Proton Conducting Fuel Cells

Where Electrochemistry Meets Material Science

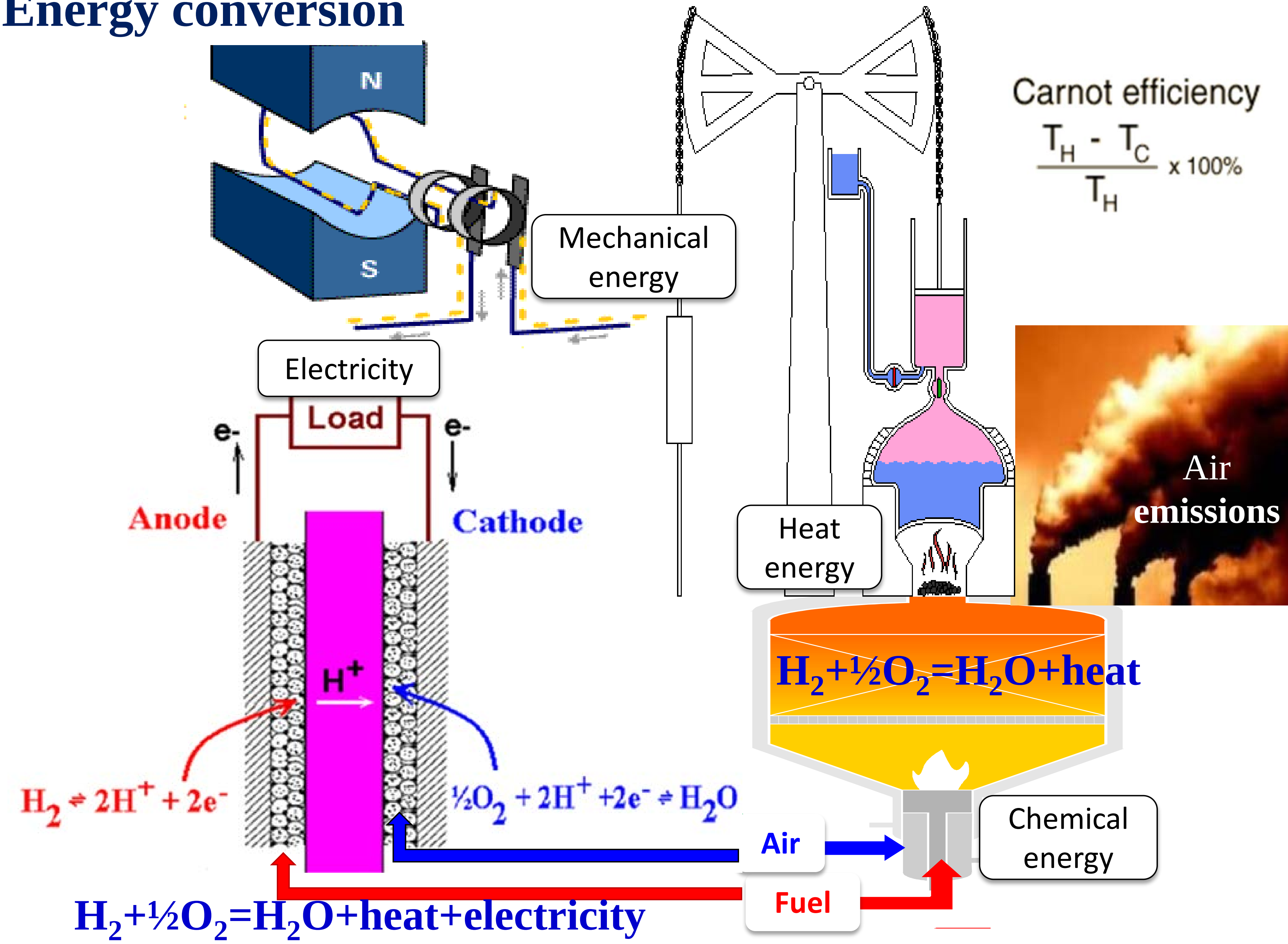
Qingfeng Li, dr. techn.

Section of Proton Conductors, DTU Energy

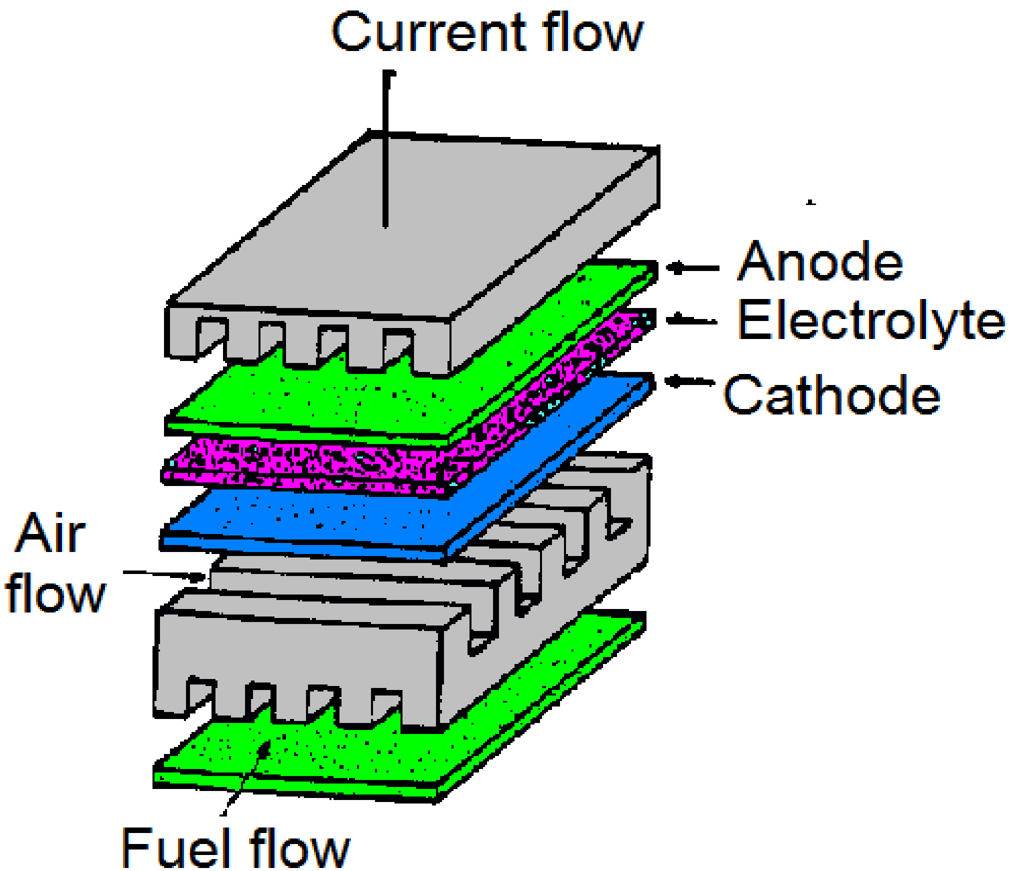
- Fuel Cells – a promise of electrochemistry
  - High efficiency, is it true?
- Hydrogen popularity
  - Hydrogen pecularity?
- Proton conductors
  - Not always proton conducting?
- DTU research
  - What further on?

- **Promise of Electrochemistry**
  - **A fuel cell, how is it working?**
  - **High efficiency, is it true?**

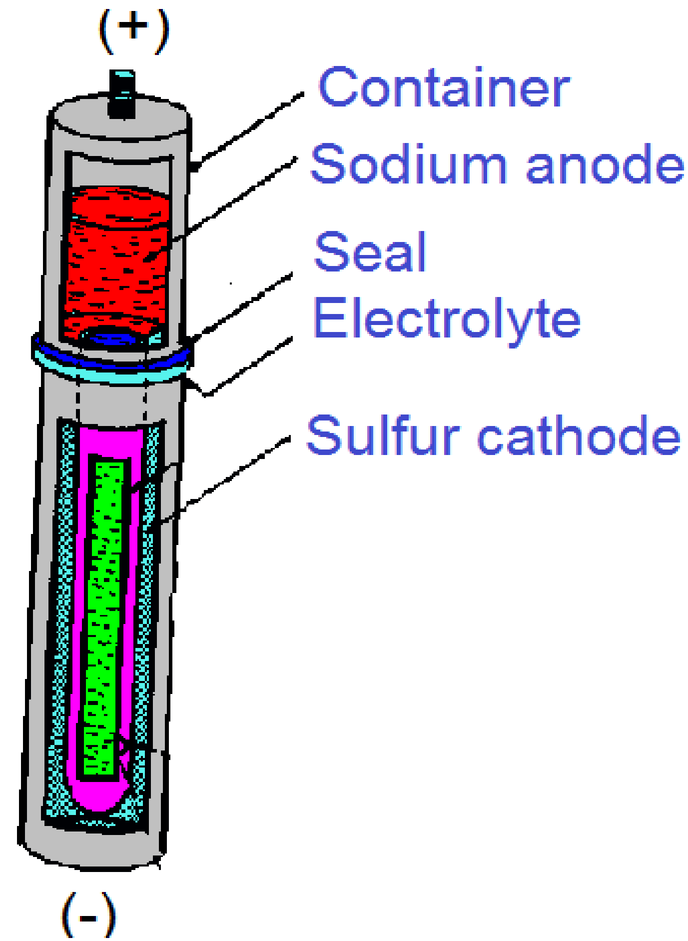
Energy conversion



Fuel Cells



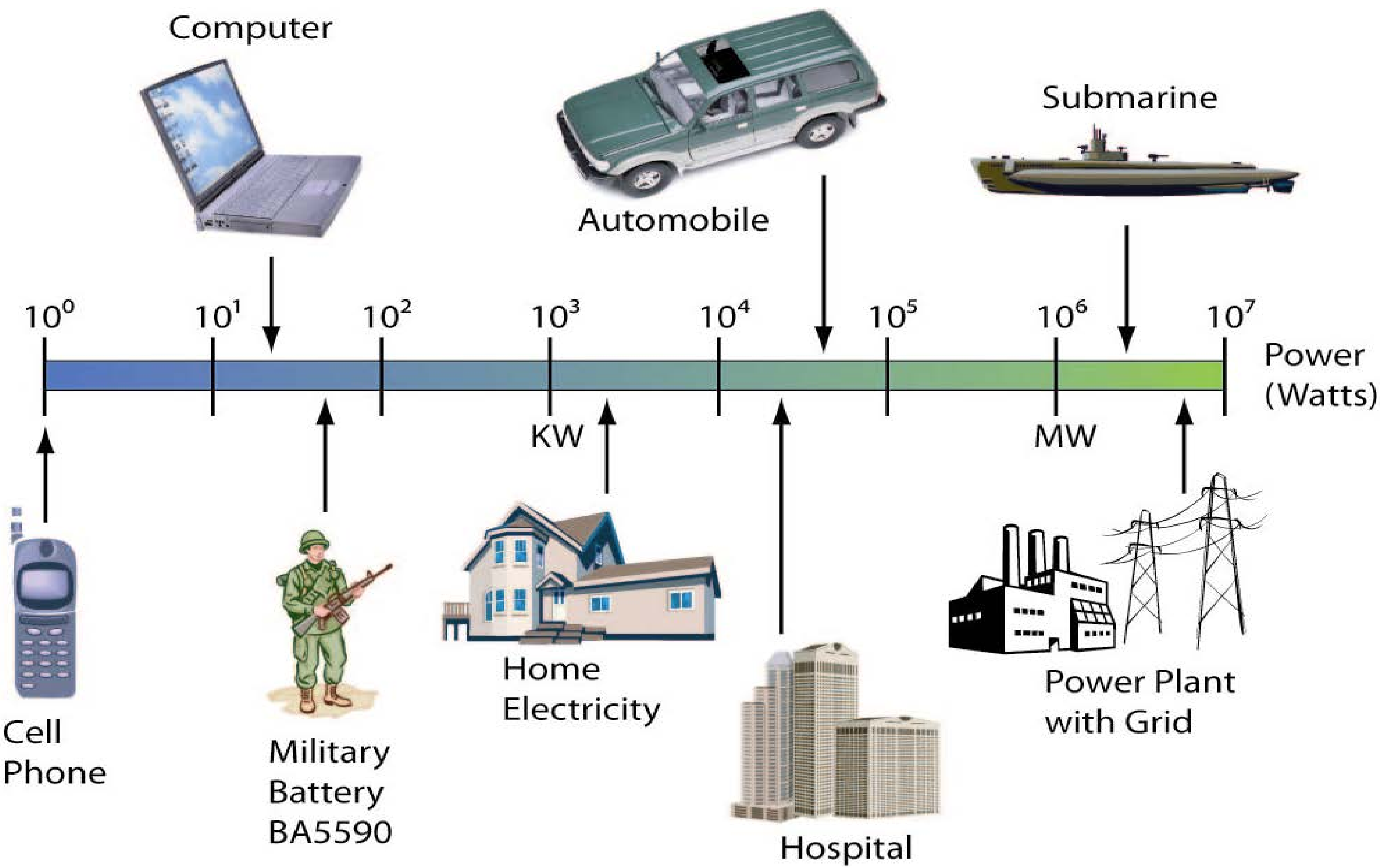
Batteries



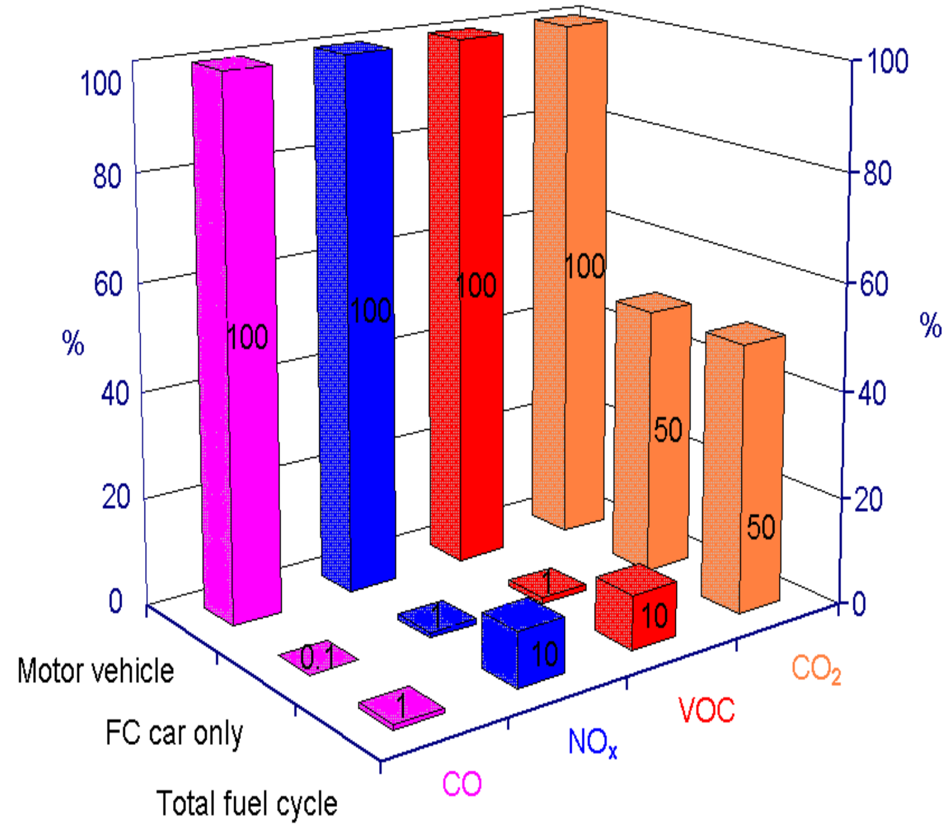
- External supplied reactants
- Continuous operation
  - fuel-tank-limited
  - quick refueling
- Reducing pollution

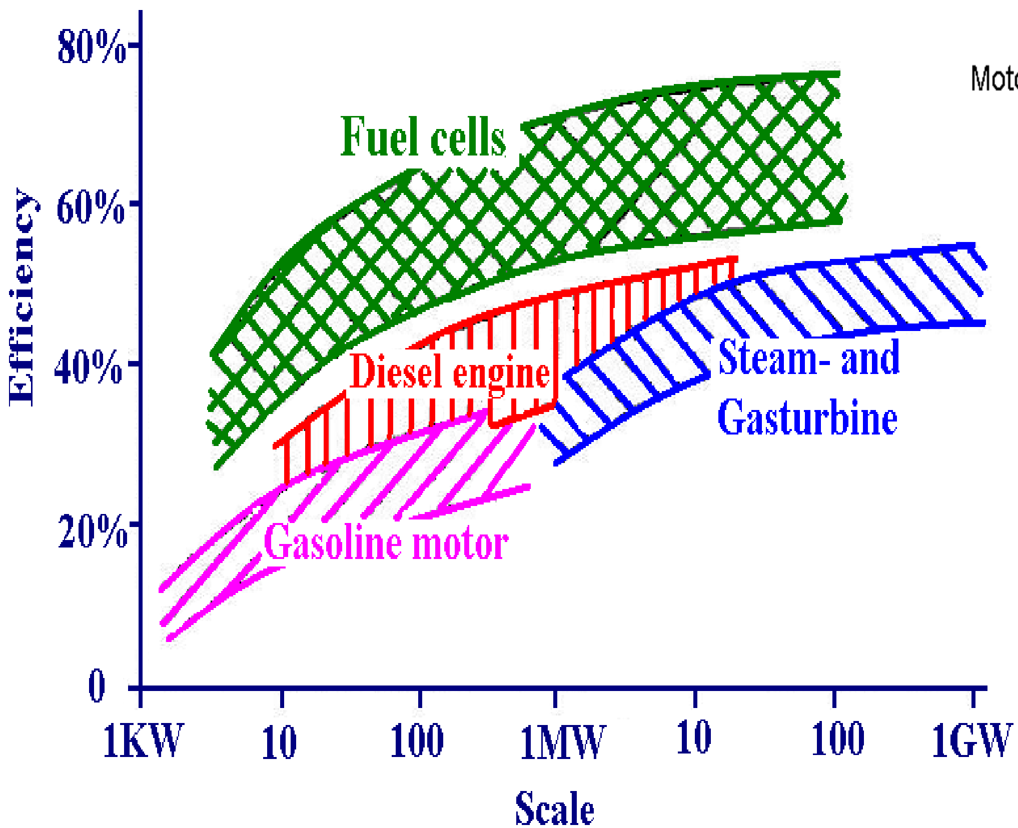
- Electrode-stored reactants
- Discontinuous operation
  - limited capacity
  - lengthy recharging
- Shifting pollution ´´

Fuel Cell Power Spectrum



Fuel cells
- Promise of electrochemistry

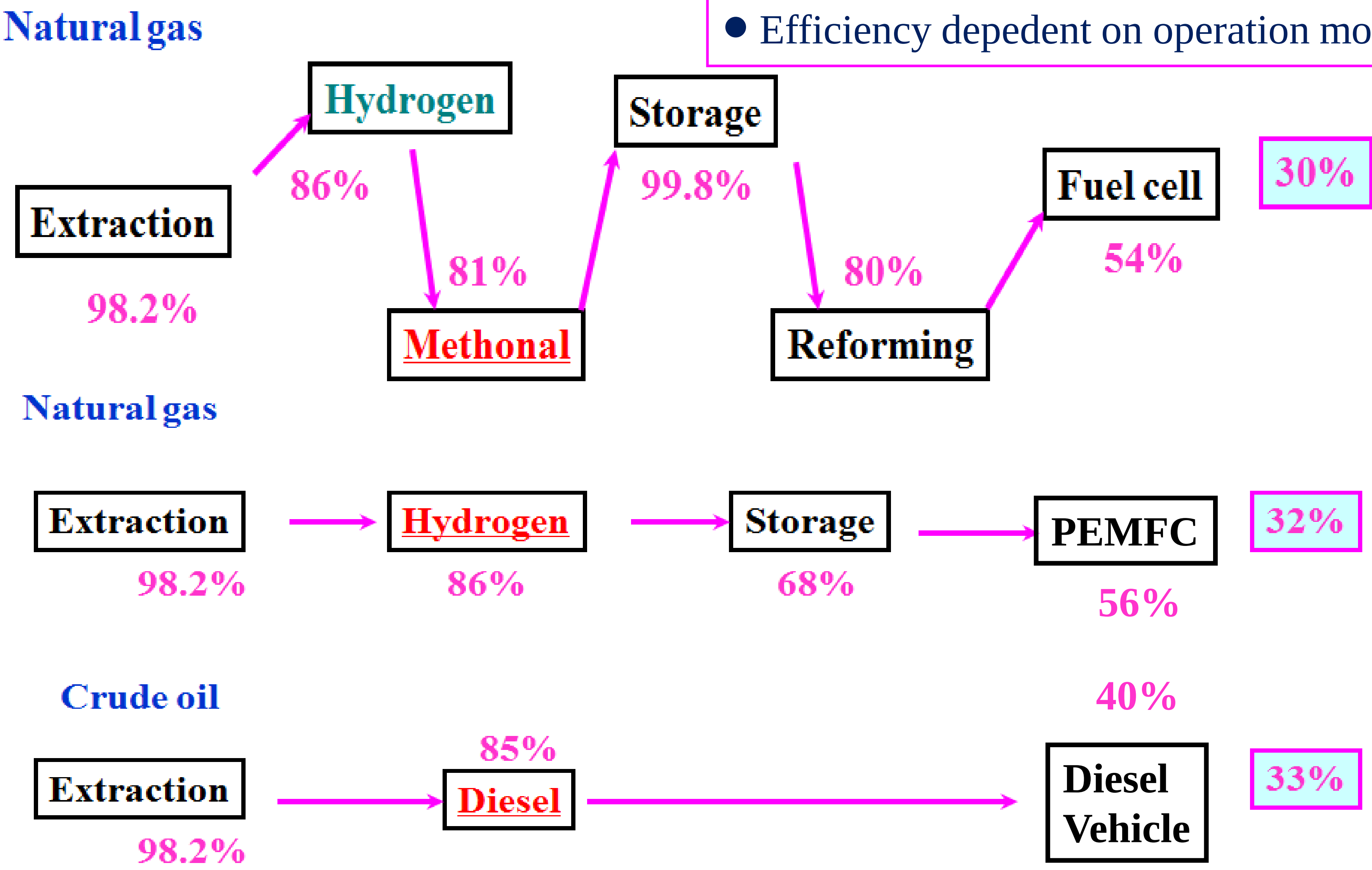




- Highly efficient
- Sufficiently pollution-free
- Flexible in size
- Compact and quiet enough
  - to be sited closer to users

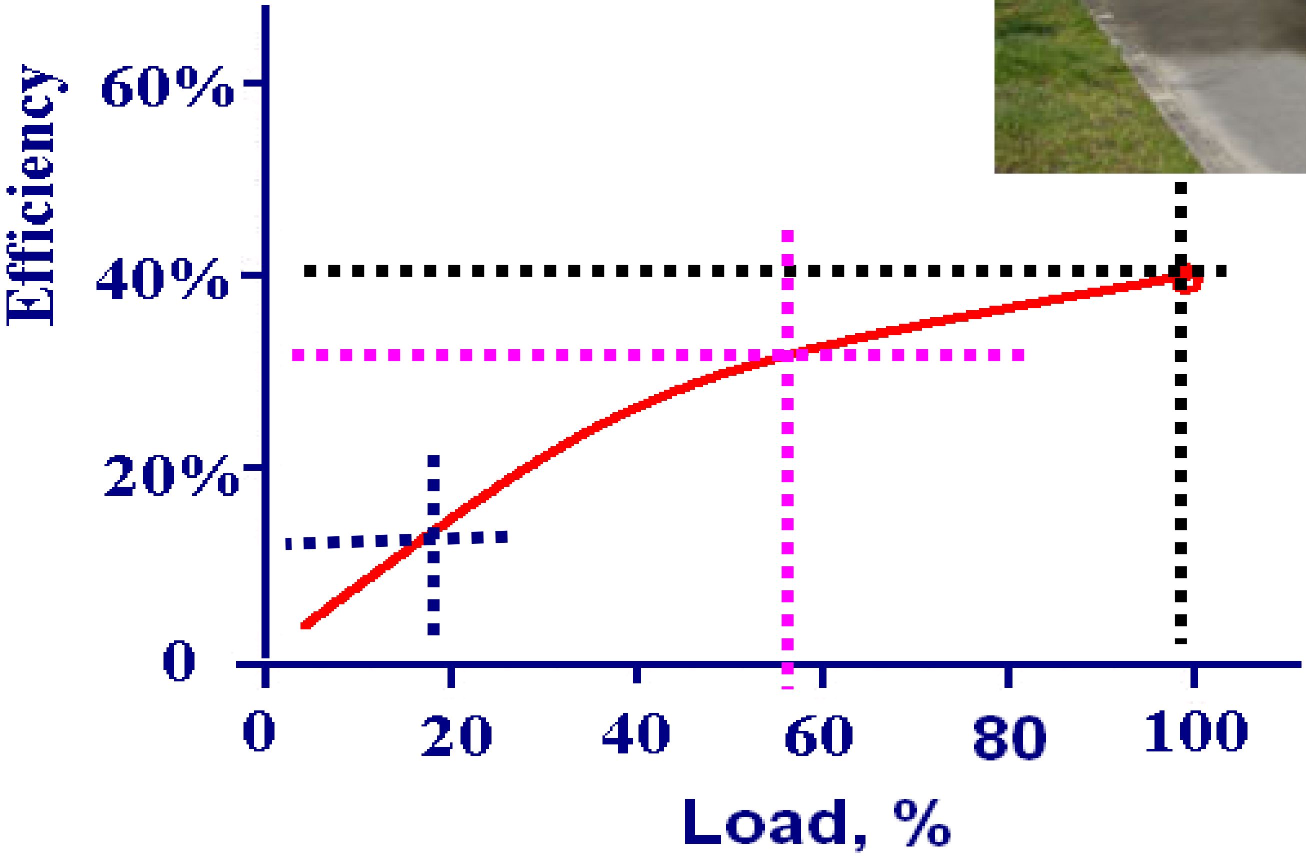
Higher efficiency, is it true?

- Good to look at entire well-wheel chain
- FC makes more sense in association with renewable energy sources
- Efficiency depedent on operation modes



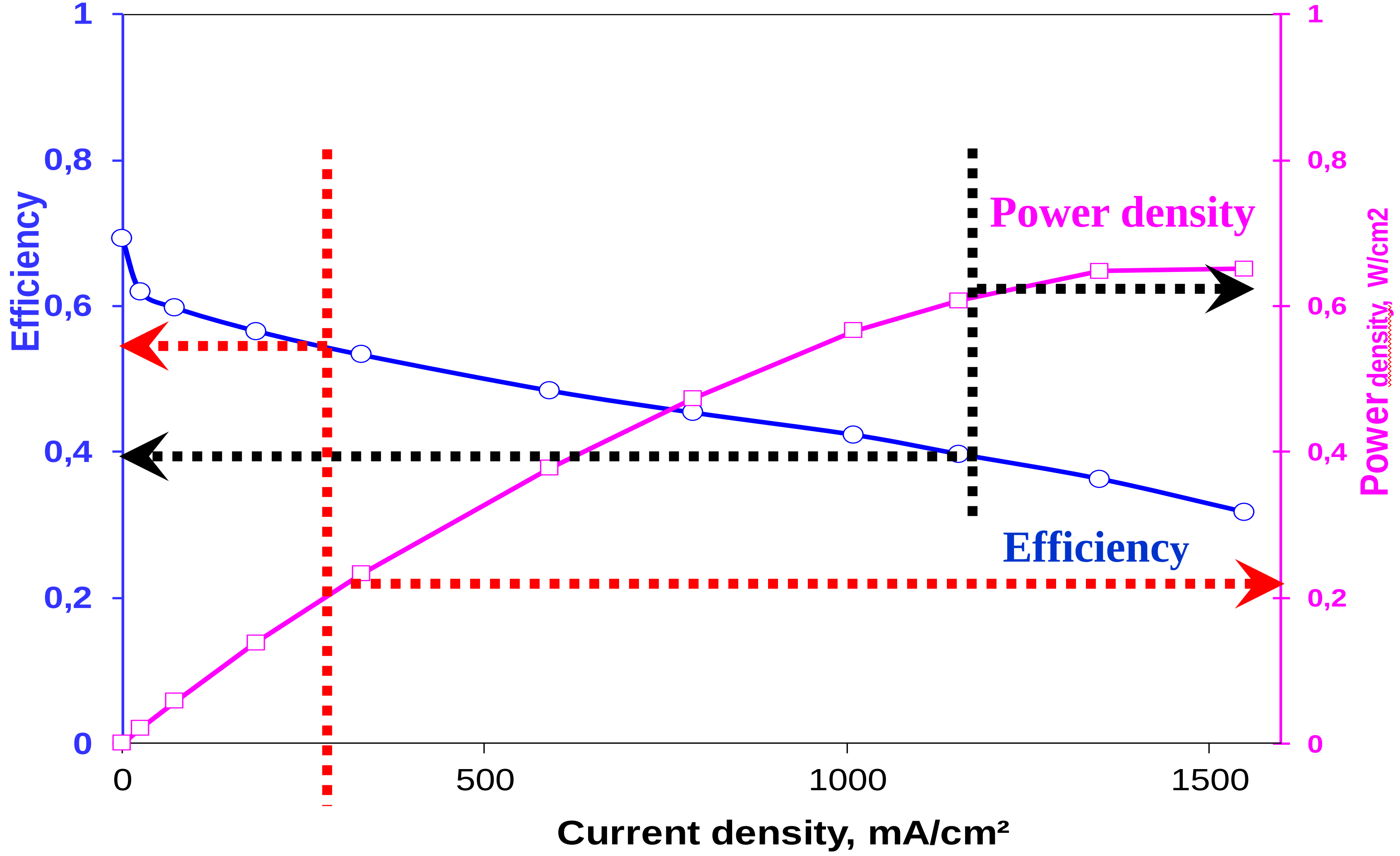
Efficiency of a thermal engine

- dependence on the load range



Efficiency of an electrochemical cell

- dependence on the load range



Efficiency under varied loading levels

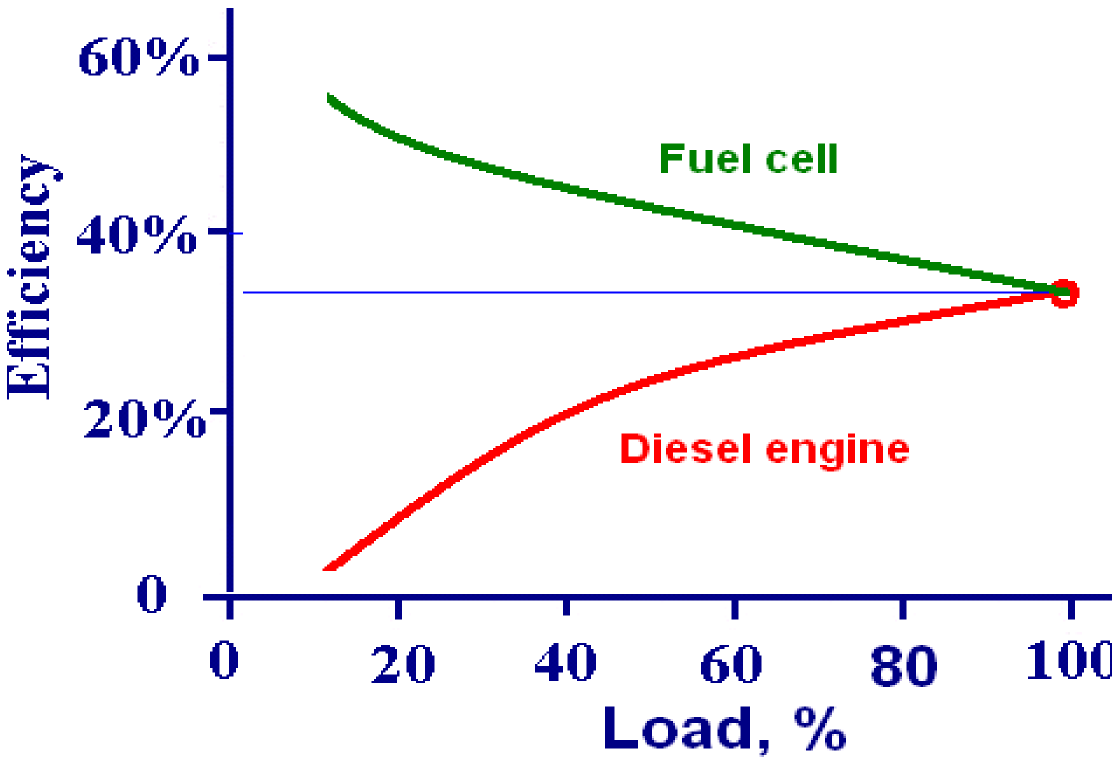
Extraction → Hydrogen → Storage → PEMFC — **32%**

98.2% — 86% — 68% — 56%

Crude oil

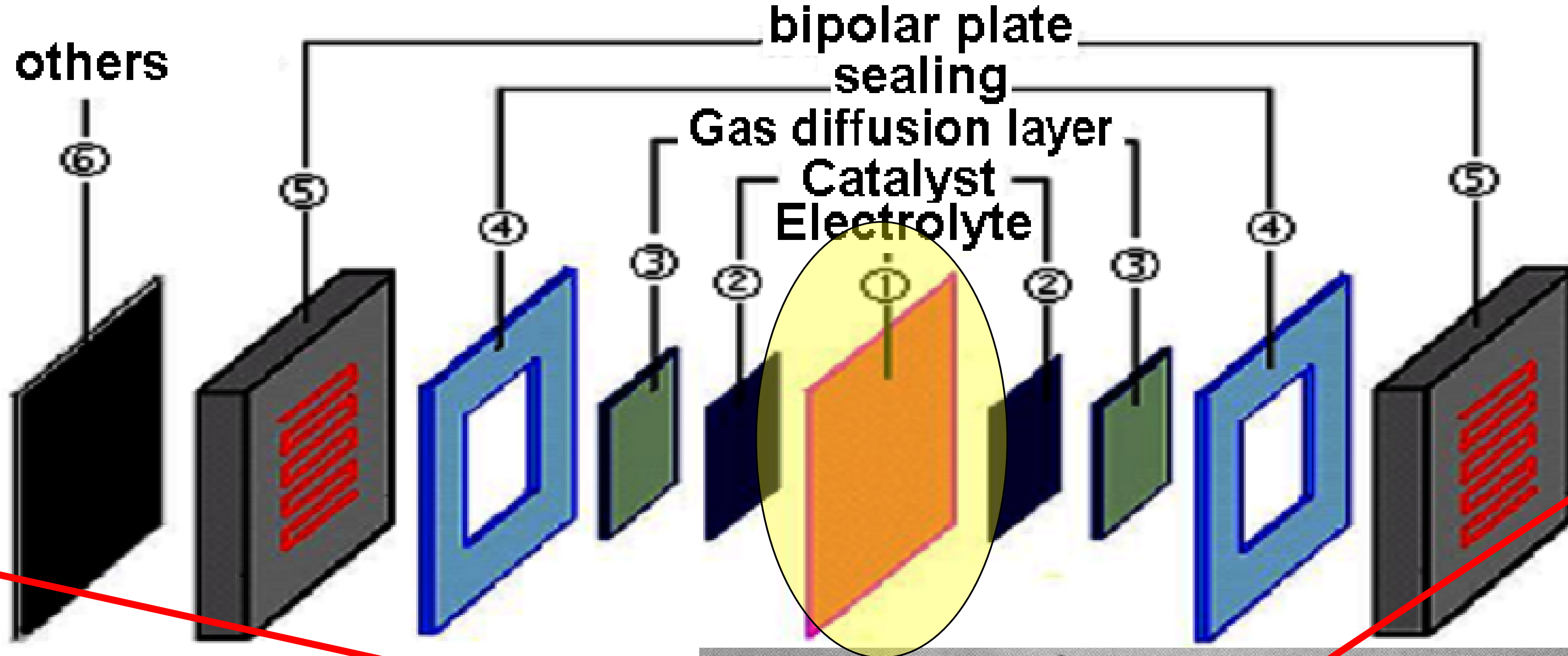
Extraction → Diesel → Diesel Vehicle — **33%**

98.2% — 85% — 40%



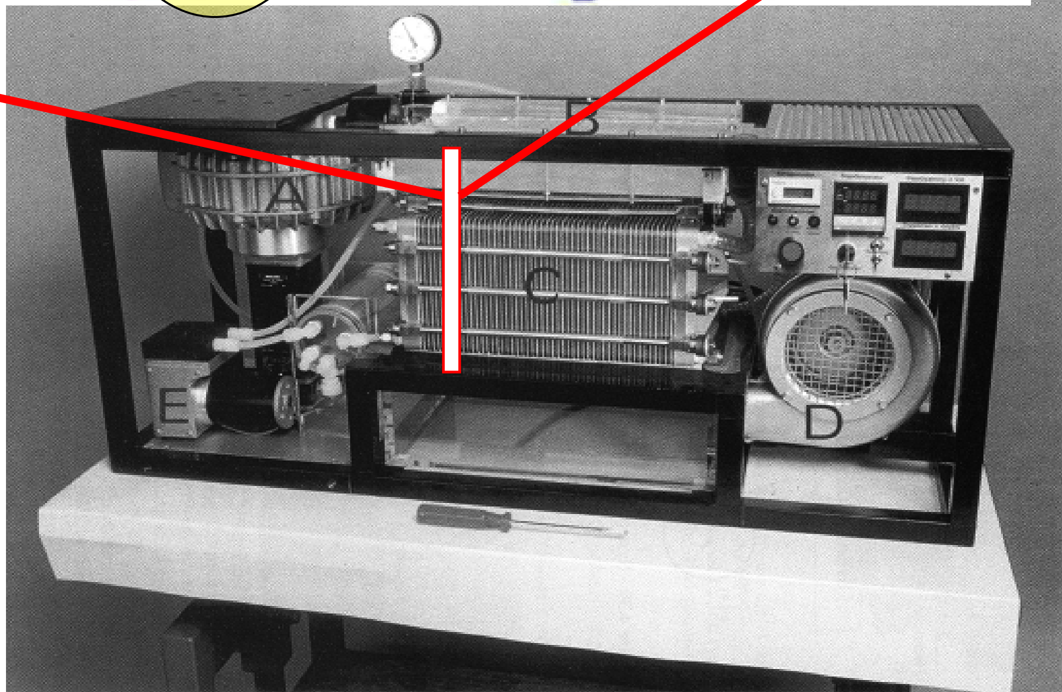
APU = Auxiliary Power Unit

- **Challenges for Materials Science**
  - **Pecularity of hydrogen and proton**
  - **Proton conducting mechanisms**
  - **Consequences of water carriers**



Material issues

- Catalysts and supports
- Electrode substrates
- Bipolar plates
- Seals and others

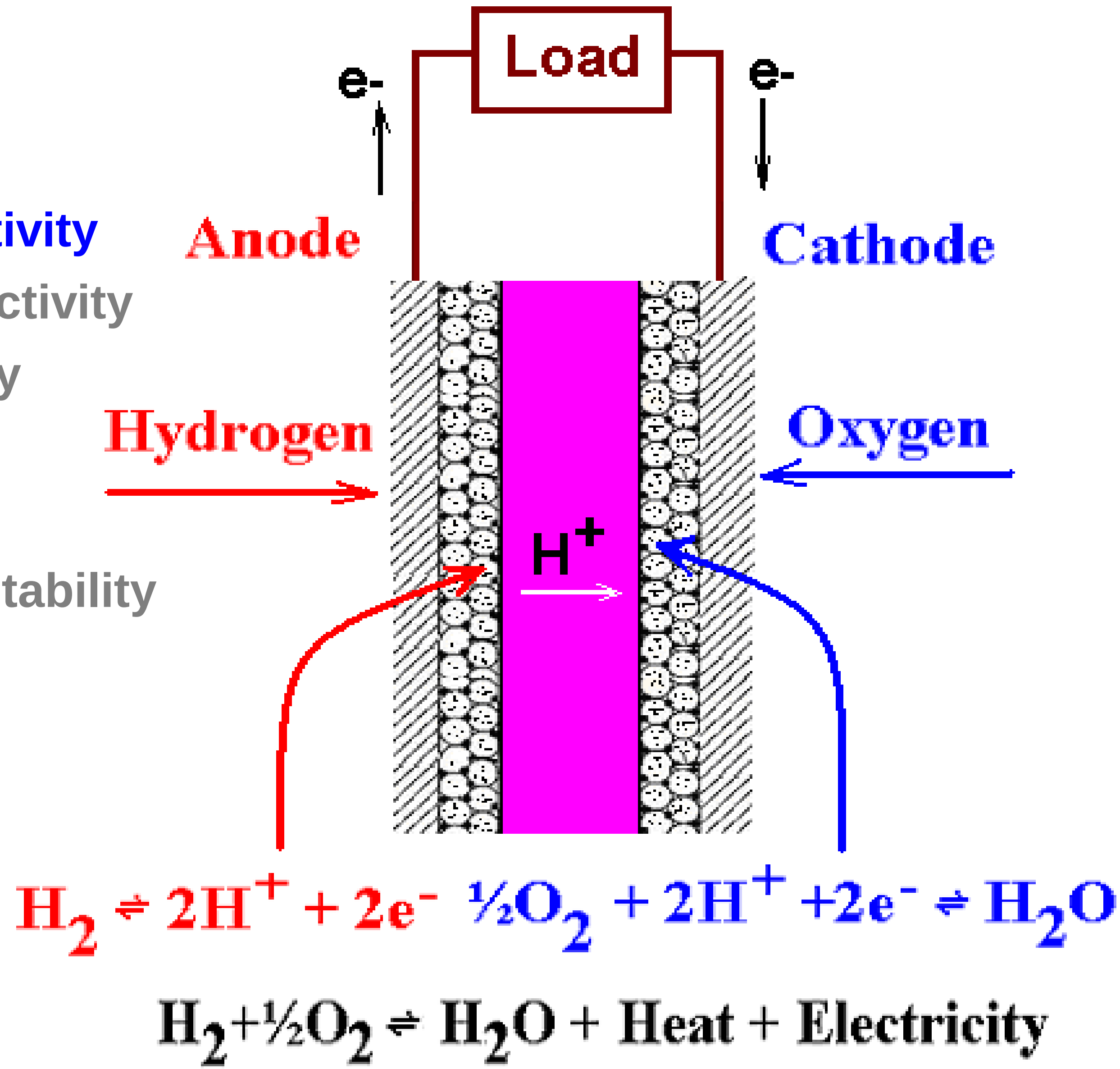


Proton conducting electrolytes

- operational from room/subfreezing temperatures

Major requirements

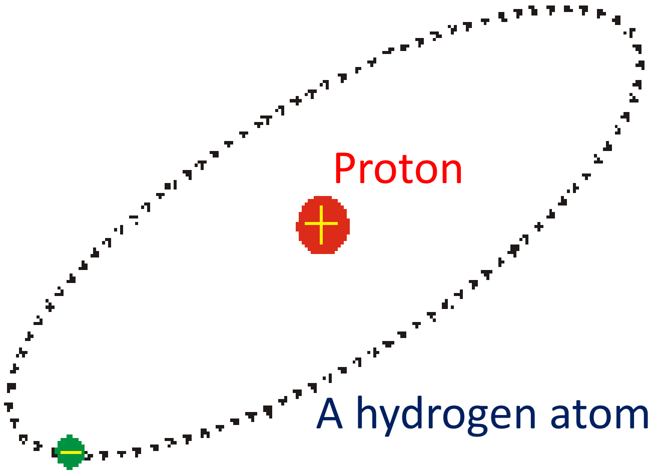
- **High proton conductivity**
- No electronic conductivity
- Low gas permeability
- Mechanical strength and flexibility
- (Electro-) chemical stability
- Availability
- Cost



Proton and conductivity

- A hydrogen atom losing one electron
  - A chemist calls it an ion, a cation H^+

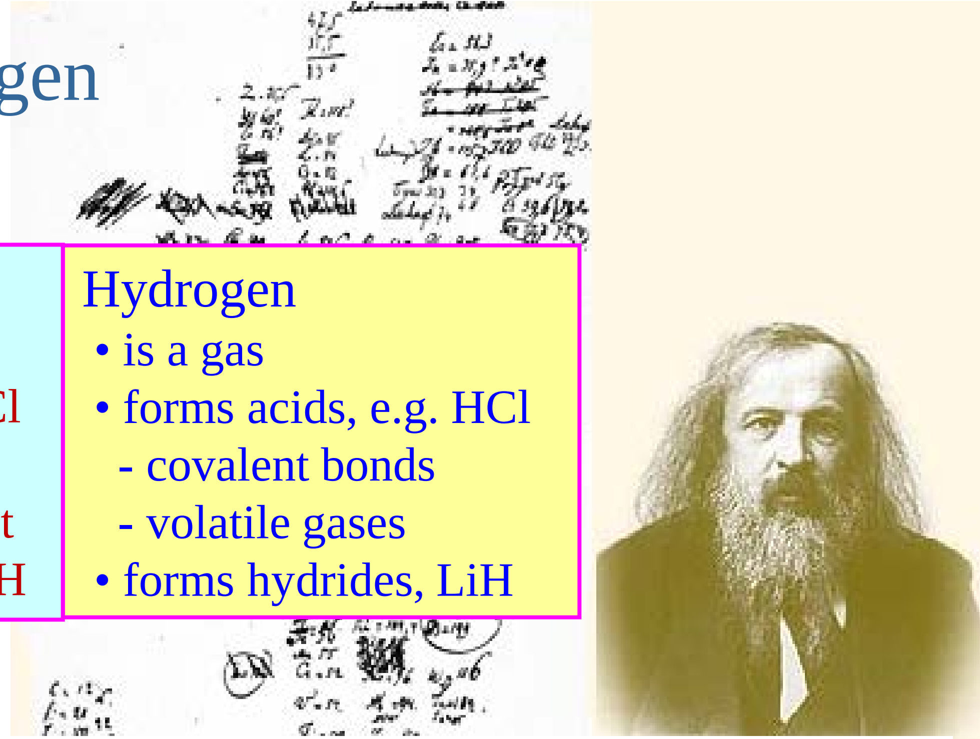
- A proton has no electron shell of its own
  - A physicist calls it a fundamental particle



→ very strongly reacting with its environment
always associated with a carrier
in condensed phases

	Electron	Sodium ion (Na^+)	Proton
Charge, C	-1.6×10^{-19}	$+1.6 \times 10^{-19}$	$+1.6 \times 10^{-19}$
Mass, kg	9.10×10^{-31}	3.82×10^{-23}	1.67×10^{-27}
Diameter, m	*ca.* 10^{-18} m (10^{-9} nm)	*ca.* 10^{-10} m (10^{-1} nm)	*ca.* 10^{-15} m (10^{-6} nm)

Pecularity of Elemental Hydrogen



Similarities

Half filled s-orbital

e.g. H $1s^1$

Li ...$2s^1$

Na ...$3s^1$

K ...$4s^1$

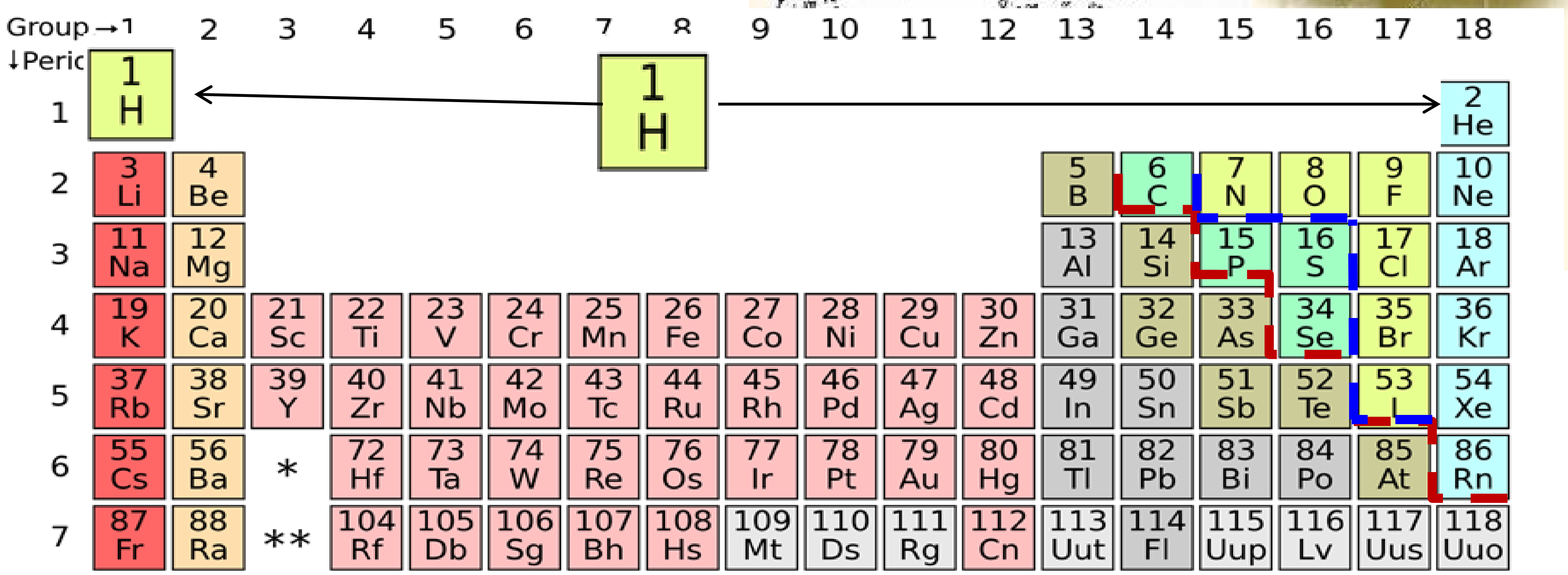
Differences

Alkali metals

- are active metals
- form salts, e.g NaCl
  - ionic bonds
  - high melting point
- forms hydrides, LiH

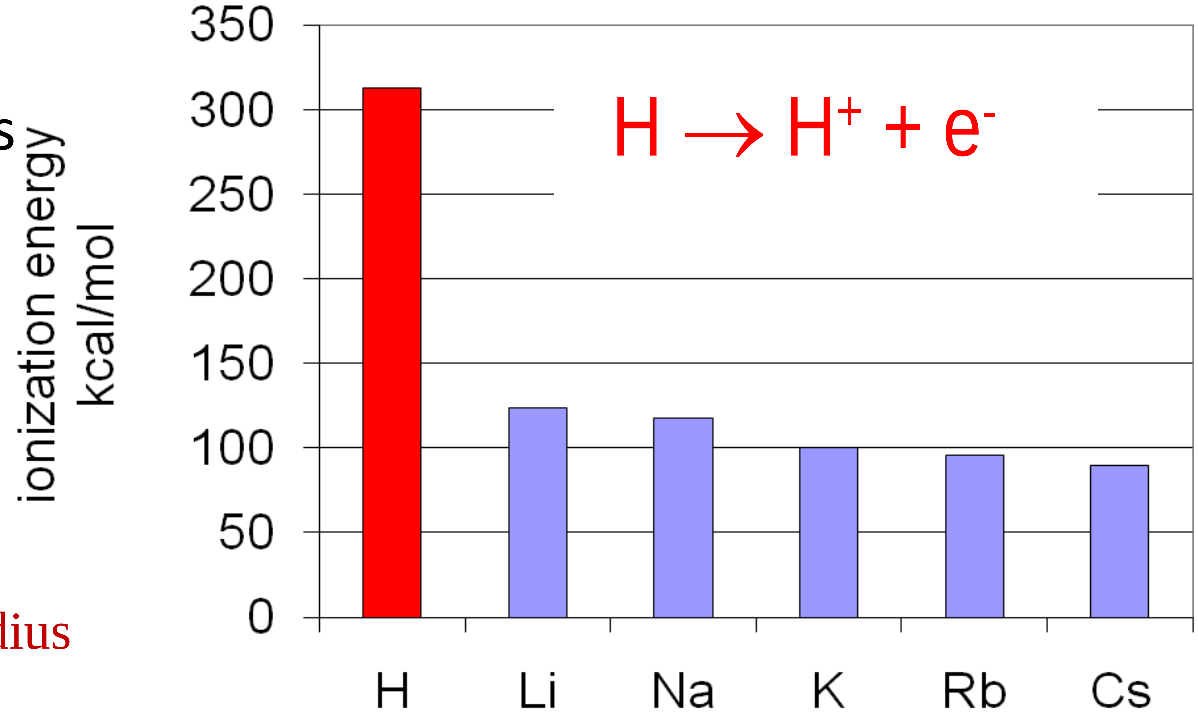
Hydrogen

- is a gas
- forms acids, e.g. HCl
  - covalent bonds
  - volatile gases
- forms hydrides, LiH



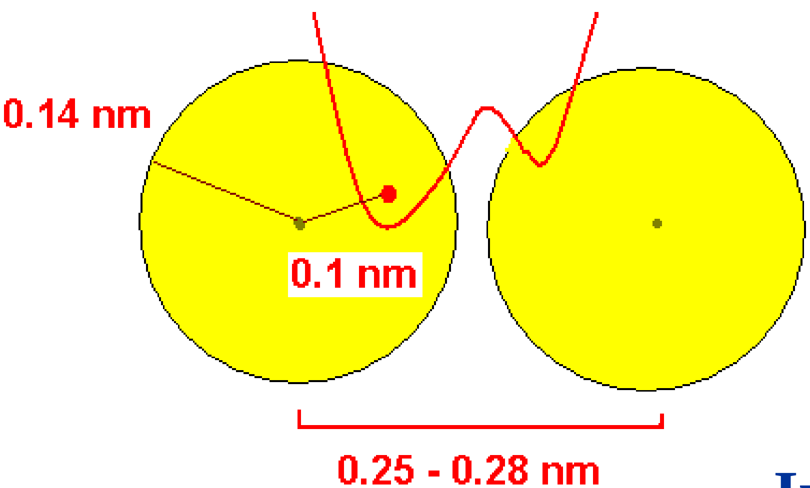
Ionization energy

of the first group elements



- Proton has strong attraction to electrons
  - forming covalent bonds by sharing e^- pairs
  - forming **hydrogen bonds**

The O-H bond, about 0.10 nm, less than 0.14 nm of the O^{2-} radius



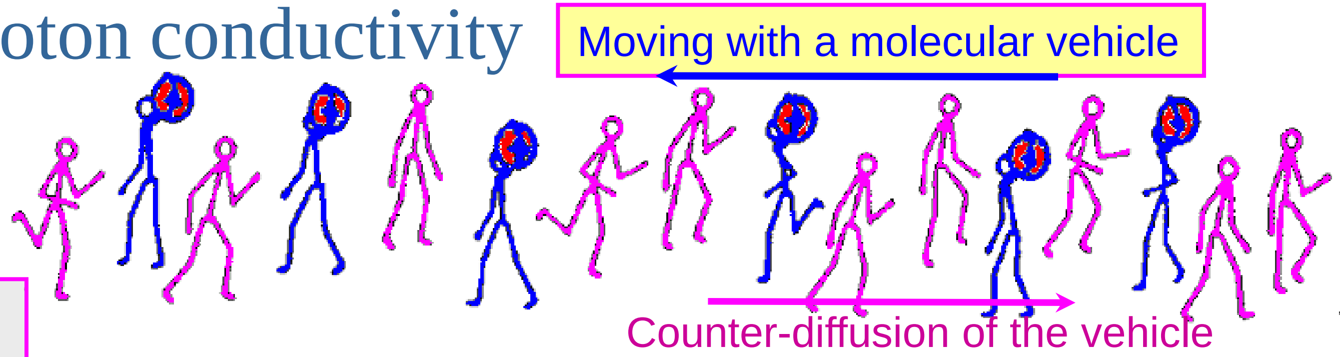
O—H-----O

In X - H...Y hydrogen bonds:

Proton donor: X - H distance ~110 pm

Proton acceptor: H--Y distance: 160-200 pm

Mechanisms of proton conductivity



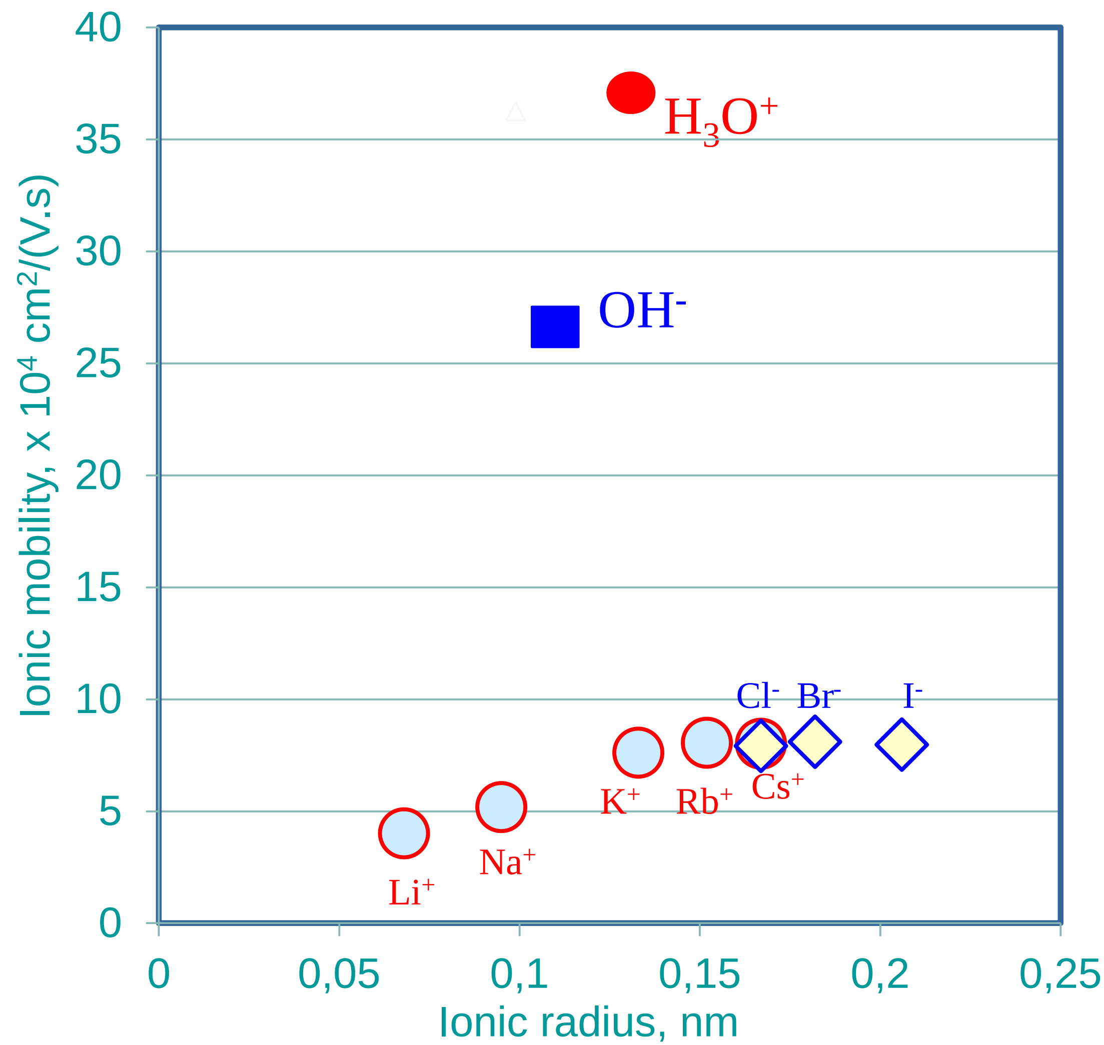
Vehicle mechanism

Stokes law:

Ionic mobility $\propto 1/r \cdot \eta$

(radius and viscosity)

Cations	Ionic radius, nm
Li^+	0,068
Na^+	0,095
K^+	0,133
Rb^+	0,152
Cs^+	0,167
Anions	
Cl-	0,167
Br^-	0,182
I^-	0,206
OH^-	**0,110**
H_3O^+	**0,136**

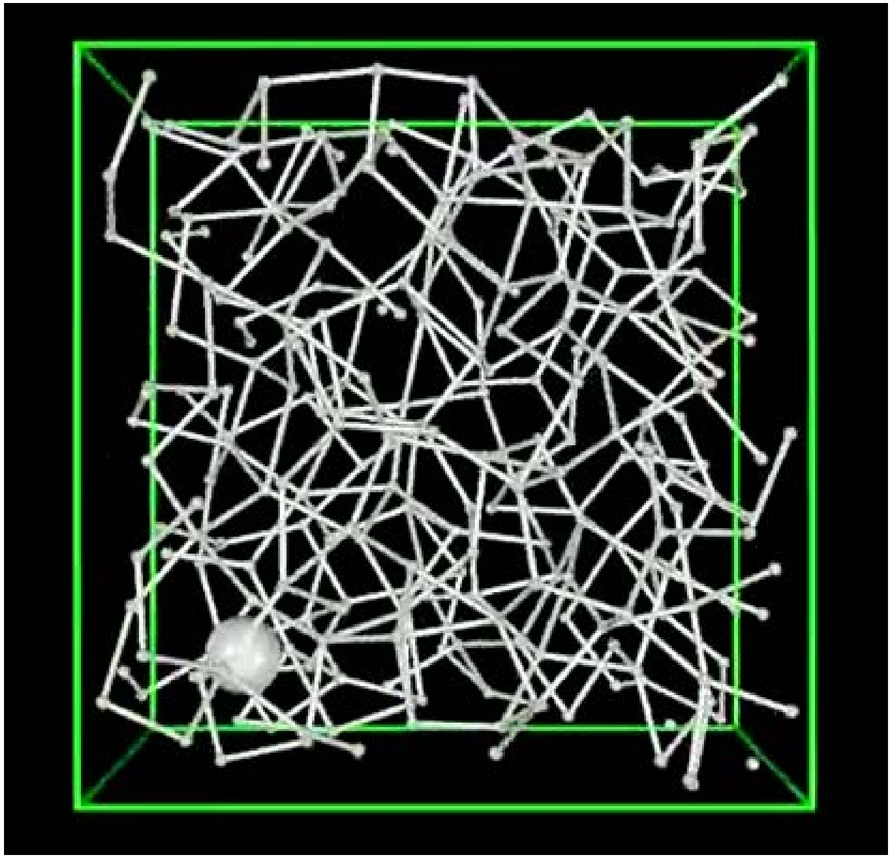


Abnormal mobility of protons

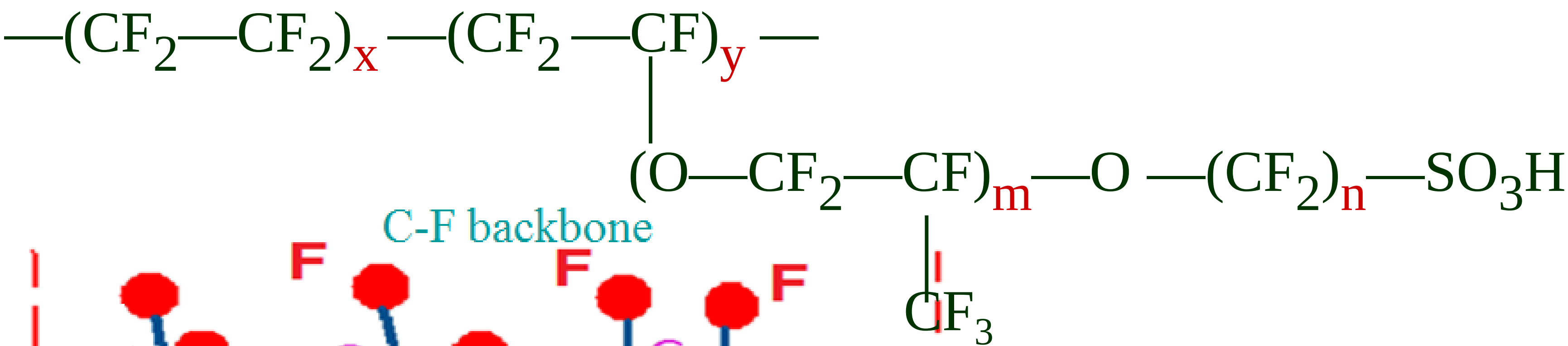
Grotthuss mechanism

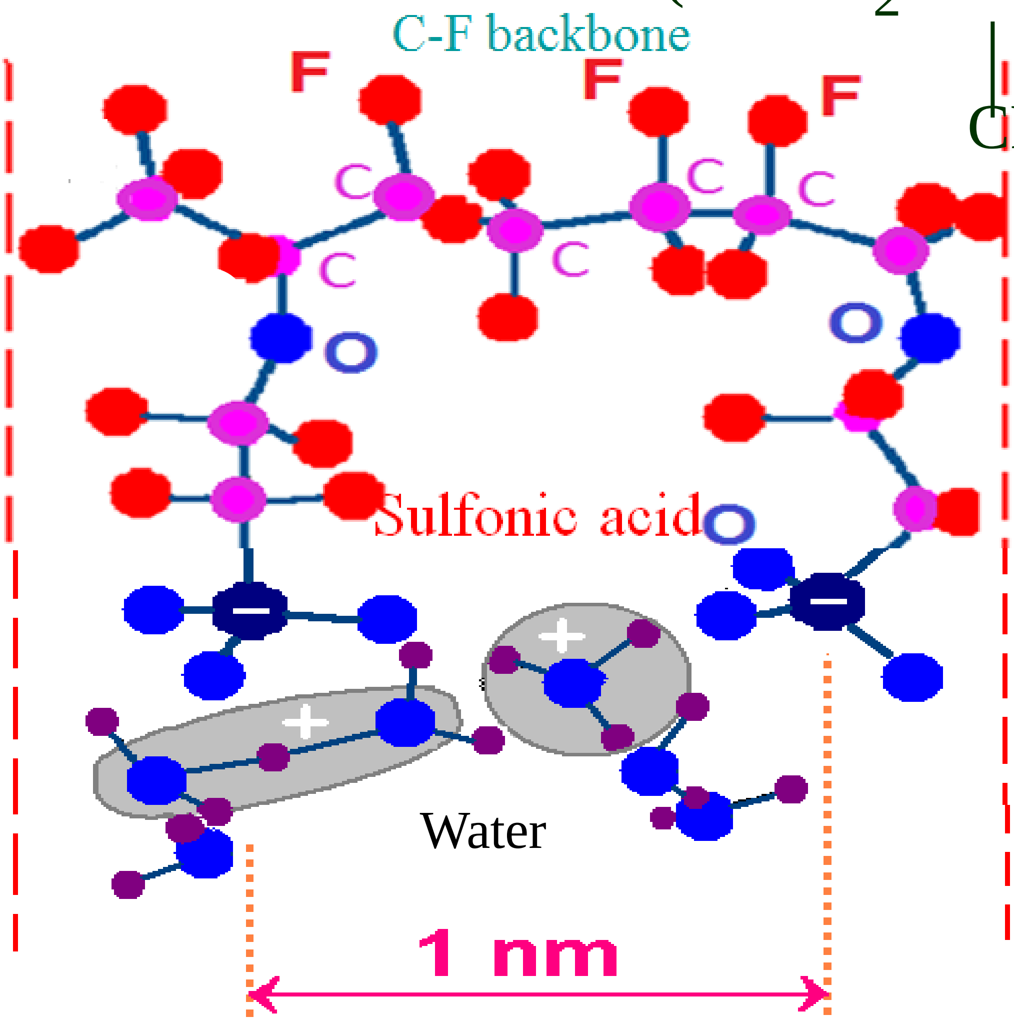
- protons hop from one site to another
- re-orientation of other molecules (structure diffusion)

Particles	Mobility $cm^2\ sec^{-1}\ V^{-1}$
Cation in water (e.g. K^+)	ca. 5×10^{-4}
Proton in water	ca. 36×10^{-4}
Cation in ice (e.g. Li^+)	<< 10^{-8}
Proton in ice	ca. 10^{-1}

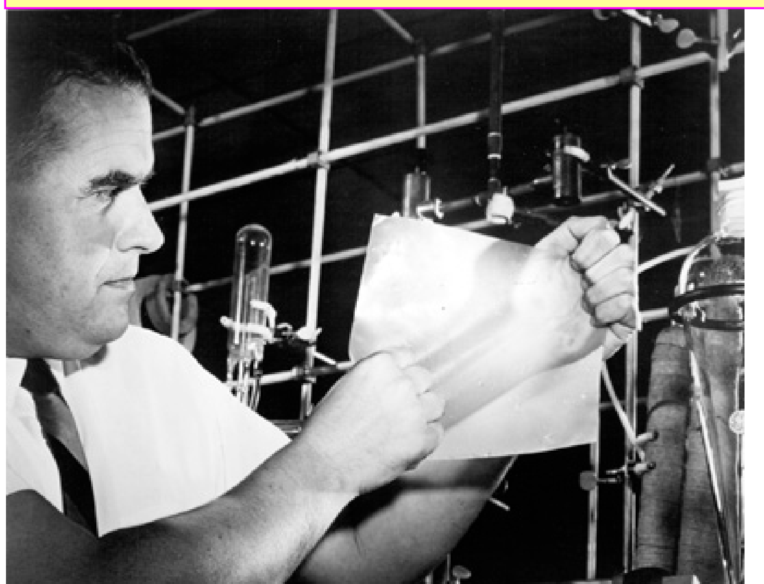


Perfluorinated sulfonic acids (PFSA membranes)





- High conductivity (0.1 S/cm)
- Mechanically strong & flexible
- Gas tight (low gas permeability)
- Long term durability



Hydrated PSFA membranes

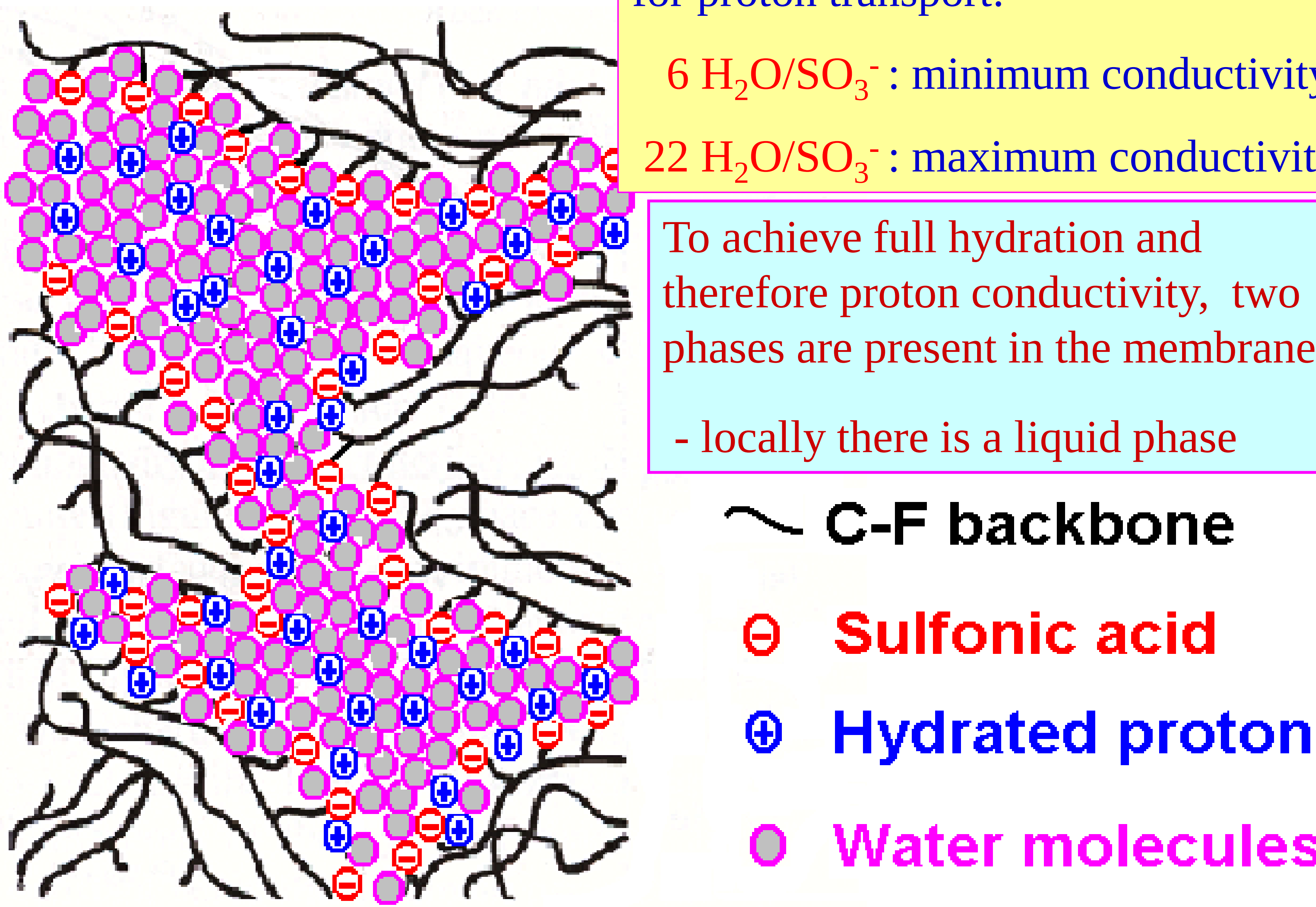
Water as bridges and vehicles for proton transport:

6 H_2O/SO_3^- : minimum conductivity

22 H_2O/SO_3^- : maximum conductivity

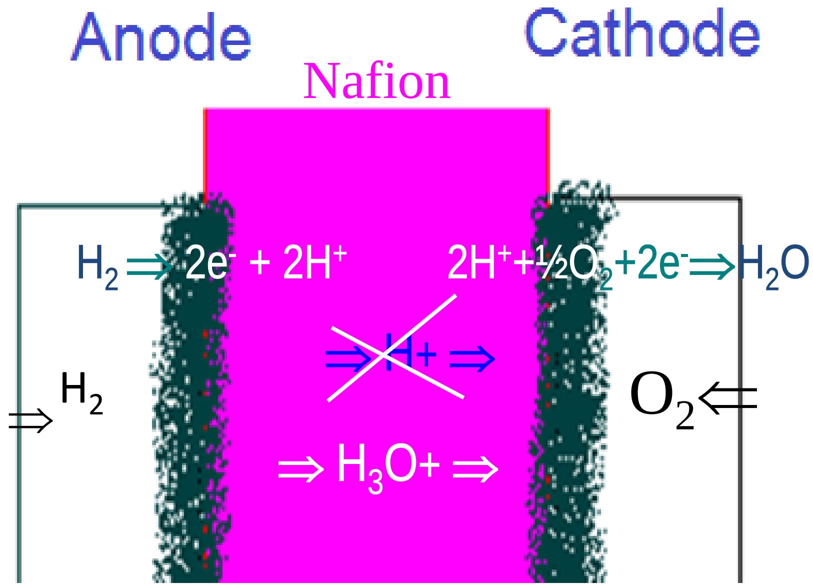
To achieve full hydration and therefore proton conductivity, two phases are present in the membrane

- locally there is a liquid phase



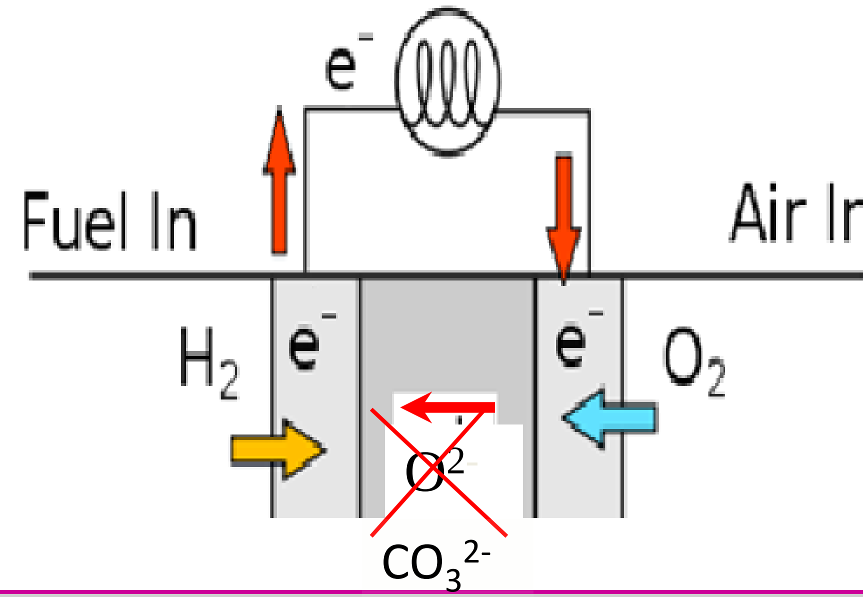
Vehicle mechanism of proton conductivity

- why it is of importance?



Similarity

- between SOFC and MCFC



H_3O^+ conducting electrolyte

Anodic: $H_2 + H_2O \rightarrow H_3O^+ + 2\ e^-$

Electrolyte: $H_3O^+_{(a)} \rightarrow H_3O^+_{(c)}$

Cathodic: $½O_2 + H_3O^+ + 2\ e^- \rightarrow 2\ H_2O$

Overall reaction: $H_2 + ½O_2 \rightarrow H_2O$

CO_3^{2-} conducting electrolyte

Anodic: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2\ e^-$

Electrolyte: $CO_3^{2-}{}_{(a)} \rightarrow CO_3^{2-}{}_{(c)}$

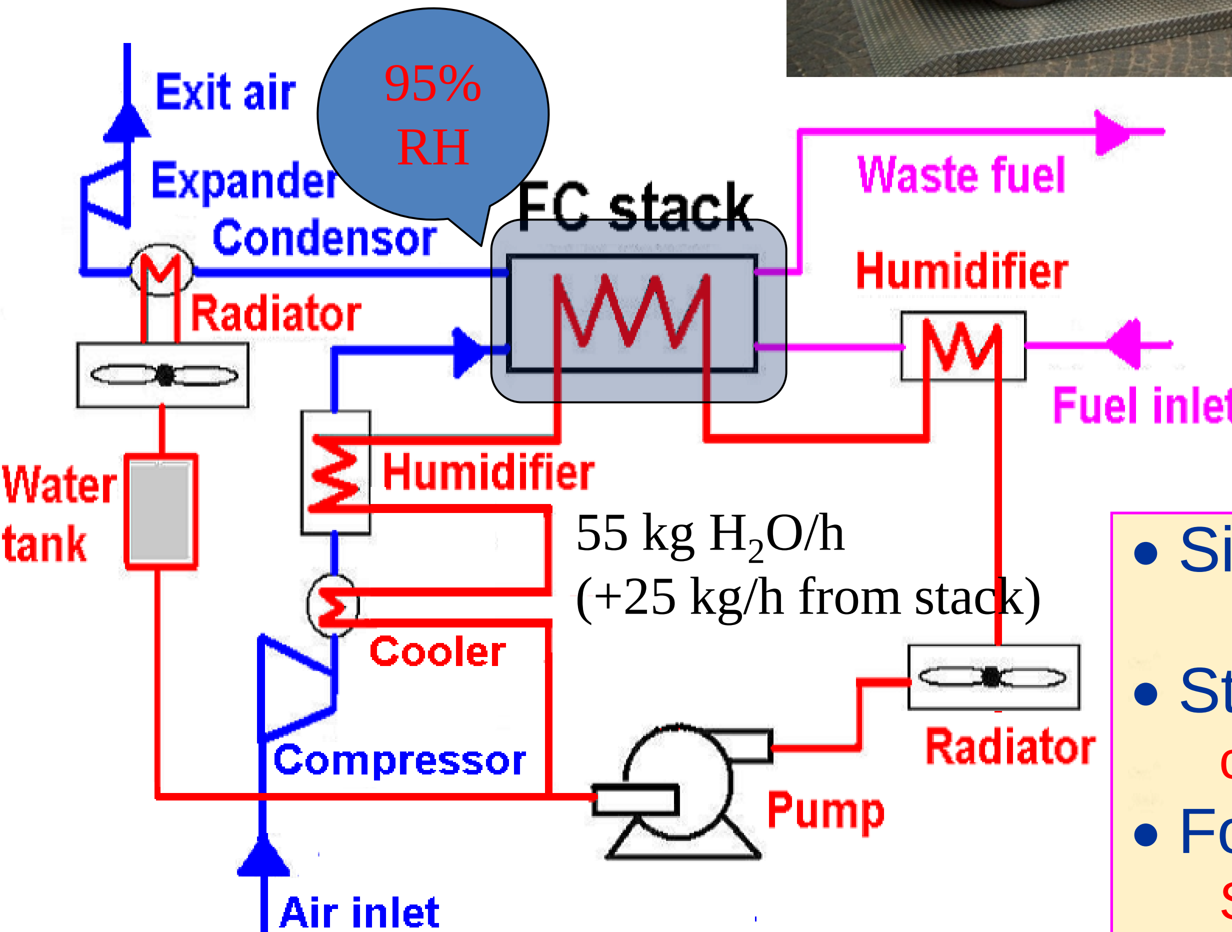
Cathode: $½O_2 + CO_2 + 2\ e^- \rightarrow CO_3^{2-}$

Overall reaction: $H_2 + ½O_2 \rightarrow H_2O$

Major system complexing due to water management

- humidification of fuel+air
- water condensation
- water storage + pumping

GM/Opel Fuel Cell Marathon
2004, 10,000 km
from Hammerfest to Lisbon



- Single cell performance
  > 1 W / cm²
- Stack performance
  ca. 1 kW/kg or 1 kW/liter
- For vehicle propulsion
  Small cars: ca. 50 kW
  A stack < 50 Kg and <100 L

More challenges associated with water

- Water management issues
- Secondary consequences

  - Temperature issue: LT/HT PEMFC

  - Fuel purity issue: CO cleanup for reformate H_2

  - Cooling issue: temperature gradient and radiator demand

  - Heat recovery: CHP and integrated fuel processors

- **DTU Research**
  - **- Proton conducting membranes via primary hopping mechanism**
  - **- Perspectives and future work**

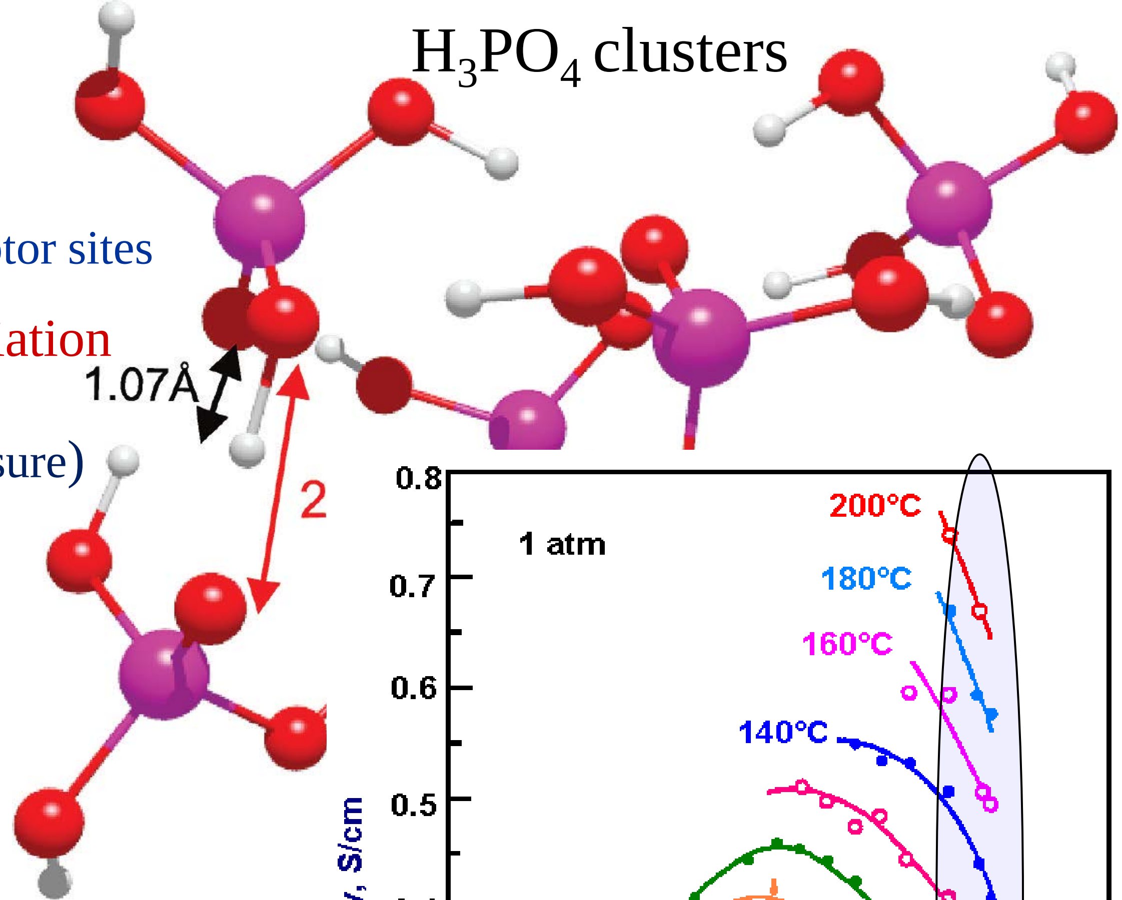
Phosphoric Acid

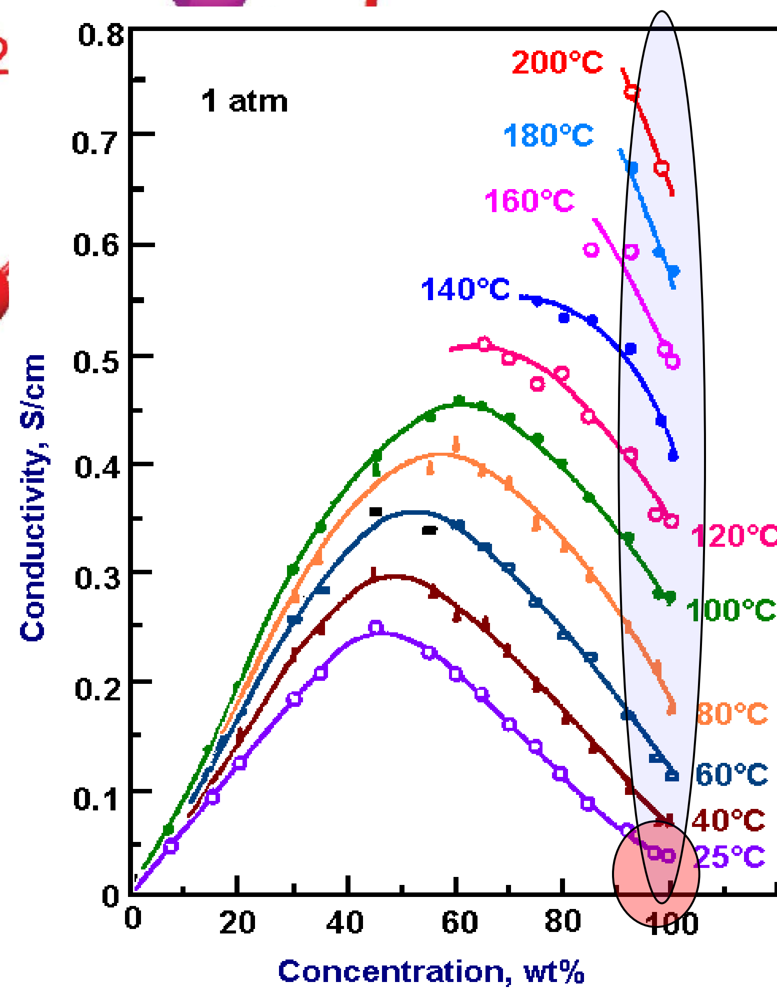
- H_3PO_4 molecules
  - three proton-donor and one acceptor sites
- Intermediate acidity, 7% dissociation
  - extensive H-bonds
  - (high viscosity & low vapor pressure)
- Hydrogen bond network:
  - Neighboring O---O: < 2.5 Å
  - O-H bond length: > 1.07 Å
- High proton conductivity
  - 98% by Grotthuss-type hopping
  - 2% by hydrodynamic diffusion of charged species
- Anhydrous conductivity
  - Charge carriers by self-dissociation

$$5\ H_3PO_4 = 2\ H_4PO_4^+ + H_3O^+ + H_2PO_4^- + H_2P_2O_7^{2-}$$

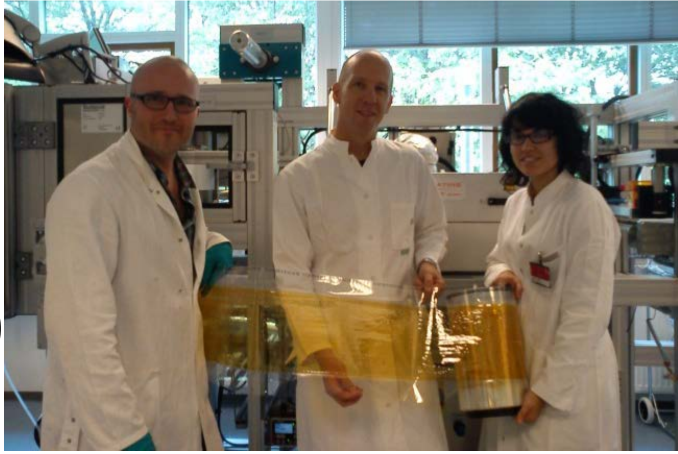
mol/l	16.815	0.890	0.461	0.429	0.461

H_3PO_4 clusters



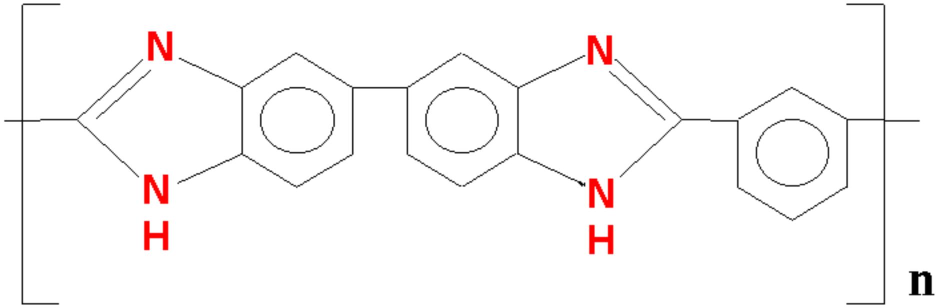


High Temperature Polymers



Polybenzimidazoles $T_G = 425\text{-}435°\ C$

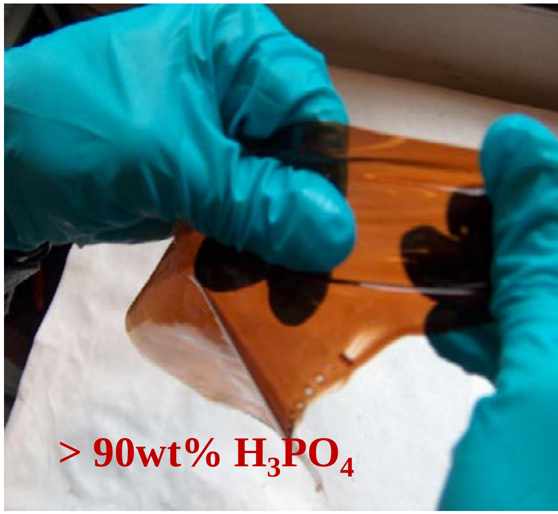
(Poly (2,2´-m-(phenylene)-5,5´´-bibenzimidazole (PBI))

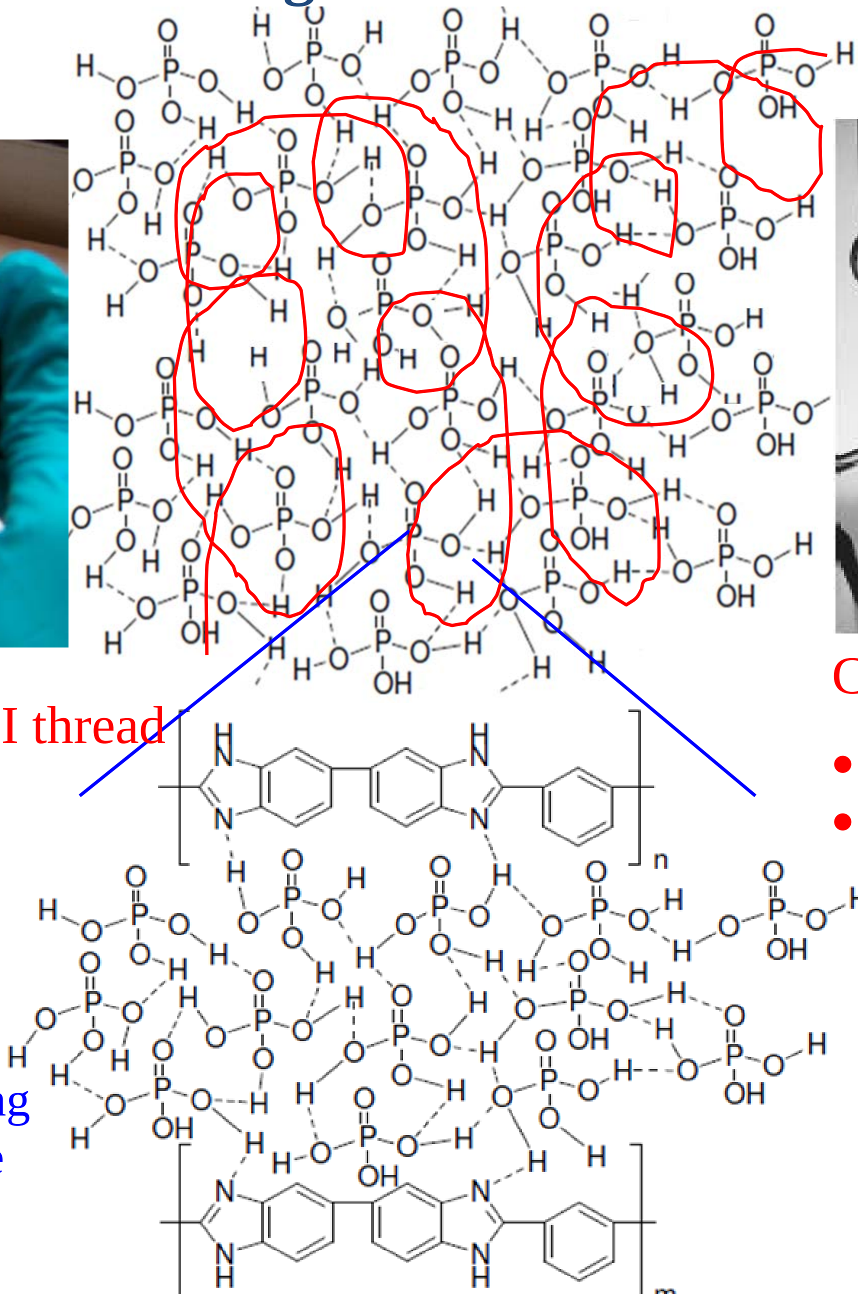


Applications

- As seals, insulator, valves ...
- As fibers for protective garments to astronauts, race-car drivers, fire-men...
- As films & membranes for reverse osmosis and ultra-filtration...
- Becoming conductive when ......

Acid doping
- more than immobilizing matrix





Concentrated H_3PO_4

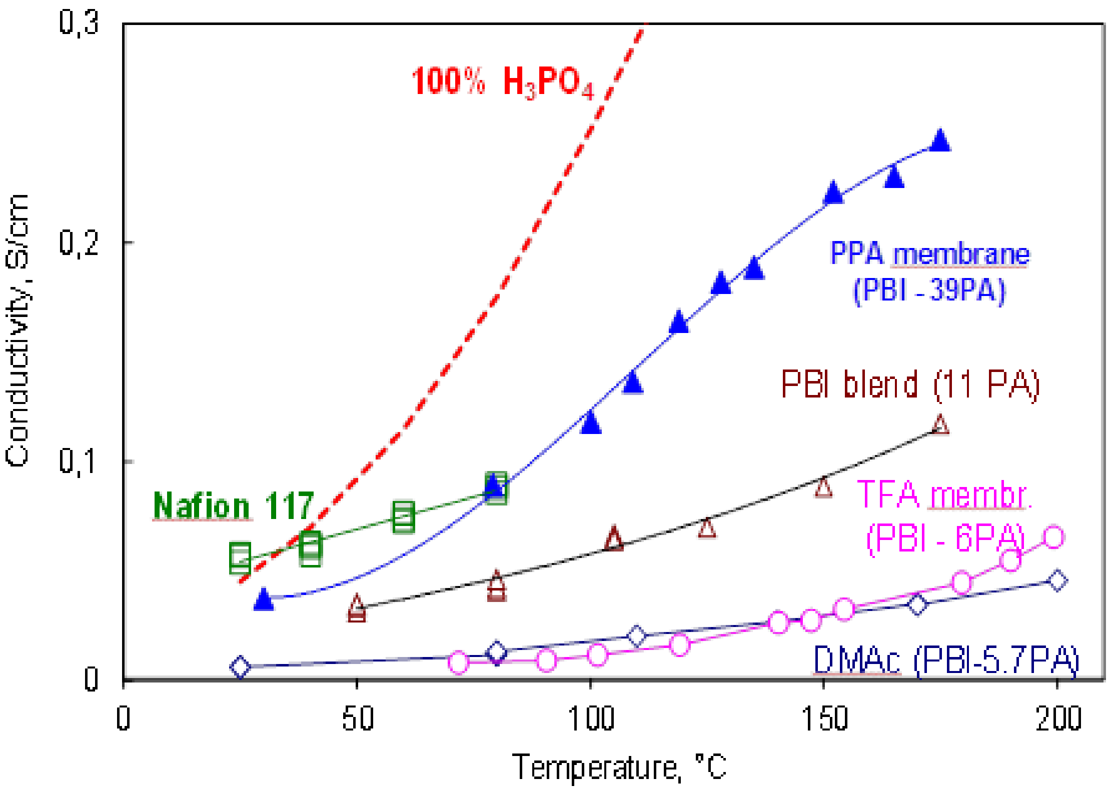
- Viscous yet flowing
- Extensive H-bond network
  - high surface tension
  - high dielelectric constant
  - nearly pure hopping
  - anhydrous conductivity

PA networked by PBI thread

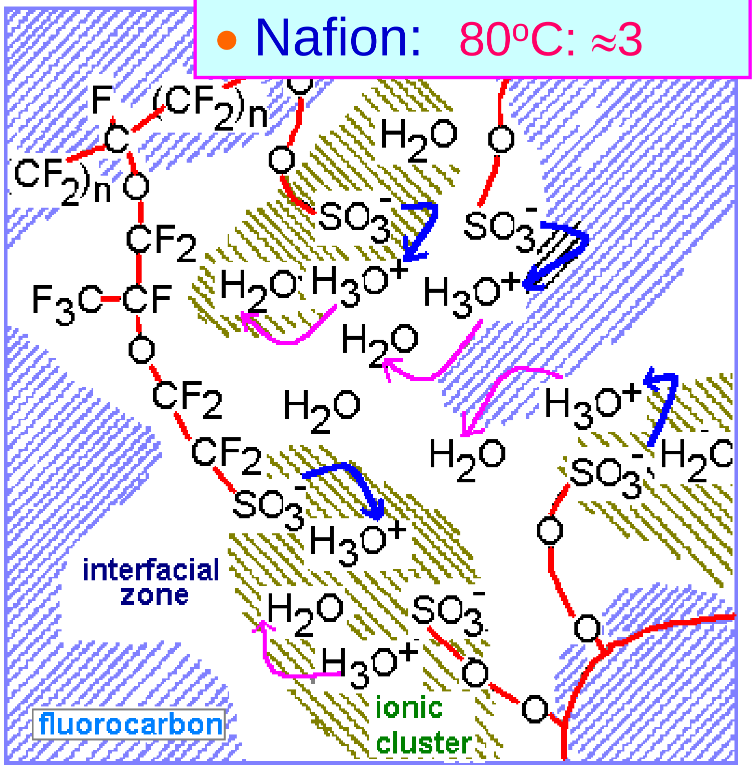
- PA/PBI = 20-40 (direct casting)
- PA/PBI = 10-12 (post doping)
- Self-standing & mechanically strong
- Essentially one phase

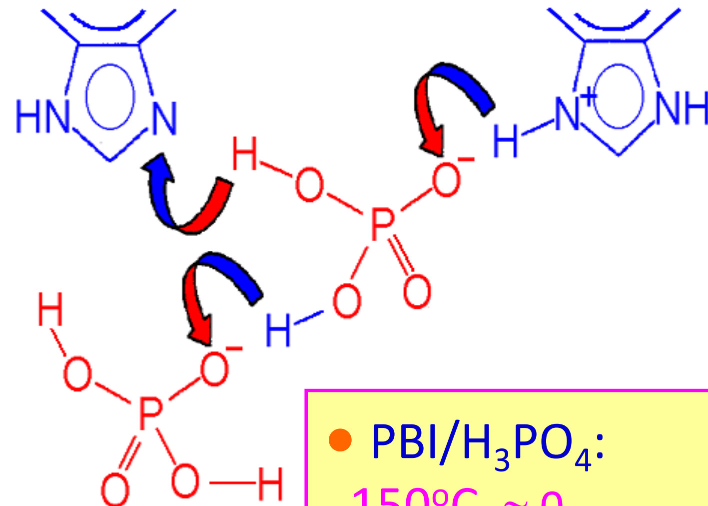
PBI-PA membranes

- Anhydrous conductivity
- Nearly zero water-osmotic drag coefficient
- 10-50% remaining conductivity
- Almost unchanged hopping mechanism



- Nafion: 80°C: ≈3

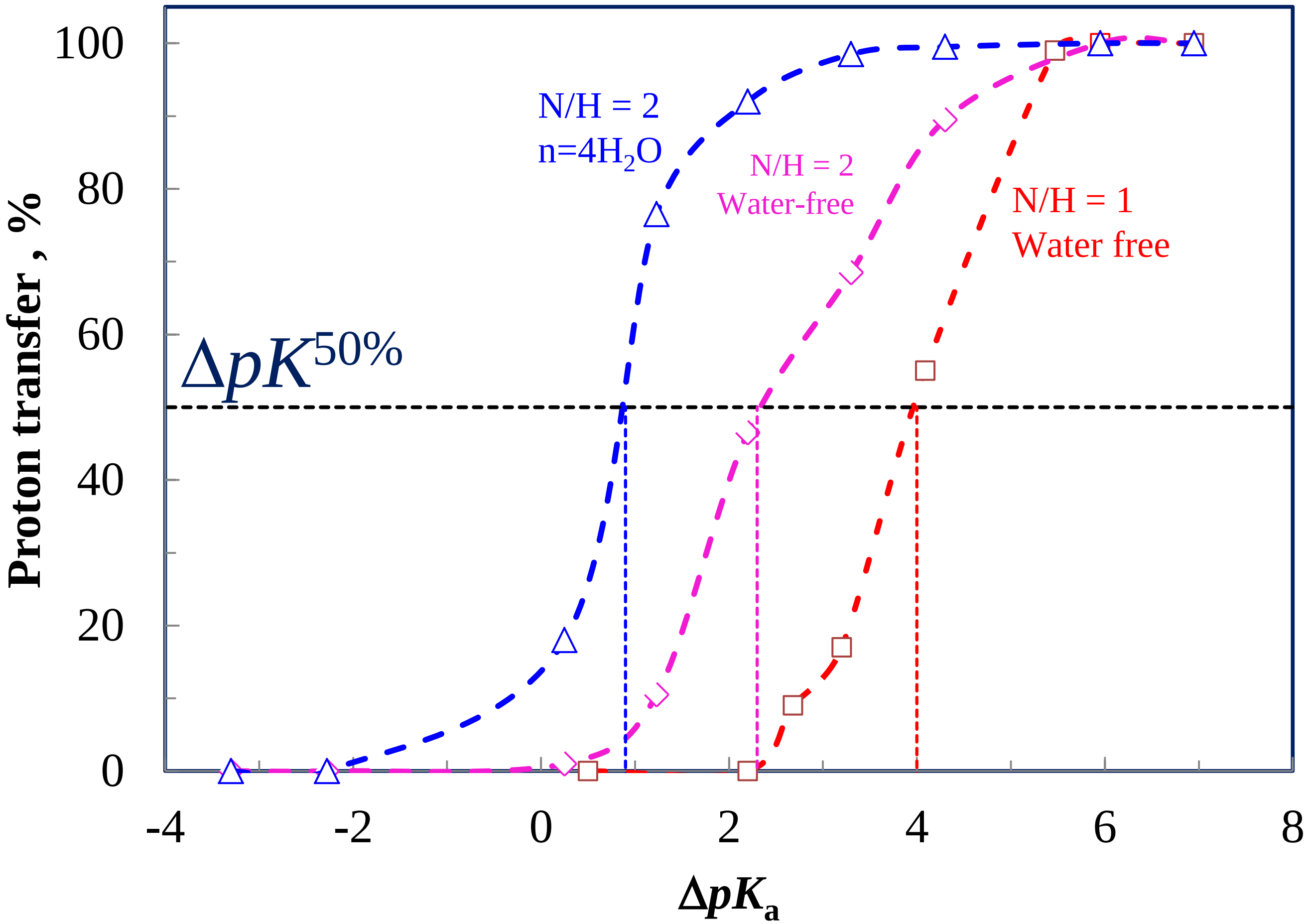




- PBI/H_3PO_4: 150°C, ≈ 0 (Li et al., 1998)

Why unchanged hopping mechanism

HA + B = BH$^+$ + A$^-$ $\Delta pK_a^{HA-B} = pK_a^{BH^+/B} - pK_a^{HA/A^-}$



Complete transfer
No H-bonding

Half-way proton transfer
Extensive H-bonding

No proton transfer
No H-bonding

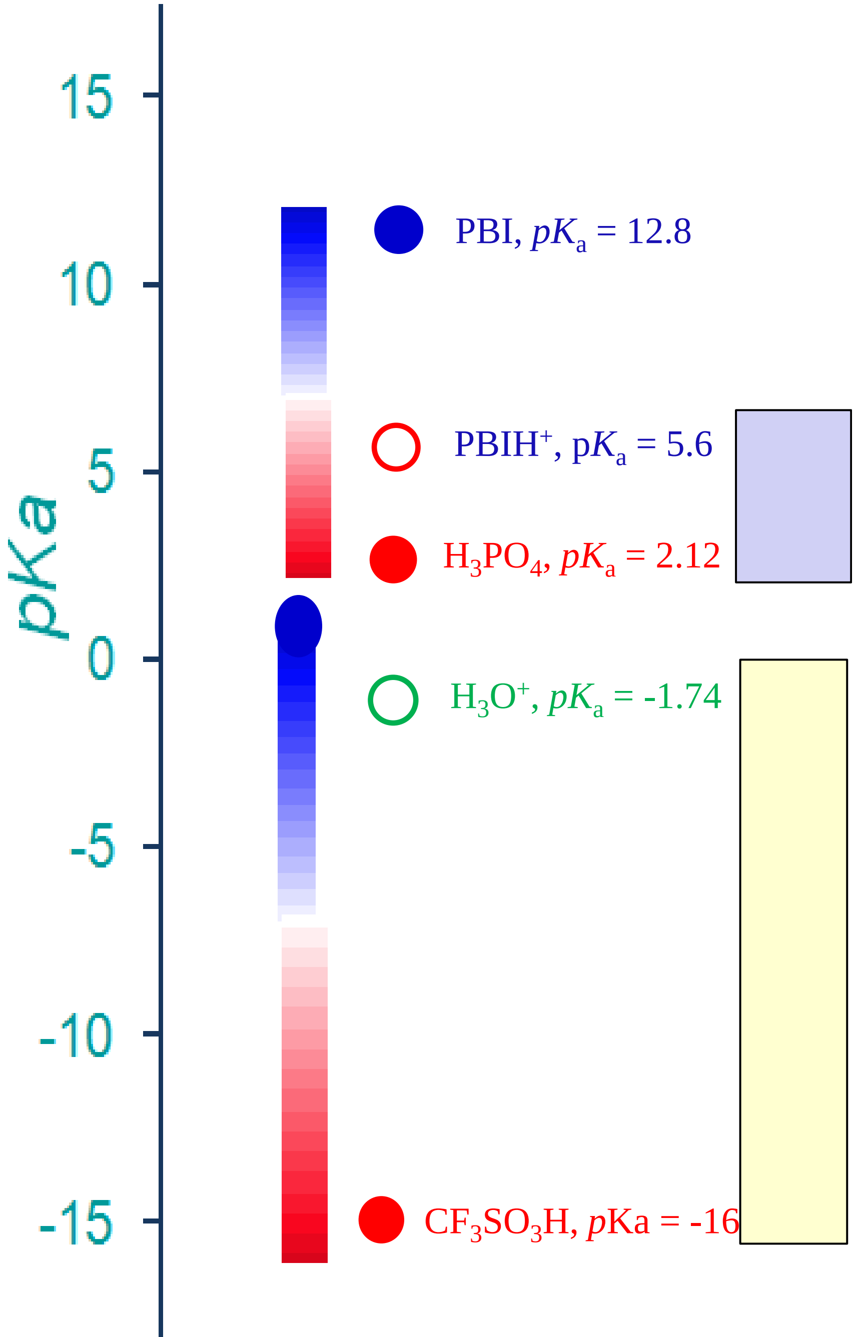
Zundel (2000), University of Munich

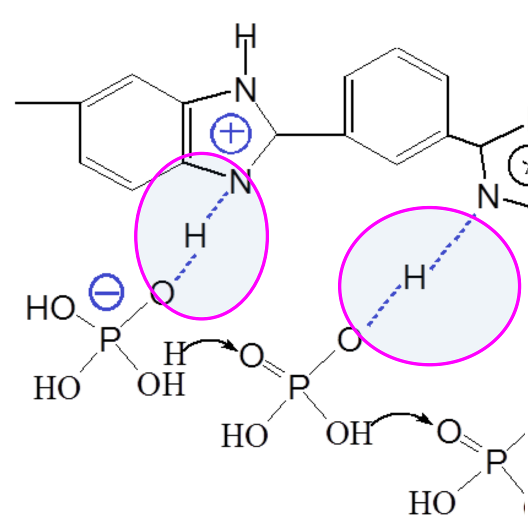
For carboxylic acids and N-bases: OH···N ↔ O$^-$…H$^+$N

MacFarlane et al. 2012

Acid-base chemistry

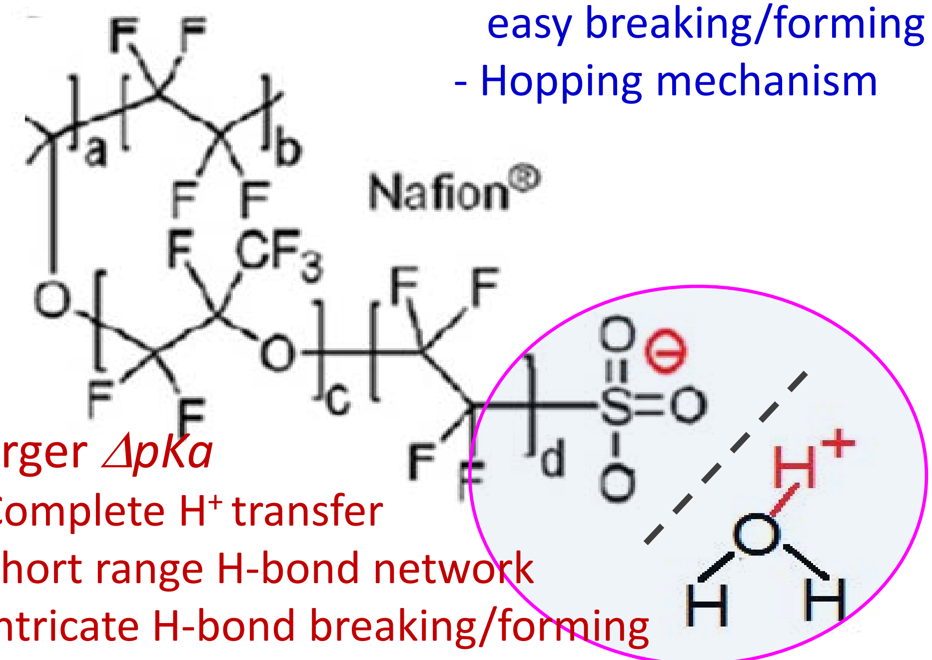
$$PBI + H_3PO_4 \leftrightarrow PBIH^+ + H_2PO_4^-$$





Intermediate *ΔpKa*

- Incomplete H^+ transfer
- H-bond network
- Mild strength of H-bond easy breaking/forming
- Hopping mechanism



Larger *ΔpKa*

- Complete H^+ transfer
- Short range H-bond network
- Intricate H-bond breaking/forming
- Vehicle mechanism of mobile H_3O^+

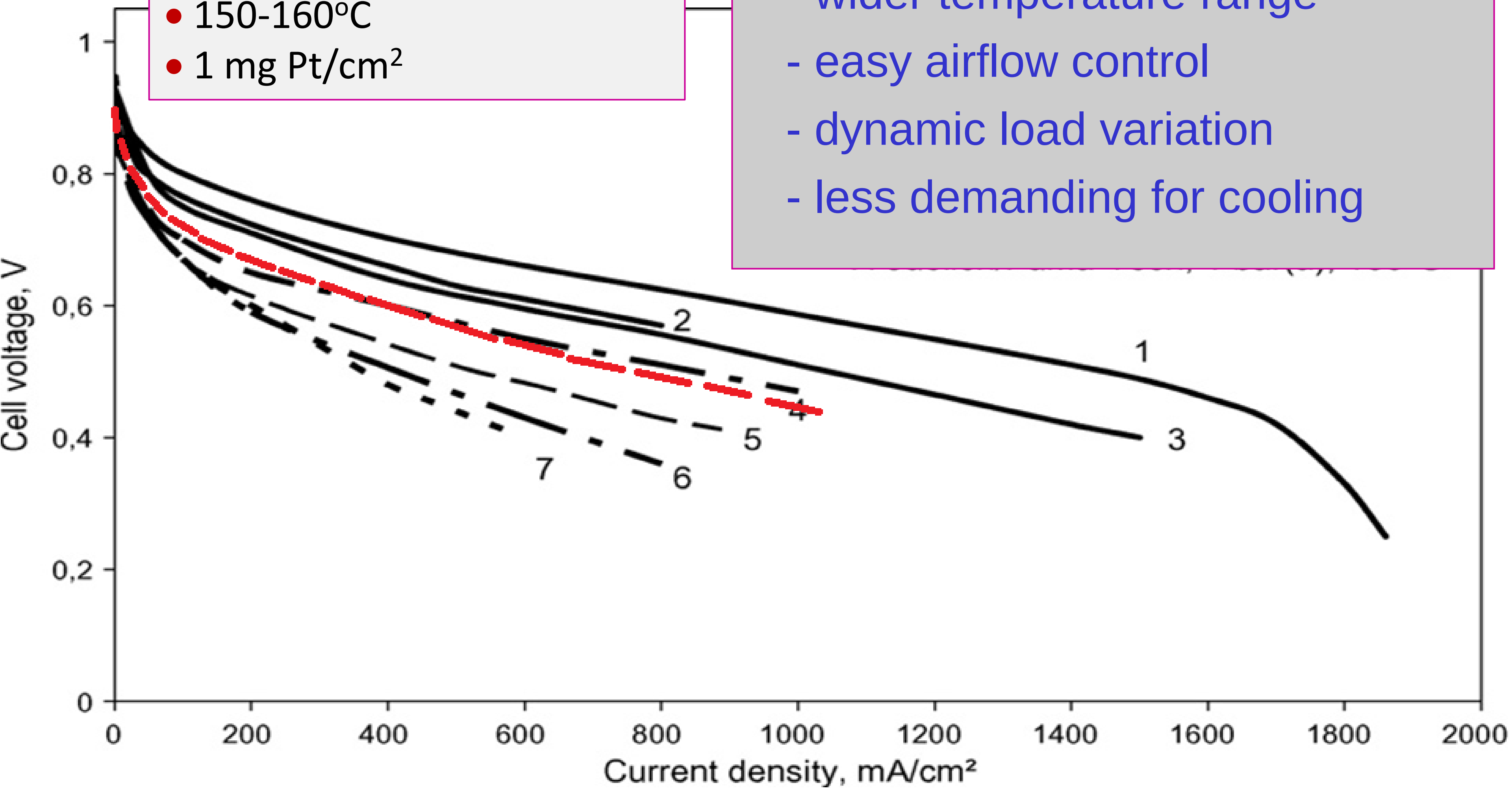
PBI cell performance

Typical performance

- 200 mA/cm^2 at 0.65-0.67 V
- H_2-Air, ambient pressure
  λ_{H2} = 1.2; λ_{Air}=2.0
- 150-160°C
- 1 mg Pt/cm^2

Operational features of PBI cells

- **No humidification**
  - dry hydrogen & air
- **Wide temp. range** (130-210°C)
  - wider temperature range
  - easy airflow control
  - dynamic load variation
  - less demanding for cooling



Status and Challenges

Further challenges

- Membranes
  - Proton generative functionalities
  - Acid-base chemistry vs. protonics
  - Immobilization of doping acids
  - Durability orientated efforts
- ORR kinetics
  - Acid anion adsorption
- Catalysts and electrodes
  - Activity: Low loading Pt
  - Stability: Support and synergies
  - Non-precious metal catalysts
  - Electrode engineering
- Fuelling strategies and its impact on lifetime
- Construction materials and stack engineering

Status - DPS datasheet

Membrane and MEA Performance

Acid doped membranes with excellent chemical, thermal and mechanical stability. High proton conductivity at 140-200 °C and nearly zero water drag:

- Temperature of operation up to 200 °C
- No humidification required
- Very high CO tolerance above 150 °C

MEA lifetime and durability:

> 8,000 hours by continuous operation

> 140 start-up cycles during 7,000 hours

http://daposy.com/pdf/DPS-Dapozol-ENG-okt13.pdf

HT-PEM in Denmark

4M Centre
Machanisms
Materials
Manufacturing
Management

GDL
Polymer
Catalyst
Bipolar plates
Sealing materials

Red. kinetics
Ox.kinetics

Cathode
Membrane
Anode

Fuel Cell modeling

MEA

Stack

System simulation
integration strategies

Integration

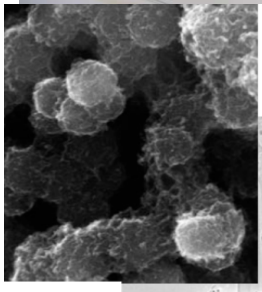
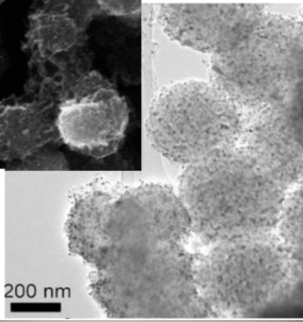
ystem

Stationary system

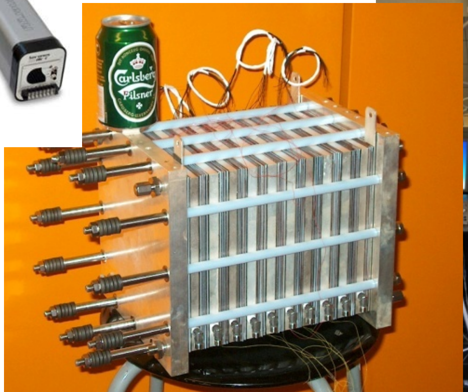
Applications

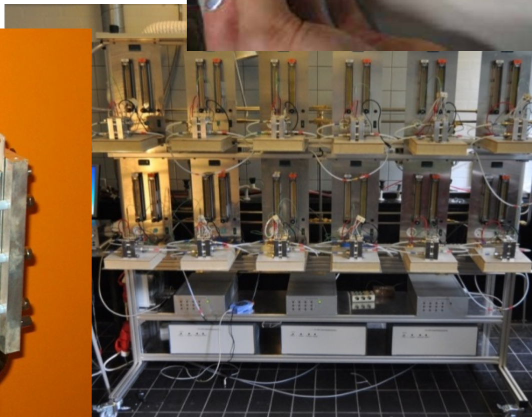
DTU – Proton conductors, Catalysts
KU – Catalysts
SDU – Components
DPS – Polym. Membr. MEA.

AAU – model & simulation
Serenergy – stack & modules
IRD – MEA, Stack, system



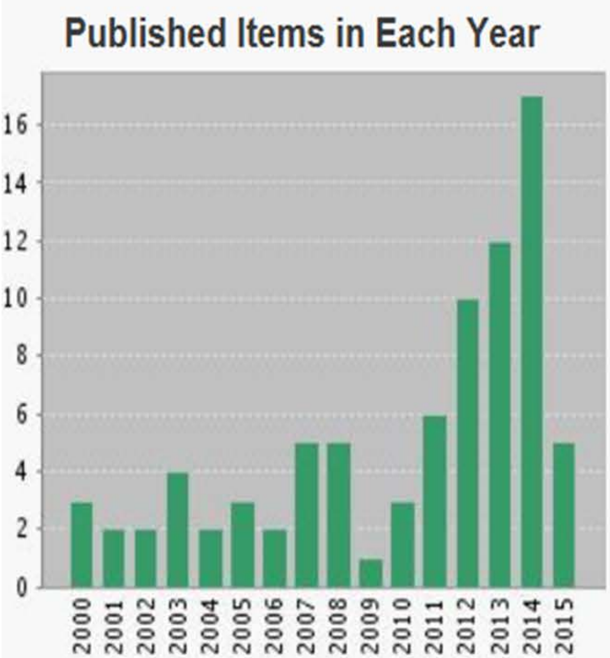


The group contribution to the subject

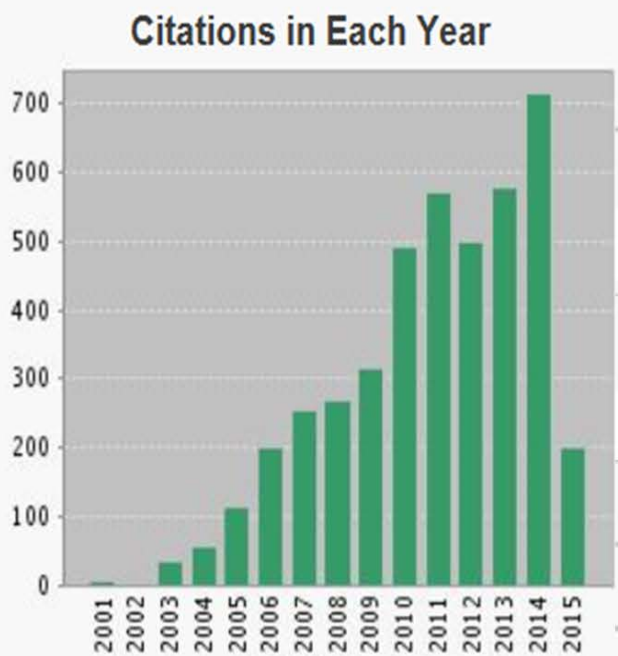
Proton Conductors and FC/EC Applications

- **Polymer chemistry**
- **Acid doping**
- **Membrane degradation**
- **Phosphates**
- **Catalysts**
- **Electrodes**
- **Fuel & electrolyser cells**
- **Durability**

Citation report: 82
You searched for: Proton conductor, fuel cell, PBI, phosphoric acid, phosphate, cayalysts, etc.
Group authors
Address: Lyngby



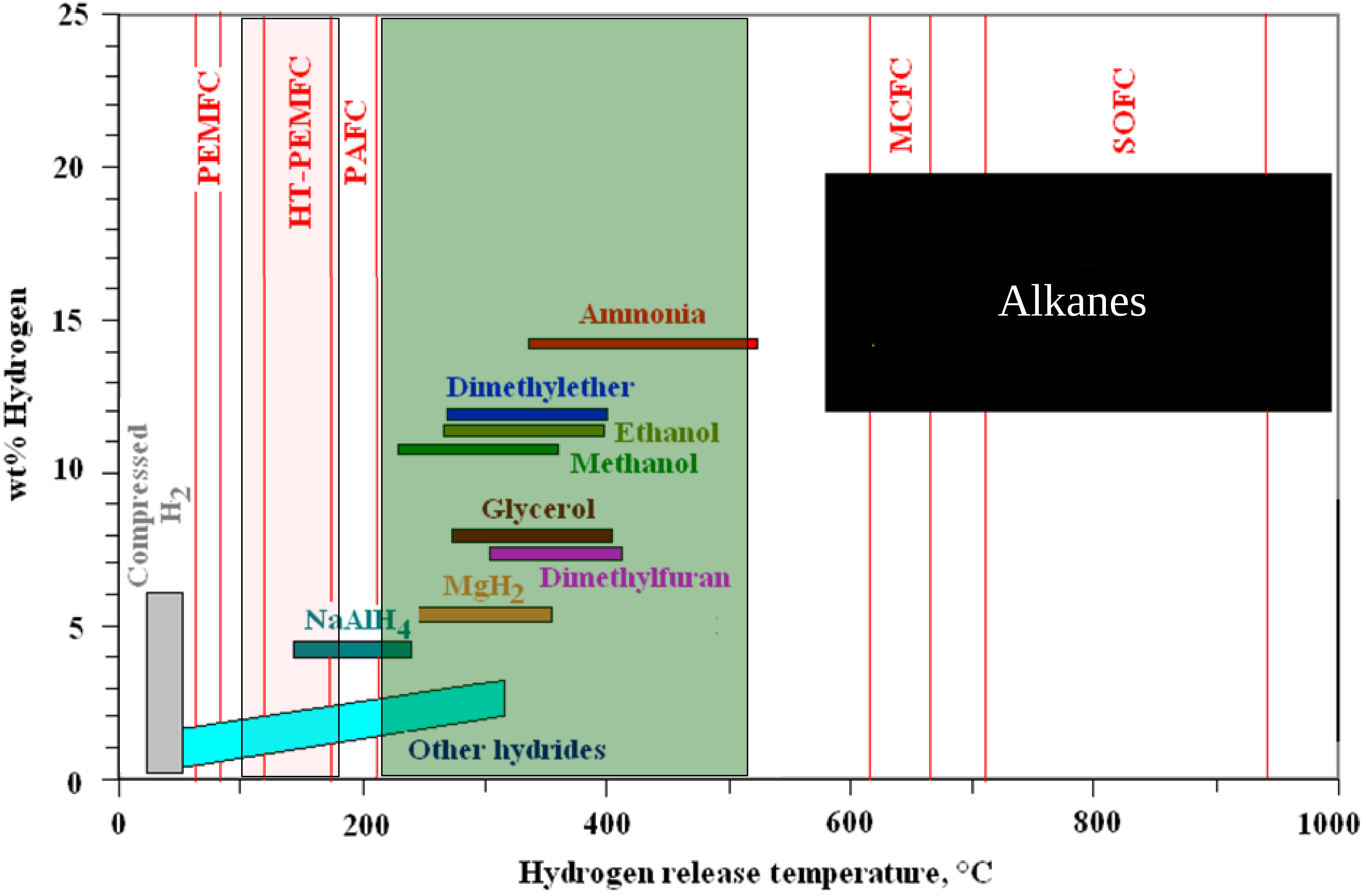
The latest 20 years are displayed.



The latest 20 years are displayed.

Results found: 82
Sum of the Times Cited [?] : 4305
Sum without self-citations [?] : 3875
Citing Articles [?] : 2413
Citings without self-citations [?] : 2345
Average Citations per Item [?] : 52.50
h-index [?] : 25

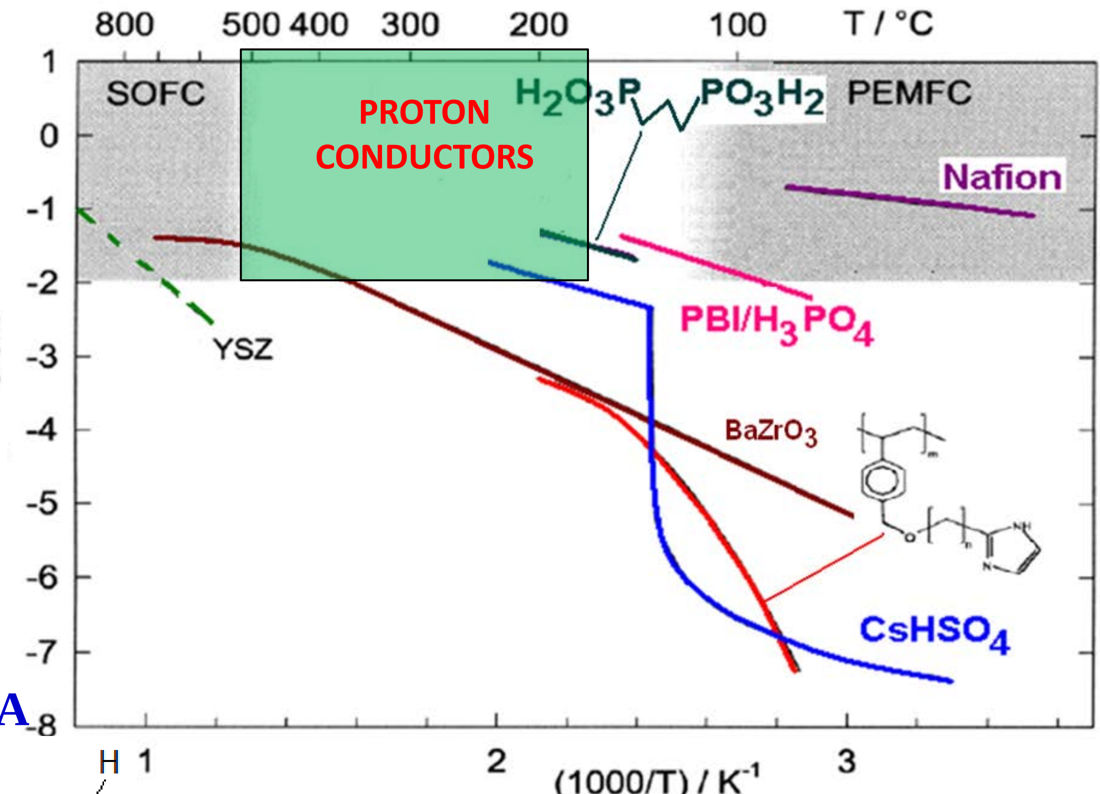
Approaching intermediate temperatures



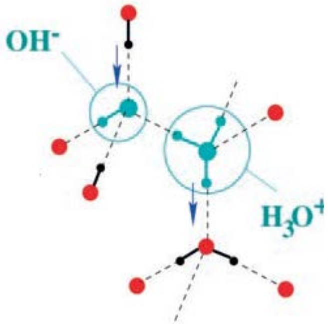
Proton conductors

to fill up the temperature gap

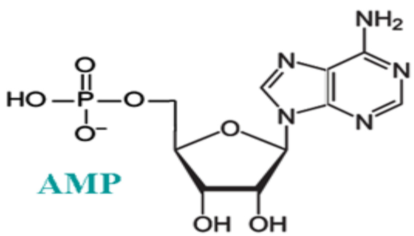
Kreuer et al. Chem. Rev. 2004, 104, 4637

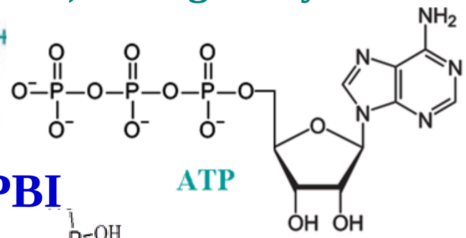


a) Aqueous solutions

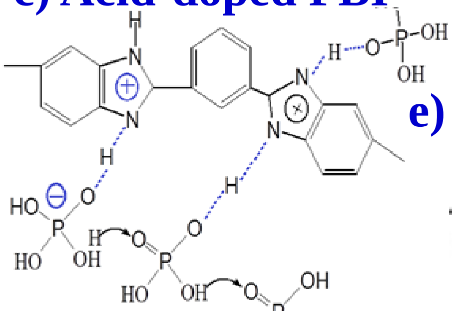


d) Biological systems

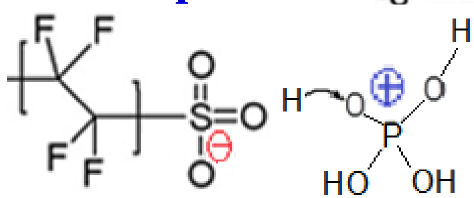




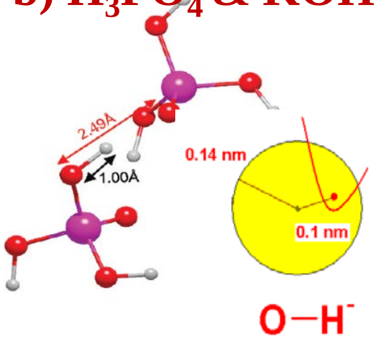
c) Acid-doped PBI

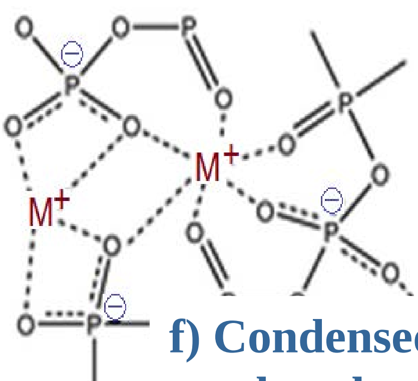


e) Acid-doped PFSA

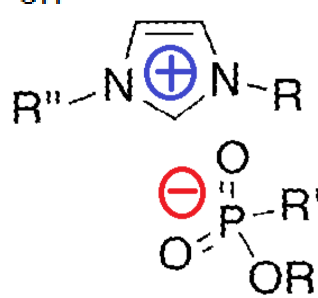


b) H_3PO_4 & KOH





f) Condensed phosphates



g) Protic ionic liquids and protic plastics

Research of interest

- acid-base chemistry versus proton conductivity
- polymer & membranes
- condensed phosphates

Summary

- **Fuel cells**

  An electrochemical device for energy conversion
  of high efficiency and less emission

- **Many material challenges**

  Proton conductors
  - Vehicle and hopping mechanisms
  - Water as a proton vehicle
    - management and system complexation
    - temperature limitation and secondary effects

- **DTU research**

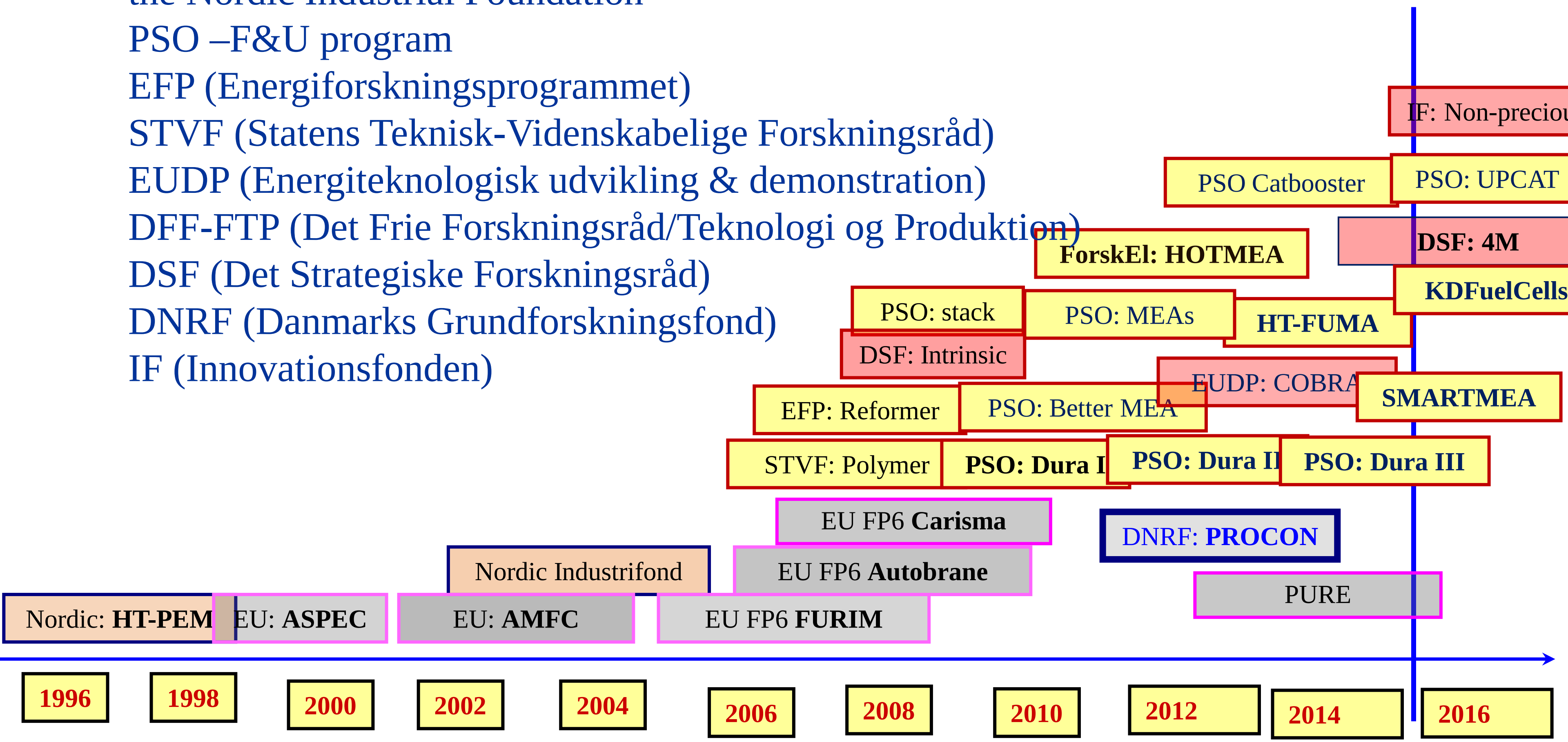
  Proton conductors of primarily hopping mechanism
  - allowing for higher temperatures
  - no humidification
  - other potential system simplification

  Further work
  - improvement of performance and durability
  - fundamental understanding
  - approaching intermediate temperatures

Acknowledgements

- **Financial support**

  the Nordic Energy Research Programme
  the European Commission, the **4th – 7th** framework Programmes
  the Nordic Industrial Foundation
  PSO –F&U program
  EFP (Energiforskningsprogrammet)
  STVF (Statens Teknisk-Videnskabelige Forskningsråd)
  EUDP (Energiteknologisk udvikling & demonstration)
  DFF-FTP (Det Frie Forskningsråd/Teknologi og Produktion)
  DSF (Det Strategiske Forskningsråd)
  DNRF (Danmarks Grundforskningsfond)
  IF (Innovationsfonden)



Acknowledgements

- All members, previous and present, in this picture or behind, Section of Proton Conductors
- Colleagues in Risø campus

- Danish Power Systems ApS
  Hans Aage Hjuler, Thomas Steenberg, Carina Terkelsen
- DTU Chemistry
  Jens Ulstrup, Rolf W. Berg; Jingdong Zhang; Qijin Chi,
- IRD Fuel Cells ApS
  Laila Grahl-Madsen, Mikkel Juul Larsen, Steen Yde …
- Tatanline A/S, Søren Eriksen

The way of my research career was paved by the continuous guidance, encouragement and support from Professor Niels J. Bjerrum. Through this long period of time we have had, with active participation of Dr. Hans Aage Hjuler, hundreds of technically orientated meetings, most of which took place in the long Thursday evenings in professor Bjerrum´s office. I highly appreciate these discourses, which sometimes lasted hours long with many detours and also unexpected outcomes. It has been my privilege, through these informal discussions, to learn the scientific discipline and technical expertise from professor Bjerrum and Dr. Hjuler, to whom my special thanks are first extended.

Q. LI

High Temperature PEMFC

2005

Qingfeng Li

High Temperature Proton Exchange Membranes For Fuel Cells