NPRE 498ES: Energy Storage Systems

Term Presentation

Micro/nanofluidic fuel cells

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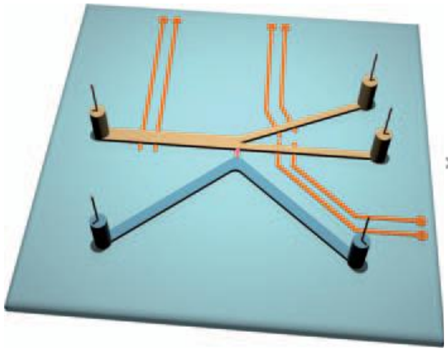
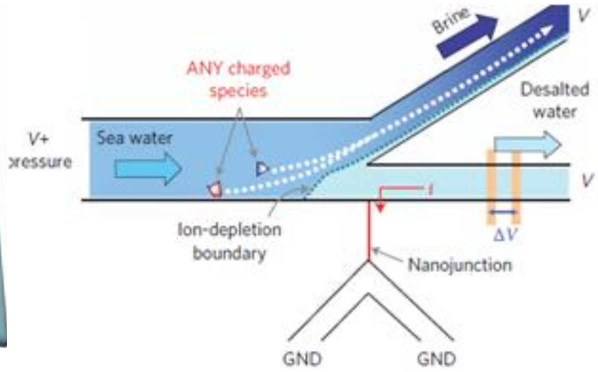
OUTLINE

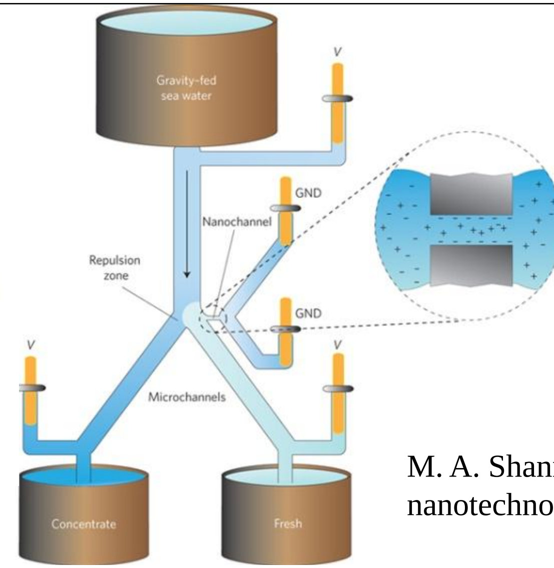
- Introduction
- Micro/nanofluidic fuel cell
  - Fabrication techniques
  - Fuel cell membrane characteristics
  - Performance
  - Merits and Demerits
- Conclusions

Micro/Nanofluidic membranes

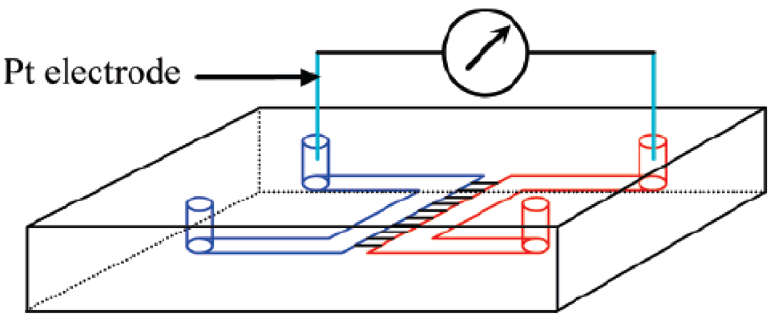


S. J. Kim, J. Han, Nature nanotechnology, vol 5,2010.

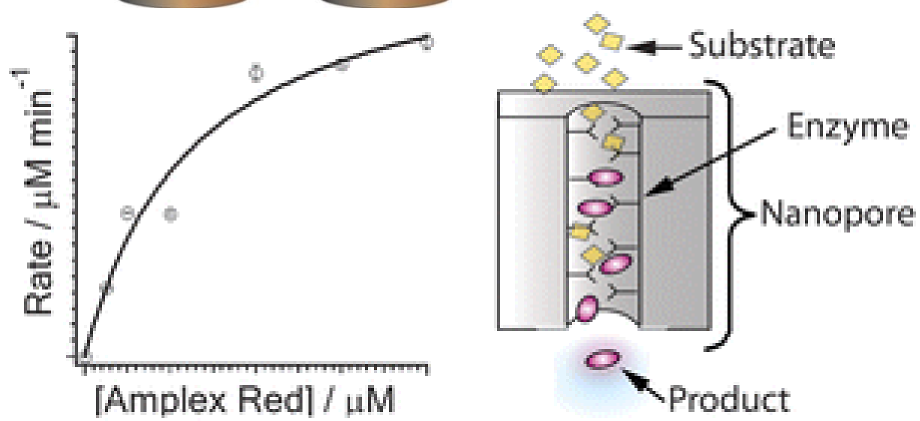




M. A. Shannon, Nature nanotechnology, vol 5,2010.



Shaorong Liu, Carolyn Matzke et al, Nano Lett. 2005, 5, 1389-1393.



Zhen Wang, Paul W. Bohn et al, ***Analyst***, 2009, **134**, 851-859

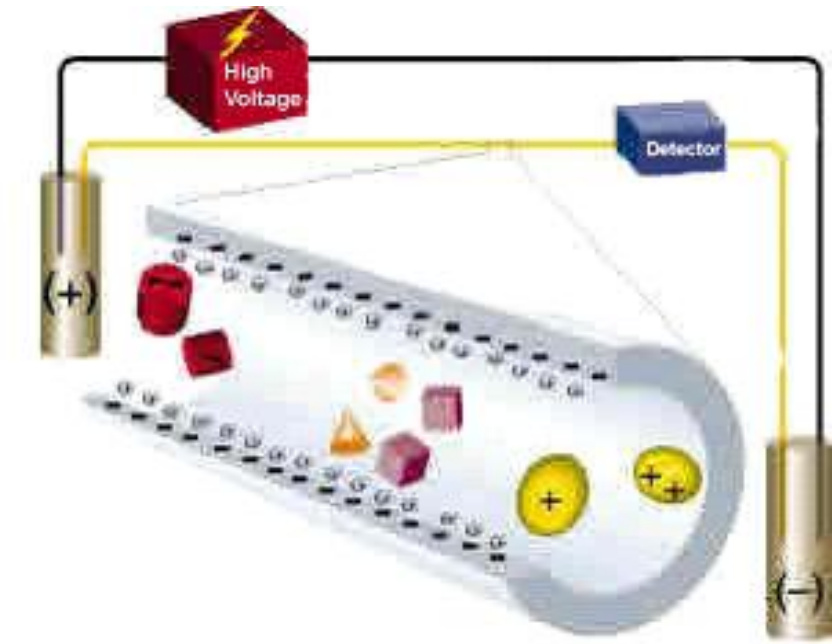
- Size → **1 – 100 nm**
- Flow Induced → **Electric Voltage** → ***Electroosmosis***, ***Electrophoresis***
- Pressure Induced Flow (Desirable) → **NO**

Change in Pressure (ΔP) ~ 1/H³. Hence, high pressure/ power is required to drive flow at low channel diameters.

Electroosmotic flow

- ***Electro osmosis is the bulk flow of liquid due to the effect of the electric field on cations/anions adjacent to the negatively/positively charged capillary wall.***

(a)



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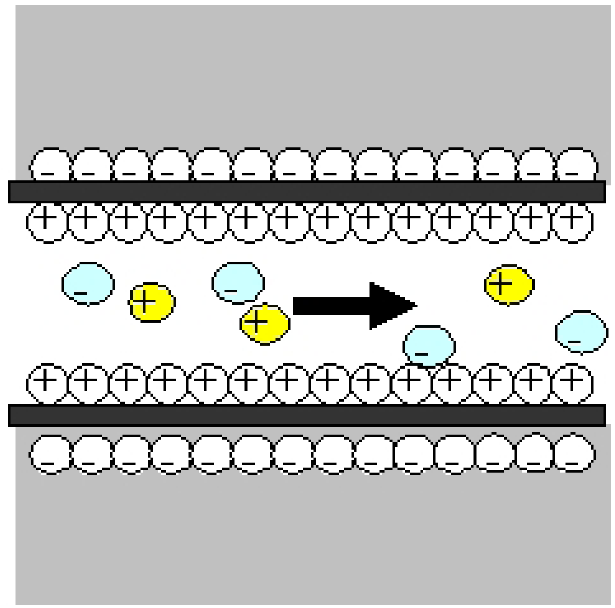

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(b)

(a) Ref: Picasso et al. 2006. “Numerical Simulation of electroosmotic flow through micro – channel using adaptive finite elements”
(b) Ref: “Numerical Simulation of Electrokinetically driven micro flows” – PhD Dissertation of Jungyoon Hahm

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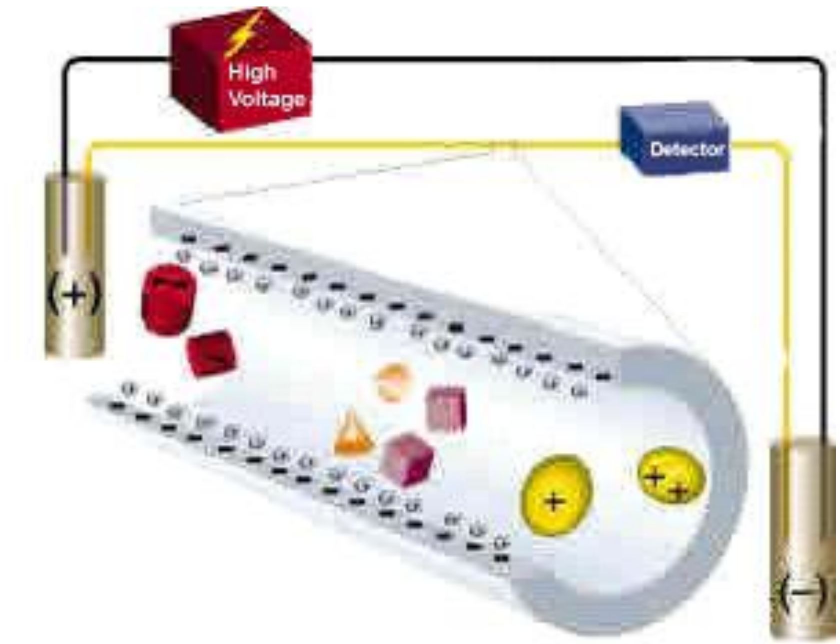

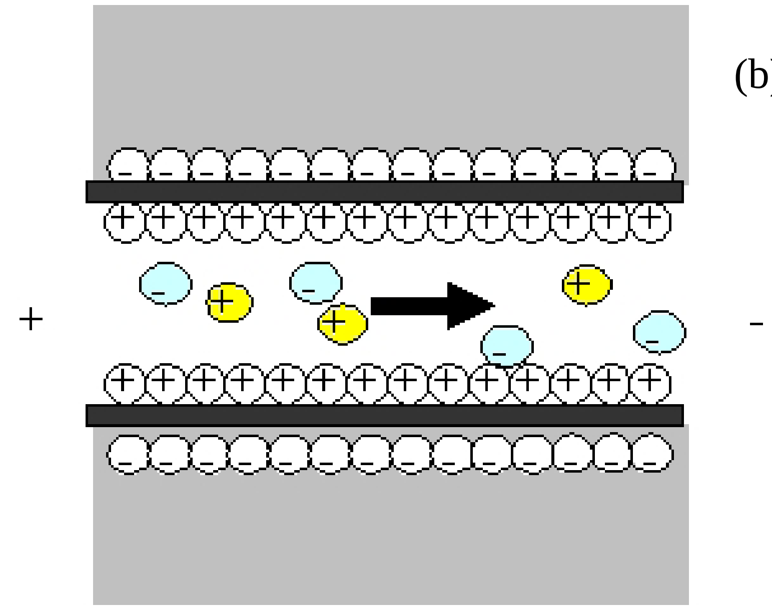

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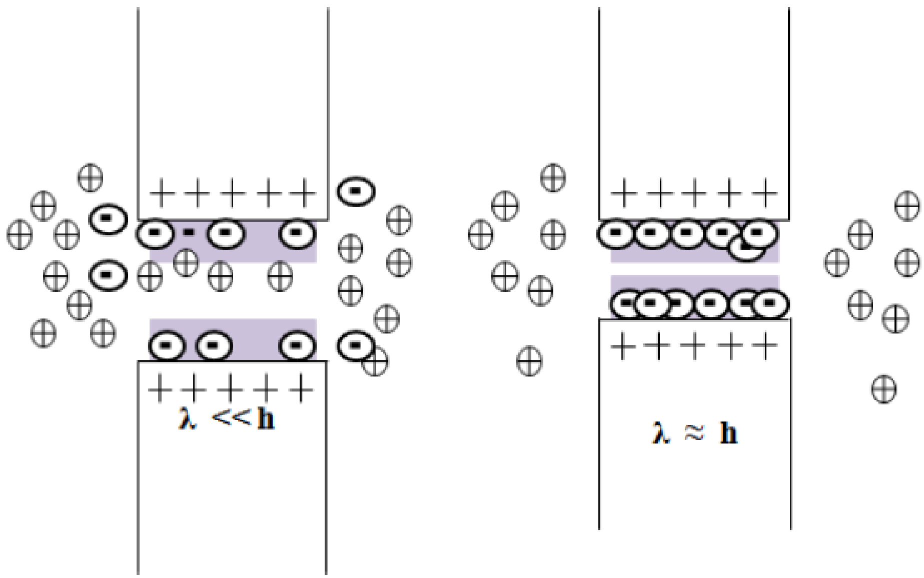
Low Re - Flow is Laminar

Electric Double Layer (EDL) / Debye Length (λ)



Debye – length (λ)

$$\lambda = \sqrt{\frac{\varepsilon \varepsilon_0 k_b T}{e^2 \sum_i c_i z_i^2}}$$

where

c_i - Bulk concentration of each ionic species

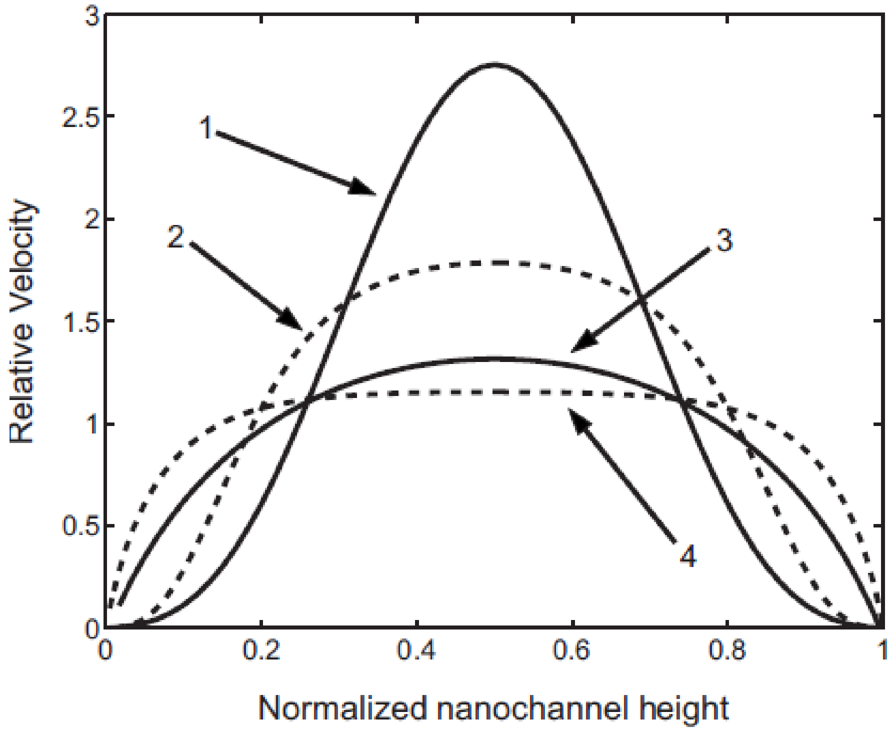
z_i - Ionic valence

k_b - Boltzmann constant

T - Temperature

- ❑As channel height decreases the Debye length or EDL overlaps.
- ❑As EDL overlap, the channel becomes ion – selective resulting in a higher concentration of counter – ions inside the nanochannel.
- ❑EDL increases with decrease in the concentration of the bulk species.

Fluid flow

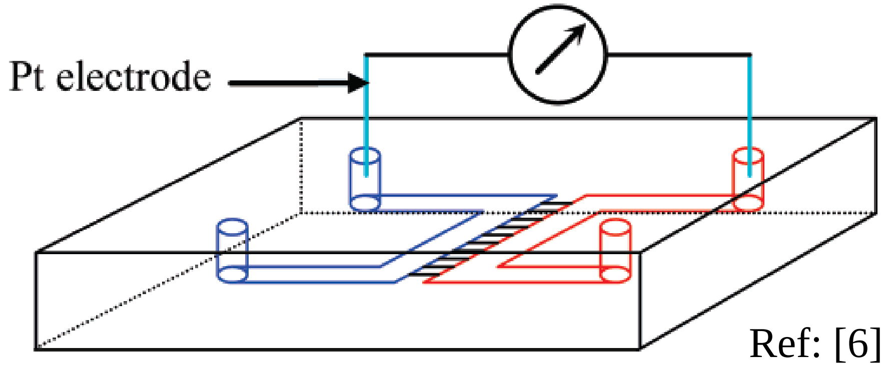


- ❑Macro channels – parabolic flow
- ❑Microchannel – Plug like flow due to small EDL.
- ❑ Nanochannel – parabolic flow as the EDL overlap.

Dimensionless species velocity due to electro-osmosis as a function of the normalized nanochannel height, for an anion in (1) 60 - and (2) 200-nm-high channels, and for an uncharged molecule in (3) 60- and (4) 200-nm-high channels. Adapted from [4].

Nanofluidic fuel cell

Preparation



Ref: [6] Liu et al, Texas Tech University

❖Two U – shaped channels (1mm wide and 100μm *deep)* were micro machined on the bottom surface of a silica substrate.

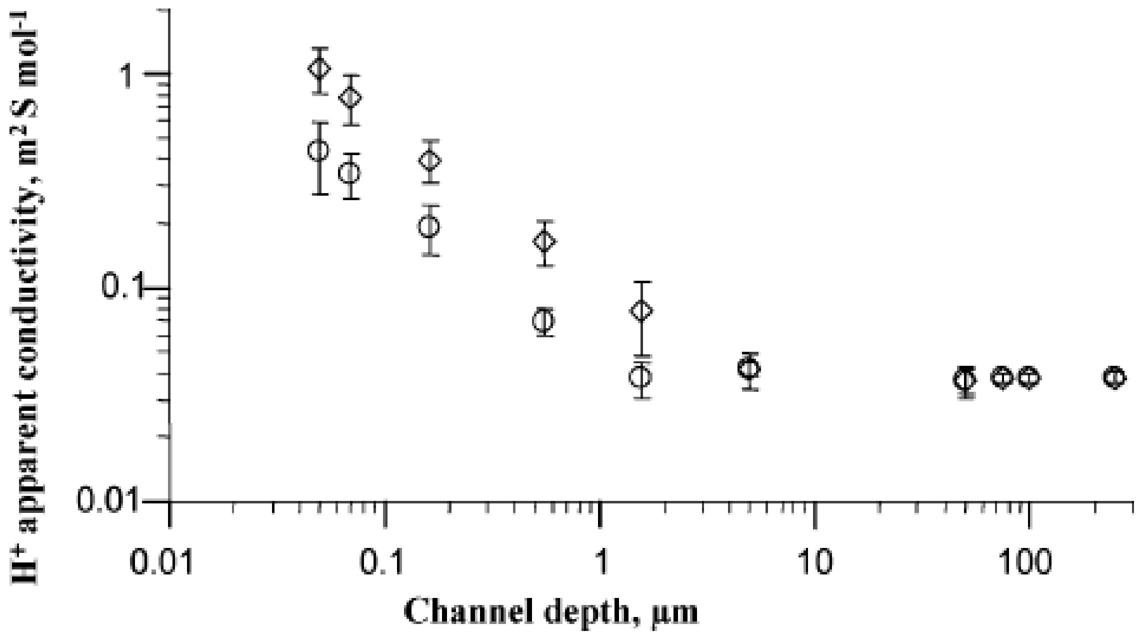
❖Four through – holes were drilled at the ends of the U – channels.

❖An array of 55 parallel nanochannels (1mm long and 100μm wide) with a depth between 50 nm to 50 μm was etched on the top surface of another silica substrate.

❖The two U – channels were connected by the nanochannels.

❖All channel surfaces were derivatized with $–SO_3H$ groups.

Enhancement of proton conductivity in nanochannels



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▪The diamond symbols represent the conductivity values obtained using 10 µM $HClO_4$, while the circular symbols indicate the conductivity data obtained using 1 mM $HClO_4$.

- ❖ Proton conductivity increases due to the increase in the concentration of the [H^+] ions with decrease in depth.
- ❖ Reason – EDL overlaps when channel height decreases.

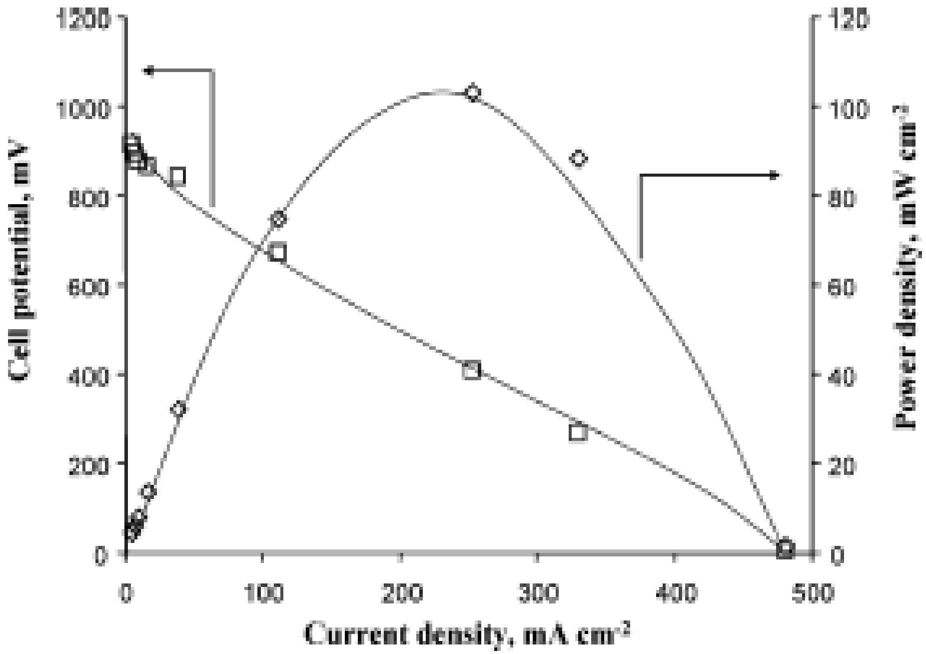
Fuel cell membrane characteristics

- High proton conduction
- Good mechanical/thermal strength, and
- low fuel crossover
- Array of nanochannels forms an excellent proton conductive membrane.
- 1-mm-long nanochannels (equivalent to a 1-mm-thick membrane), result in high mechanical/thermal strength of the membrane compared to micro meter thick Nafion membranes.
- Low Re results in suppressing fuel crossover.

Fuel Cell Specification

- Channel depth – 50 nm.
- Fuel – aqueous solution containing 1.0 M methanol in 1.0 mM H_2SO_4
- Oxidant – 1 mM $KMnO_4$ solution.
- Conventional fuel cells use high concentrations of acids in the fuel solutions while in nanochannel based proton conductive membrane enhanced proton conductivity is obtained at low concentrations due to EDL overlap.
- High concentrations of acids reduce EDL thickness and hence the degree of the proton conduction enhancement.
- A Ru/Pt (Pt deposited with Ru) electrode as anode
- Pt electrode as cathode (placed in the oxidant solution).

Performance



❑Operating Temperature – 60^0 C.

❑Maximum power density – 130 mW/cm^2

Advantages

❑ provides high proton conductivity,

❑ improved mechanical strength,

❑ capable of operating at elevated temperatures.

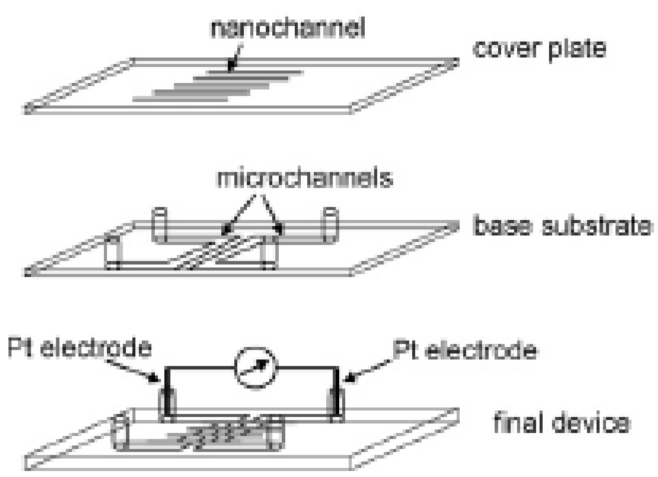
❑ can be monolithically integrated with other micro/nanofluidic devices and microelectromechanical systems using common manufacturing processes, improving its performance.

Limitations

- High power density, but limited power output (3nW) due to one-dimension-array configuration,.
- Can be improved by increasing the number of the parallel channels.
- Example, 105 nanochannels with a width of 100 µm and a length of 1 mm arranged in a 10 × 10 cm^2 area.
- The entire assembled fuel cell will occupy a space of 10×10×10 cm^3 and generate a power > 100 mW.
- Alternate technique – Using 2 – D array nanochannel membranes such as the nanoporous membranes

Novel fabrication techniques

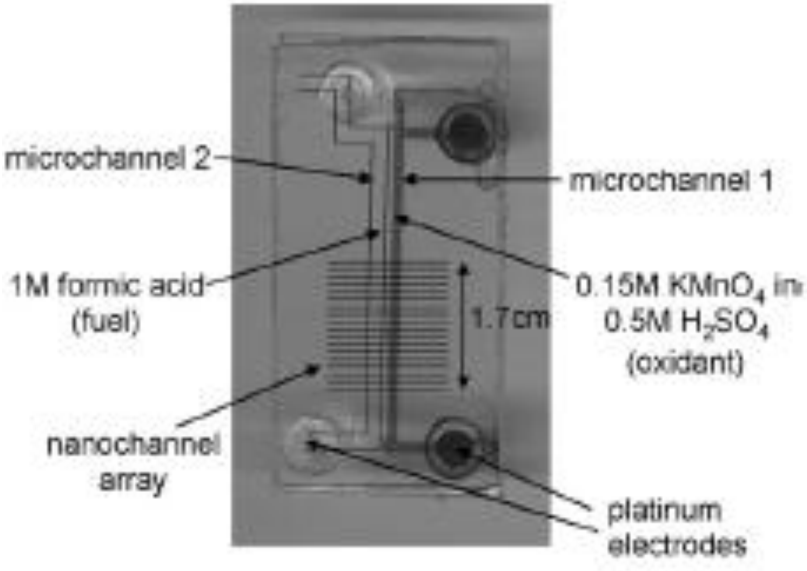
- ✓ Nanochannel arrays as supports for proton exchange membranes (PEM) in microfluidic fuel cells.
- ✓ PEM - created by selectively retaining sodium silicate precursor material within a nanochannel array that bridges two microchannels carrying the fuel and the oxidant streams via capillary forces.
- ✓ Suitable physical/chemical treatment is provided to precursor to transform it into an ion – selective membrane.



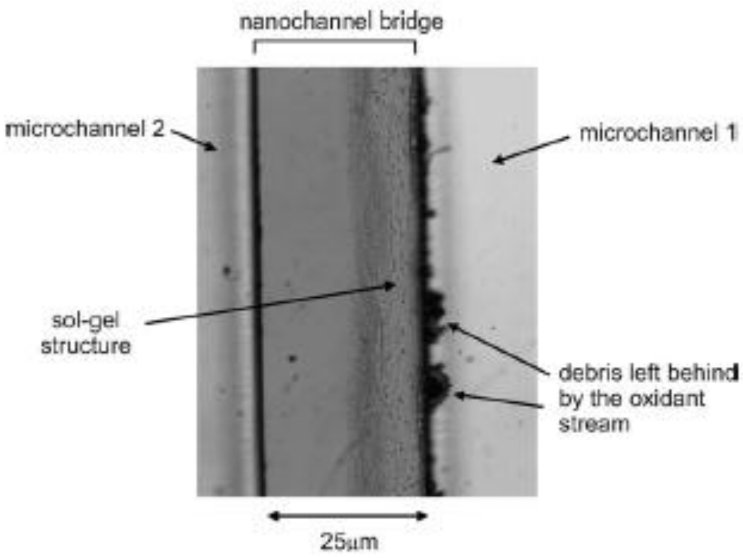
Nanochannel - 233 nm deep and 500 µm wide

Microchannel - 298 µm deep and 1300 µm wide

Ref: [7] C.J. Wadsworth et al. University of Wyoming, U.S.A.

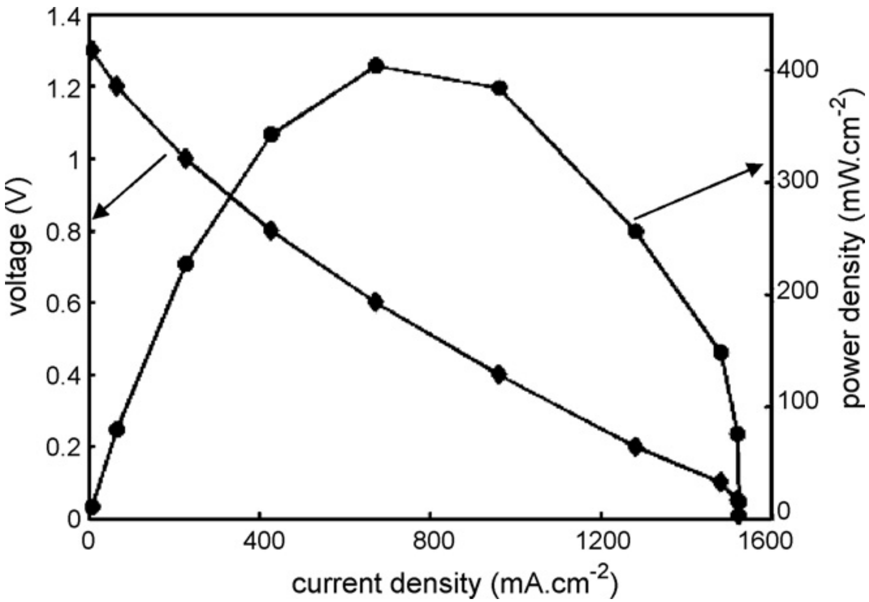


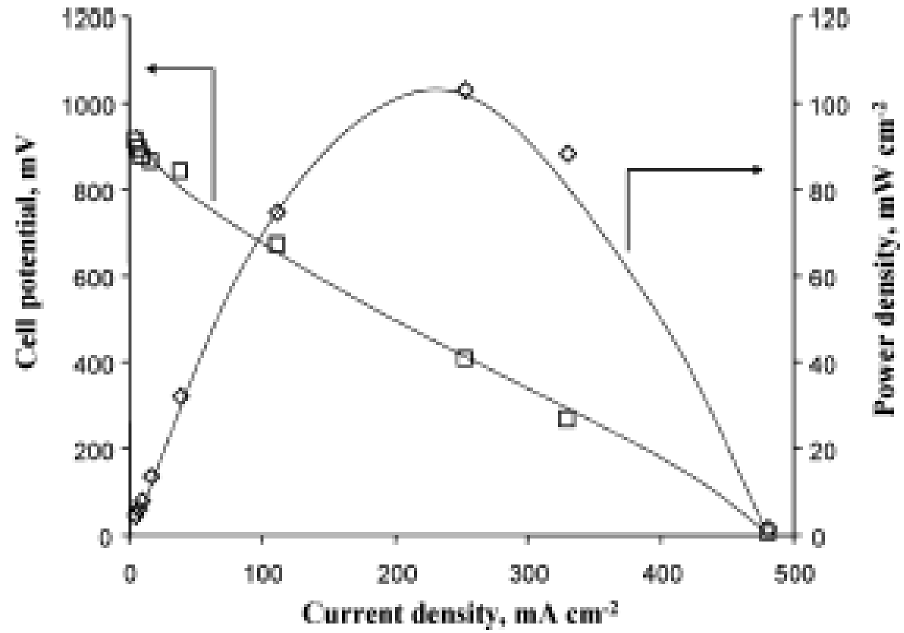
Micro/nanofluidic fuel cell device



Optical image of the sodium silicate derived sol–gel membrane fabricated within the nanochannel array of the microfluidic fuel cell device.

Performance





Operating temperature **25^0 C.**
Fuel - solution of **1M formic acid**
Oxidant - solution of **0.15M $KMnO_4$ in 0.5M sulfuric acid**

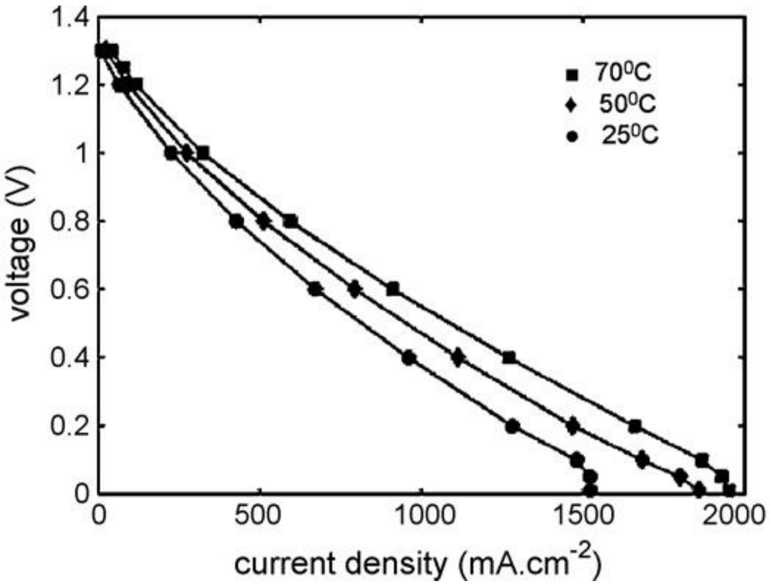
Operating temperature **60^0 C.**
Fuel – 1 mM methanol in **1mM sulphuric acid**
Oxidant - solution of **1mM $KMnO_4$**

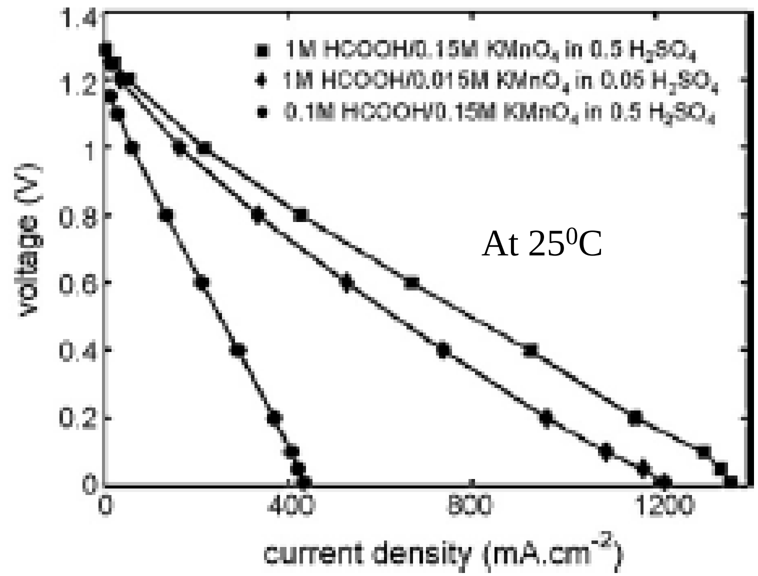
- ➢The current density was calculated based on membrane area rather than that of the electrodes.
- ➢**Reason**: No increase in the electrical current was observed with increase in surface area of electrode.
- ➢Thus, the electrical current was not limited by the electrochemical reaction kinetics but by the membrane Ohmic resistance.

Performance

- Open circuit potential – 1.31V
- Maximum current density – 1487.8 µAcm^{-2}.
- Maximum power output – 405.3µWcm $^{-2}$ correspond to a maximum total current of 31.2µA and a maximum total power of 8.5µW.
- Power increased by a factor of 2833 compared to previous model.
- **Reason:** Primarily due to the use of a low resistance PEM structure.
- High concentration of fuel and oxidant can be used using this structure enhancing the kinetics of the electrochemical reactions as well as minimizing the internal Ohmic resistance of the fuel cell.

Effect of Temperature and fuel/oxidant concentration





❖ Increase in maximum current density from 1487.8μAcm^{-2} to 1955.2μAcm^{-2} with increase in temperature from 25^{0}C to 70^{0}C.

❖Temperature has minimal effect on open circuit potential.

❖ Decrease in concentration of the fuel or the oxidant decreases the power output of the fuel cell.

❖ **Claim:** Increase in power output with increase in concentration and temperature was due to an increase in the membrane conductance and not due to enhancement in reaction kinetics.

Drawbacks

- ✓ Oxidant ($KMnO_4$) – Led to the deposition of brown debris (namely MnO_2 particles) around the sol–gel membrane.
- ✓ Did not affect the performance of the fuel cell but suspect reduction in the fuel cell life.
- ✓ In a real application, membrane fouling by $KMnO_4$ can be avoided by using different oxidant system, e.g., hydrogen peroxide.

Conclusions

- Novel micro/nanofluidic based fuel cell devices was discussed.
- Nanochannel membranes provides high proton conductivity
- Have improved mechanical strength,
- Can be stacked together into array of nanochannels to increase the power output.
- Low resistance nanochannel polymer exchange membranes could be fabricated to further increase the current and power output.

Conclusions

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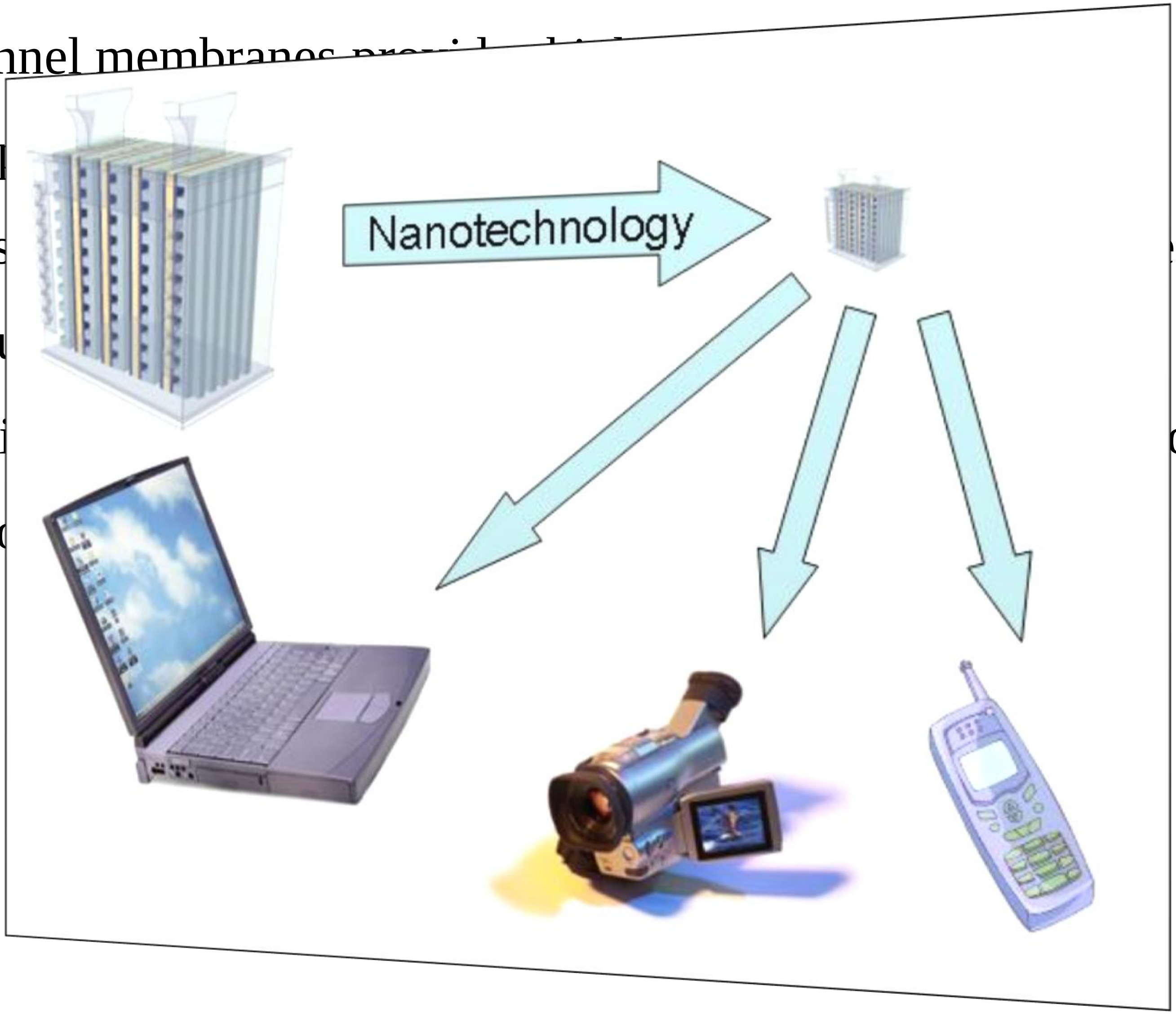

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Thank You