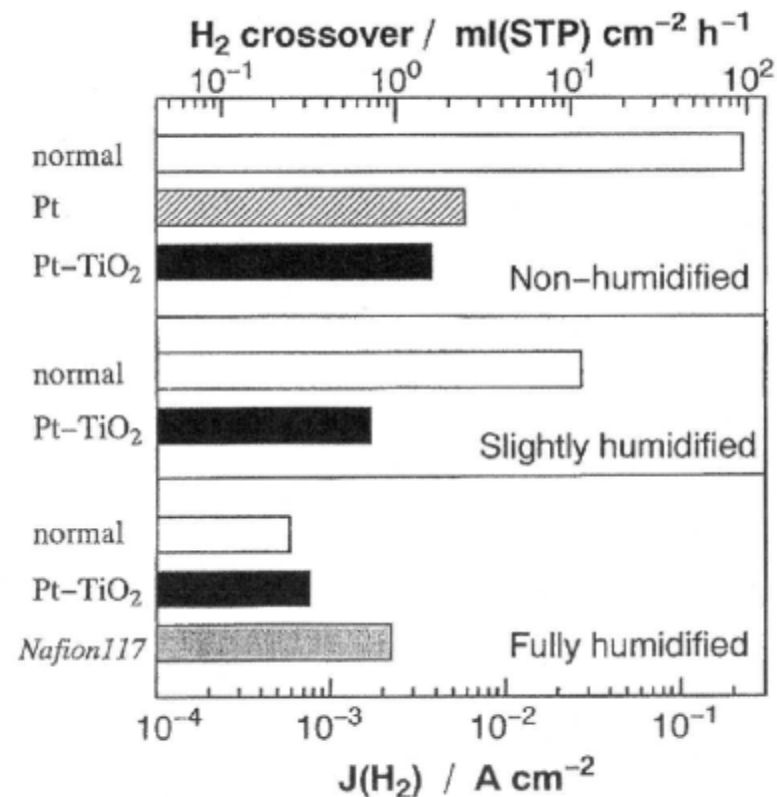Yang, Int. J. Hydrogen Energy, 2008.

Fuel Cell Performance

Platinum

Fig. 7. Comparison of current densities for the oxidation of crossover H_2, $J(H_2)$, at various PEMs (thickness = 50 μm) in PEFCs operated at 80°C with the reactant gases humidified under different conditions. Nonhumidified: dry H_2// dry O_2 (condition e in Table I). Slightly humidified: wet H_2 (T_h = 20°C)//dry O_2 (condition d in Table I). Fully humidified: wet H_2 (T_h = 90°C)//dry O_2 (condition c in Table I). The loss of hydrogen by the crossover (in the unit of ml (STP) cm^{-2} h^{-1}) is also indicated on the upper axis. The value for Nafion 117 is calculated based on the diffusion parameters which appear in Ref. 22 (thickness = 50 μm, T_{cell} = 80°C, wet H_2//wet O_2, T_h = 80°C for both gases).

The presence of Pt or Pt on TiO_2 reduces the cross-over gases.

Watanabe, J. Electrochem. Soc., 1996.

Conclusions

The inclusion of relatively small amounts of inorganic nanoparticles acts to retain moisture in the membrane, allowing higher performance of aqueous based PEMs like Nafion at elevated temperatures.

If too much inorganic material is added, it has a negative effect on fuel cell performance since the inorganic material is not a proton conductor.

The structure of the material
- solid nanoparticles of silica or mesoporous silica
- different methods of incorporating titania into the membrane
- Pt or Pt on SiO_2, TiO_2 or carbon

can have a significant impact on the observed performance. A predictive understanding of this effect is not currently available.

The optimization of these systems is highly dependent not only on the nanostructure of the membrane but also on the operating conditions of the fuel cell. The improvement of these composite membranes is only observed under certain optimized operating conditions.