Future Direction of Direction of Direct Alcohol Fuel Cell

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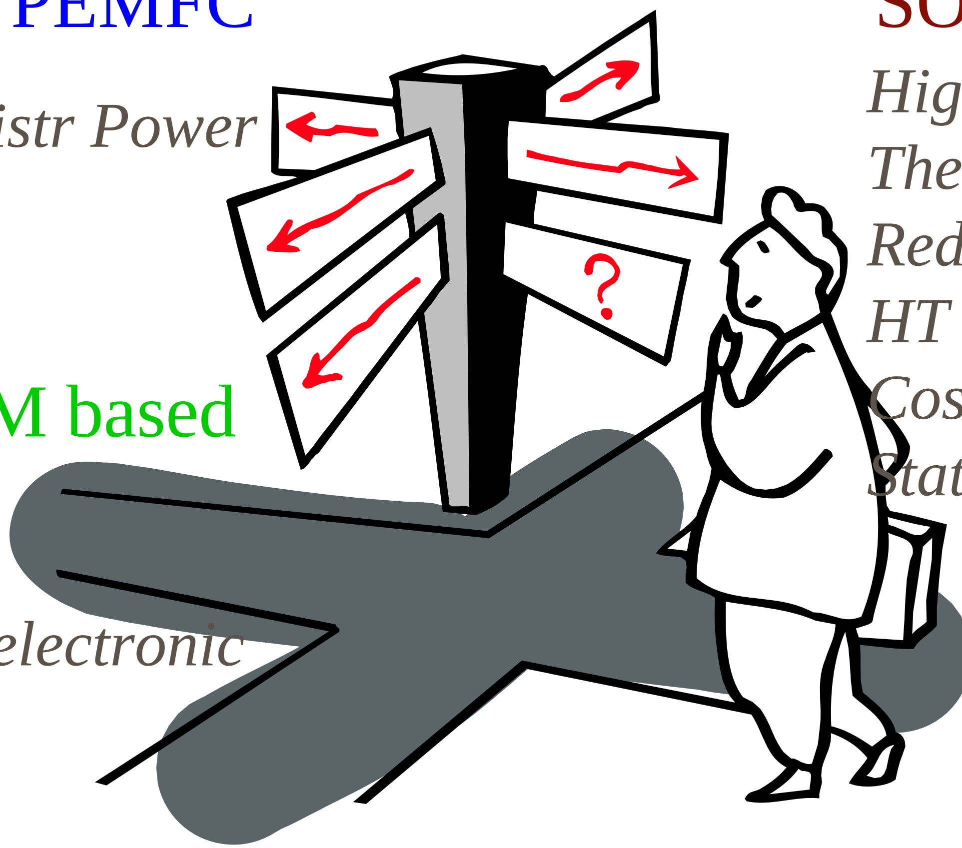
Path!

Poisoning
Operation < 80 ^{0}C
Membrane,
Cost
Automobile; Distr Power

PEMFC

SOFC

High Temperature
Thermal Cyclability
Redox-cycling
HT Sealants
Cost
Stationary power



DAFC
PEM, AEM based

Micro-fluidic
Cost
Portable micro-electronic equip

MCFC
AFC

Basu, S. (Ed.) Recent Trends in Fuel Cell Science and Technology, Springer/Anamaya (2007)

Obstacles associated with the use of hydrogen

- ☹ Generation of hydrogen gas ⟶ High cost
- ☹ Explosion hazard
- ☹ Difficult to storage and distribute
- ☹ Low power output per unit weight of the fuel cell and fuel processor
- ☹ Low energy density: **0.002772 KWh/l at atm. conditions** (33 kWh/kg)

A. Verma, **S. Basu**, "Power from hydrogen and fuel cell", July, 177-181 (2005) Chemical Weekly.

Fuel

Methanol

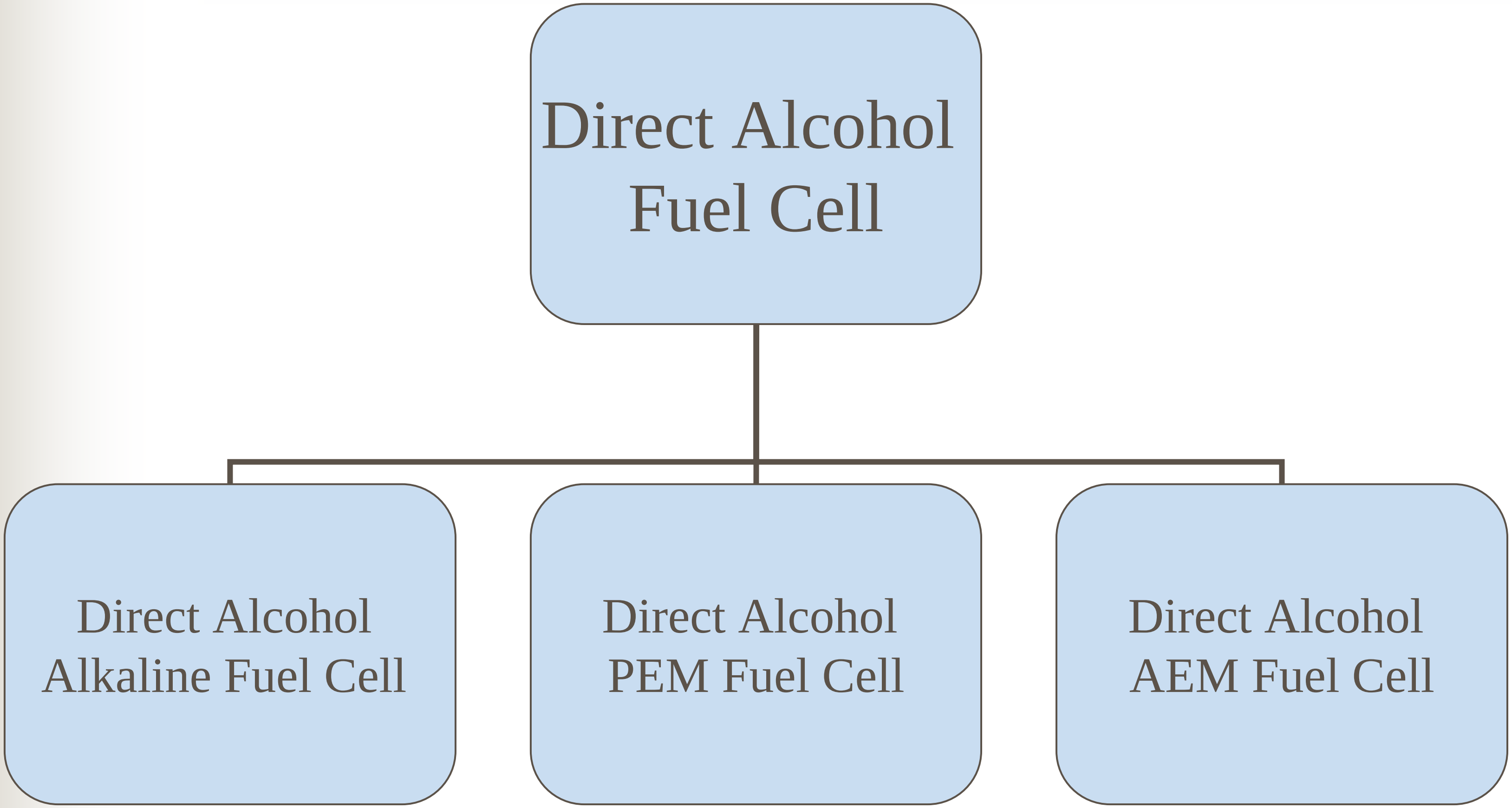
- ✓ Liquid fuel
- ✓ Easy to transport and distribute
- ✓ 5 KWh/l (6 KWh/Kg) energy density
- ✓ 6 electrons per molecule of methanol oxidized
- ✓ Electrooxidation is easy in alkaline condition

- ➢ Not a primary fuel
- ➢ Toxic

Ethanol

- ❖ Non-conventional liquid fuel - method of production is well established
- ❖ Easy to transport and distribute
- ❖ 5.9 KWh/l (7.44 KWh/Kg) energy density
- ❖ 12 electrons per molecule of ethanol oxidized
- ❖ Electrooxidation is easy in alkaline condition
- ❖ Non toxic

- ➢ C-C bond cleavage at low temperature


Direct Alcohol Fuel Cell
Direct Alcohol Alkaline Fuel Cell
Direct Alcohol PEM Fuel Cell
Direct Alcohol AEM Fuel Cell

Fundamentals of conventional alkaline fuel cell

Electrolyte: KOH solution

Anode (**Pt/C**):

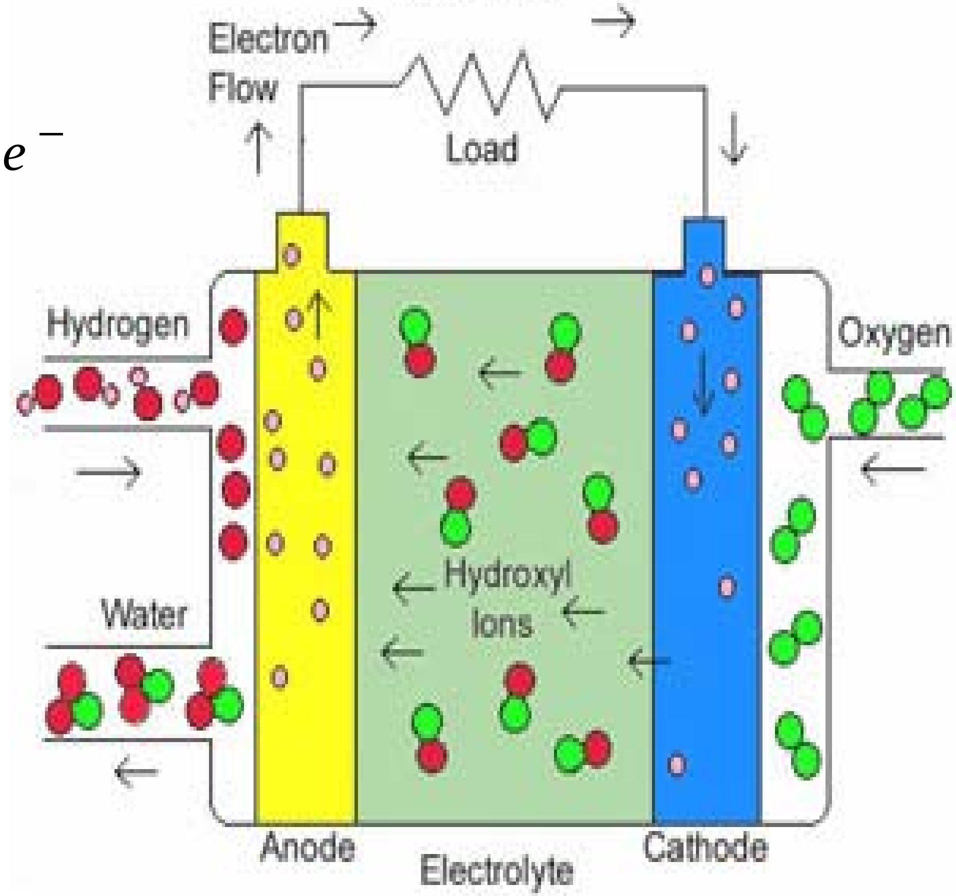
$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

Cathode (**Pt/C**):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Overall Cell Reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$



ALKALINE FUEL CELL

	Alkaline electrolyte
Anode	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Cathode	$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Overall	$H_2 + 1/2O_2 \rightarrow H_2O +$ electrical Energy +heat

Poisoning: $CO_2 + 2OH^- \longrightarrow (CO_3)^{2-} + H_2O$

- Depletion of KOH
- Poisoning of cathode surface with carbonates

Myth !

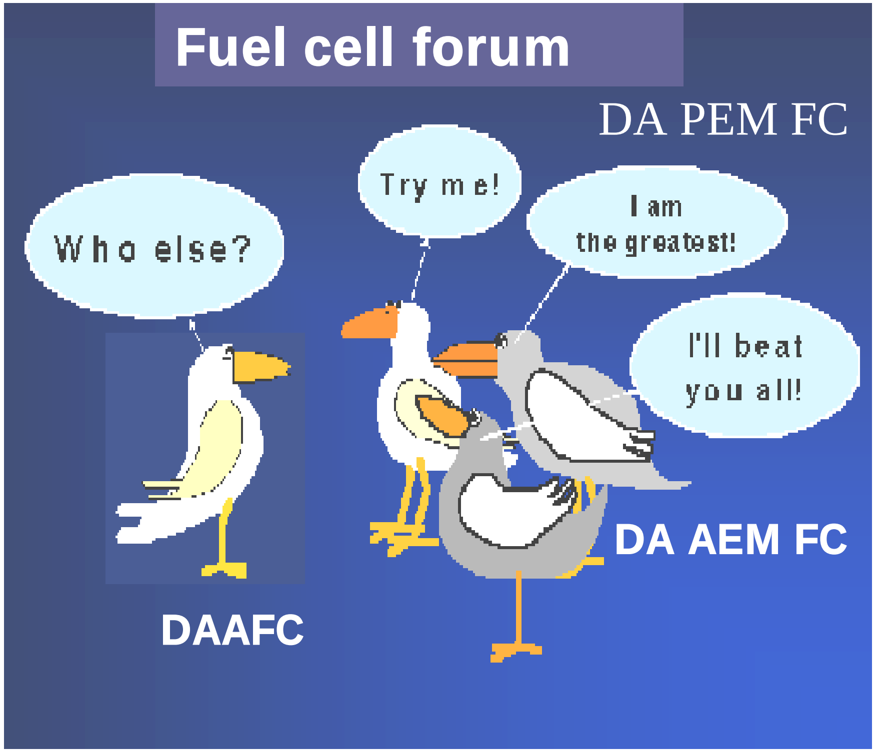
Kordesch, K., Cifrain, M., Koscher, G., Hejze, T., and Hacker, V., “A survey of fuel cell systems with circulating electrolytes”, Power Sources Conference 2004, Philadelphia, June 14-17.

McLean, G.F., Niet, T., Prince-Richard, S., and Djilali, N., “An assessment of alkaline fuel cell technology”, Int. J. Hydrogen energy, 27, (2002) 507-526

Gülzow, E., and Schulze, M., “Long-term operation of AFC electrodes with CO2 containing gases”, *J. Power Sources*, 127, (2004) 243-251

Advantages of alkaline fuel cell

- ✓Less electrode poisoning compared to acidic electrolyte
- ✓Fuel oxidation in alkaline solution by the non-noble metal catalyst is as active as noble metal catalyst
- ✓Oxygen reduction reaction is more favorable in alkaline medium than in acidic medium



Verma, A., A. K. Jha**, S. Basu** "Manganese oxide as a cathode catalyst in flowing alkaline electrolyte direct alcohol or sodium borohydride fuel cell" ***J. Power Sources*** 12. **141** 30-34 2005

Anode

✓ **Tripković et al. (1996, 2001)** suggested a general mechanism for C_1-C_4 alcohol electrooxidation in alkaline medium:

Alcohol → Reaction intermediate → Acid (in anionic form)

Reaction intermediate ↓ ‘poisoning species’ (CO) → CO_2

- Ethanol was most active on Pt surface
- **Formic acid and acetic acid** were the reaction products of methanol and ethanol electrooxidation, respectively

✓ **Torresi et al. (2003)** reported:

* the electrolysis of ethanol on polycrystalline gold in alkaline medium
* **acetaldehyde and acetic acid** were found as a reaction product
* no C-C bond cleavage

Cathode

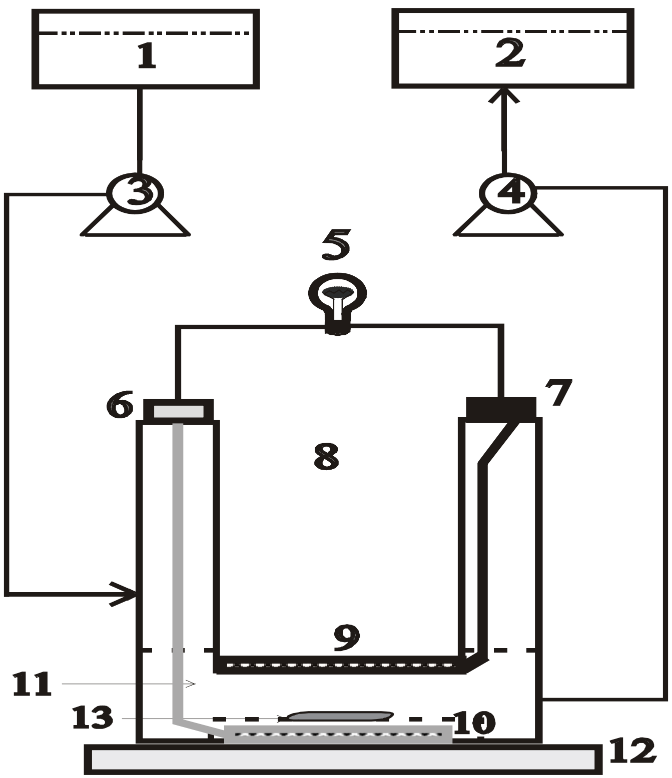
✓ **Mao et al. (2002)** reported two reduction peaks in cyclic voltammogram (CV) correspond to 2 + 2 electron mechanism for MnO_2

✓ **Verma et al. (2005)** found only one reduction peak in CV for MnO_2 cathode

Tripković, A.V., Popović, K.Dj., and Lović, J.D., “The influence of oxygen-containing species on the electrooxidation of the C1-C4 alcohols at some platinum single crystal surfaces in alkaline solution”, *Electrochim. Acta*, 46 (2001) 3163-3173.

Schematic diagram

Fuel: Methanol / Ethanol



Cathode (MnO_2/C/Ni)

$$4e^- + O_2 + 2H_2O \rightarrow 4\,OH^-$$

Anode (Pt/C or Pt-Ru or Pt-black)

Methanol

$$CH_3OH + 2OH^- \rightarrow HCHO + 2H_2O + 2e^-$$

$$HCHO + 2OH^- \rightarrow HCOOH + H_2O + 2e^-$$

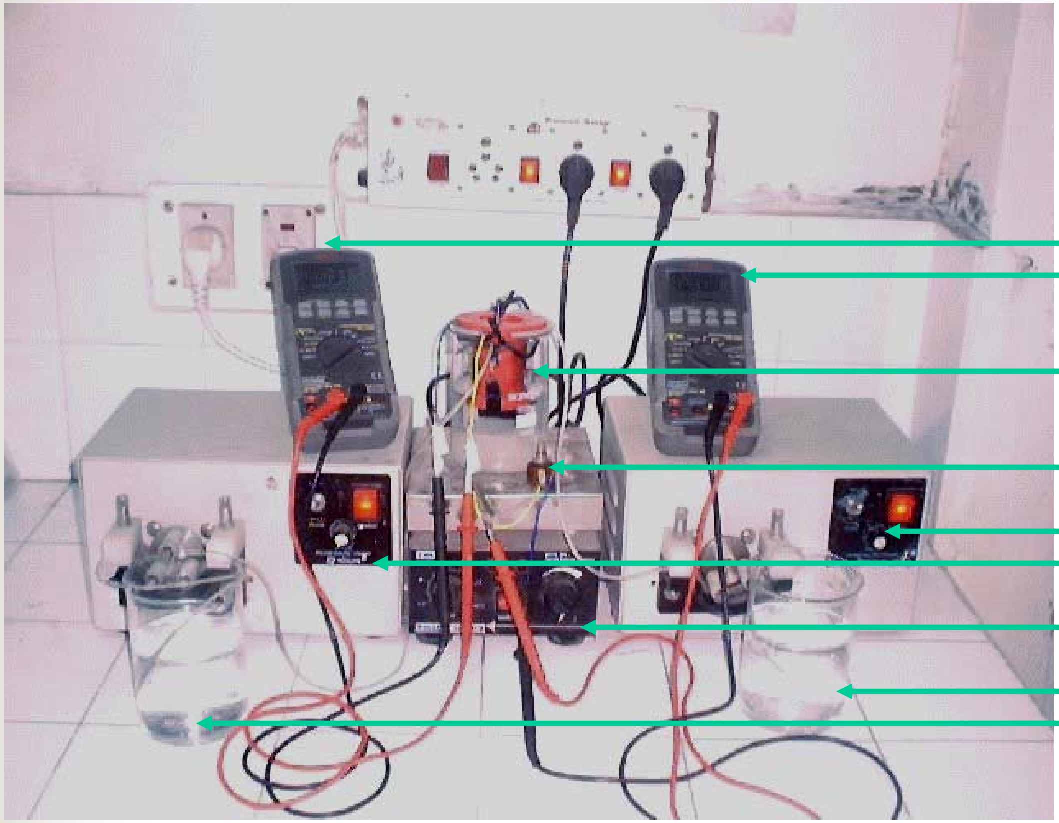
$$HCOOH + 2OH^- \rightarrow CO_2 + 2H_2O + 2e^-$$

Ethanol

$$C_2H_5OH + 2OH^- \rightarrow CH_3CHO + 2H_2O + 2e^-$$

1. Fuel-electrolyte mixture storage; 2. Exhausted-fuel-electrolyte mixture storage; 3, 4. Peristaltic pump; 5. Load; 6. Anode terminal; 7. Cathode terminal; 8. Air; 9. Anode electrode; 10. Cathode electrode; 11. Fuel and electrolyte mixture; 12. Magnetic stirrer; 13. Anode shield

Photograph of direct alcohol alkaline fuel cell



Multimeters

Fuel cell

Potentiometer

Peristaltic pumps

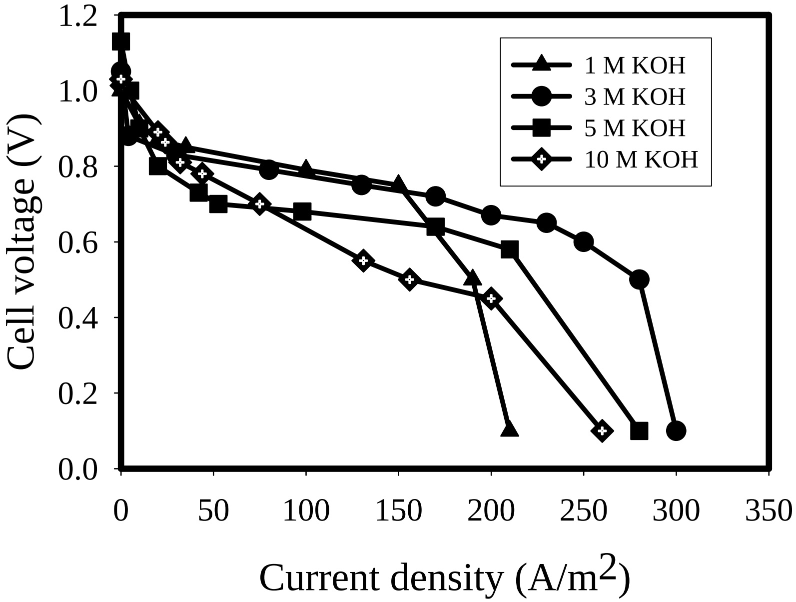
Magnetic stirrer

Fuel and electrolyte storage tanks

Verma, A., and **Basu, S.**, 'Direct use of alcohols and sodium boro hydride as fuel in an alkaline fuel cell' *J. Power Sources* **145,** 282-285 (2005)

Effect of KOH concentration

2 M Methanol, 25 ^{o}C
Pt Black: Anode, MnO_2: Cathode



2 M Ethanol, 25 ^{o}C
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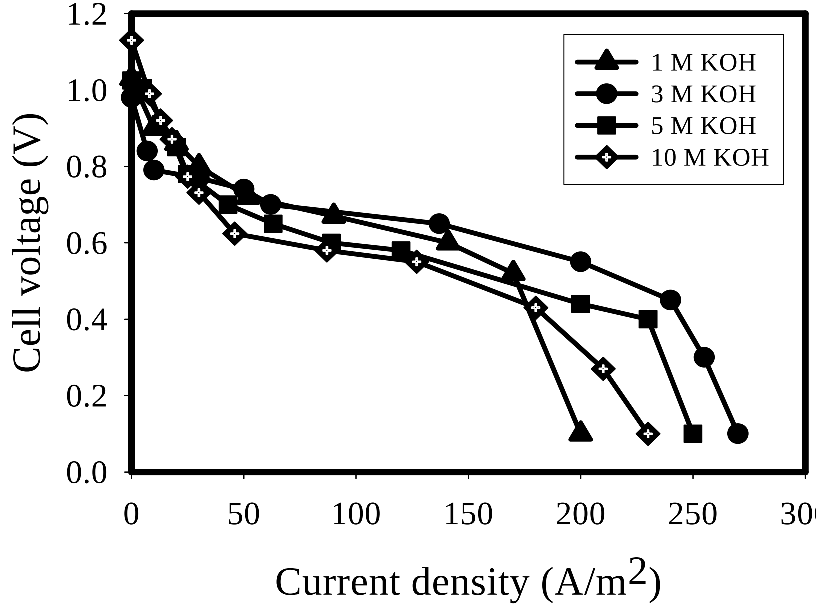
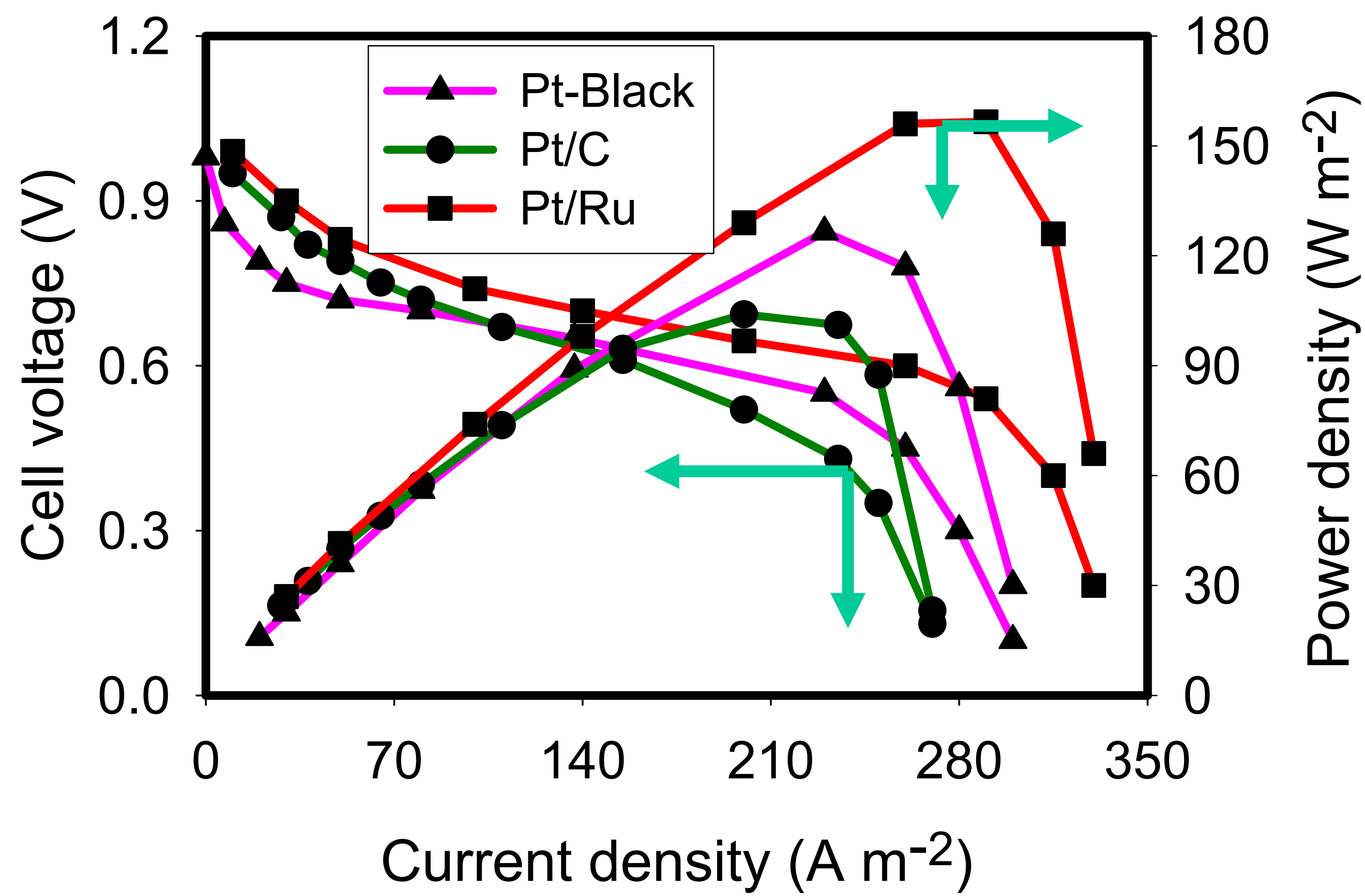


✓Verma, A., Jha, A. K., and Basu, S., 2004, Evaluation of an Alkaline Fuel Cell for Multi-fuel System, Proceedings of ASME Conf. on Fuel Cell Sci, Eng and Tech., 14-16 June, 2004, Rochester, US

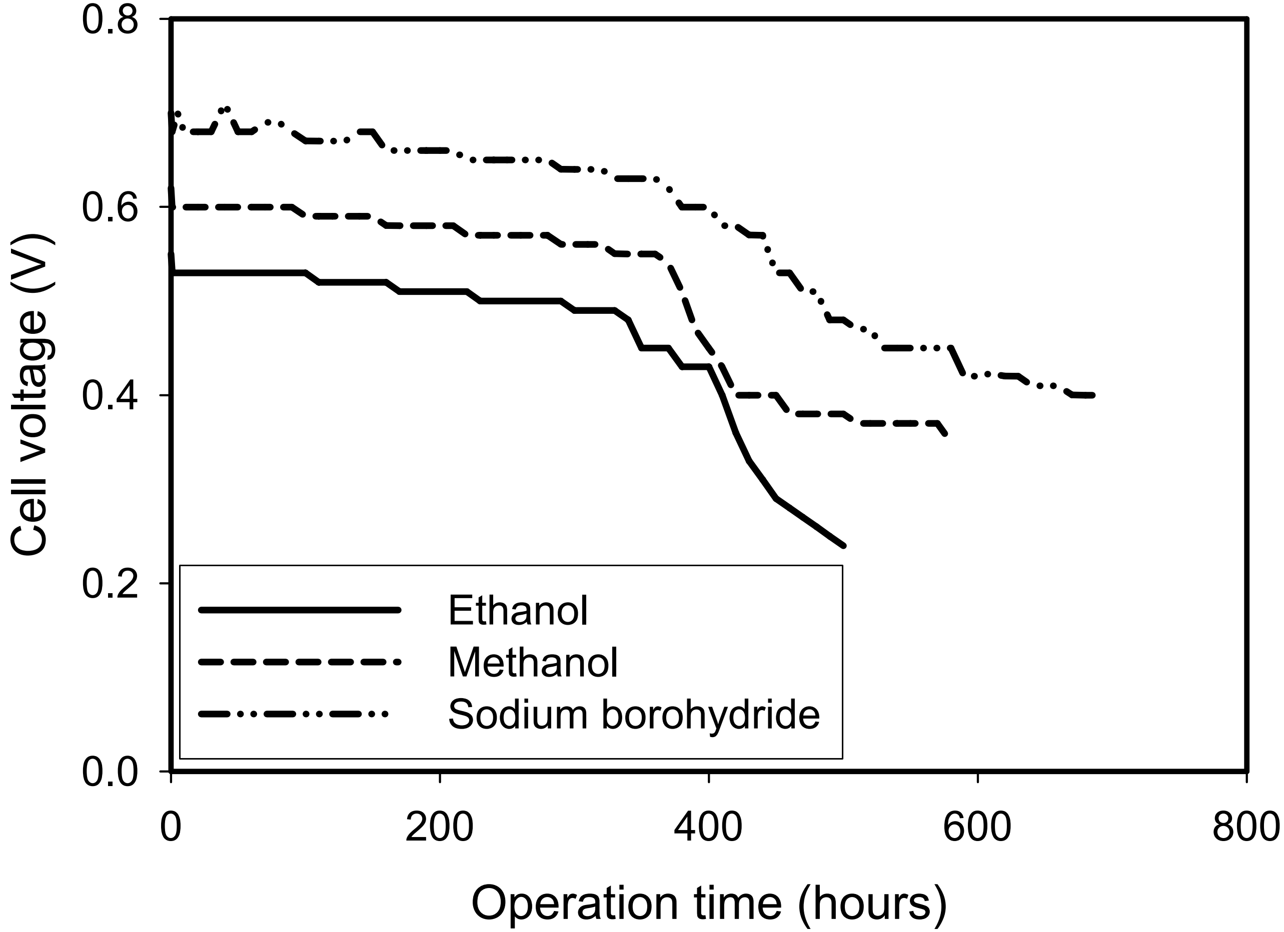
✓Verma, A., and Jha, A. K., S. Basu 'Analyses of Multi-Fuel Alkaline Fuel cell', Grove Fuel cell Symposium – Fuel cells Science & Technology, Oct. 6-7, 2004 Munich, Germany

Effect of electrode catalyst type and loading

Performance curves for anode catalysts in 2 M Ethanol/ 3 M KOH AFC



Performance of fuel cell for different fuels



A. Verma, A. K. Jha and **S. Basu** "Evaluation of an alkaline fuel cell for multi- fuel system" ASME J Fuel Cell Science & Technology, **2,** 234-237 (2005)

MODEL EQUATION

$$E_{cell} = OCV - (\eta_{ac} + \eta_{conc} + \eta_{oh})$$

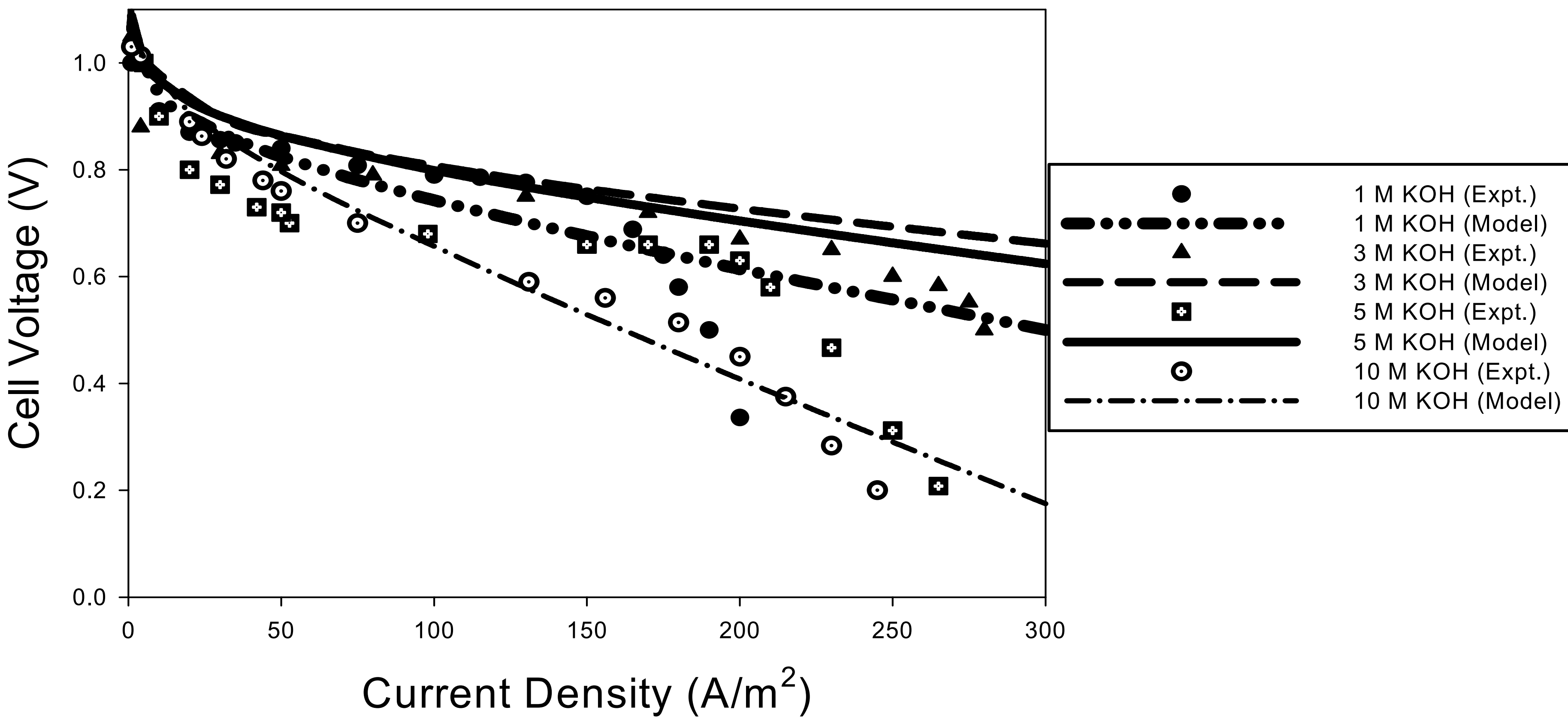
Direct methanol alkaline fuel cell

$$E_{cell} = E - \left(\frac{R\,T}{\alpha\, n\, F}\right) \ln\left(\frac{j\; C_M^{-1} \,.\, C_{OH}^{-0.5}}{K}\right) - i.(1.31737 - 9.0336\; c_{OH}$$

$$+\; 23.05735\; c_{OH}^2 - 8.107083\; c_{OH}^3 - 2.578 + 0.11875\; T_1 -$$

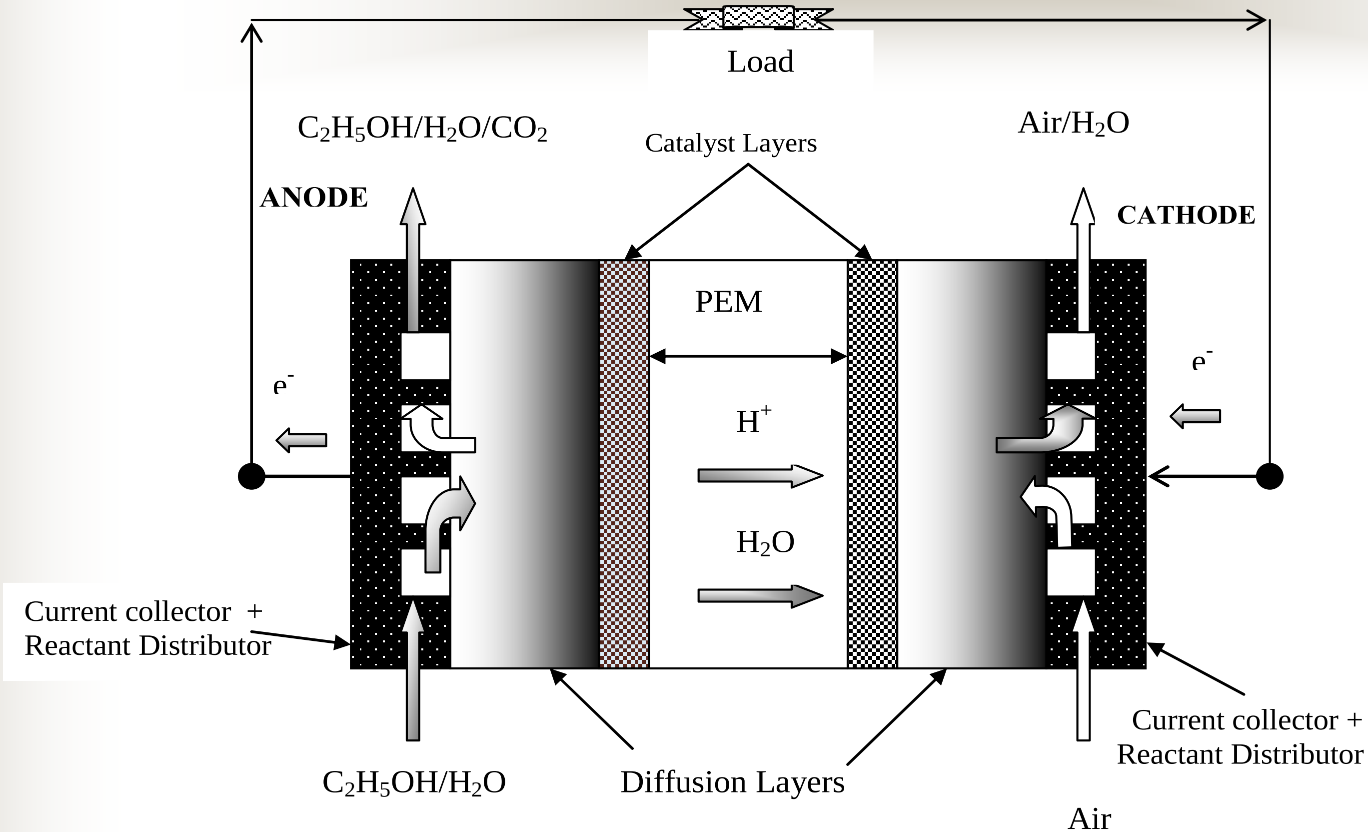
$$0.000625\; T_1) - \frac{RT}{\alpha\, nF} \ln\left(\frac{j}{j_O\left(1 - jM\right)}\right)$$

Model prediction of current-density versus cell-voltage for methanol at different KOH concentrations (t=25 °C, C_M=2M)



Direct Alcohol PEM Fuel Cell

Schematic of Direct Alcohol Fuel Cell



Anode: (catalyst : Pt / Ru / C)

$$C_2H_5OH + 3\,H_2O \longrightarrow 12\,e^- + 12\,H^+ + 2\,CO_2$$

Cathode: (catalyst : Pt / C)

$$3\,O_2 + 12\,e^- + 12\,H^+ \longrightarrow 6\,H_2O$$

Overall:

$$C_2H_5OH + 3\,O_2 \longrightarrow 3\,H_2O + 2\,CO_2$$

Preparation of Membrane Electrode Assembly (MEA)

Pt-Ru/C electrode-catalysts + Nafion ionomer + Activated carbon powder + PTFE dispersion

↓

Mix by ultrasonic agitation

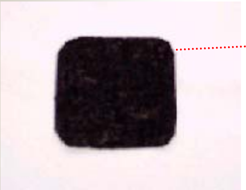
↓

Paint on diffusion layer

↓

Dry diffusion layer with electrode catalysts

↓



Anode

Pt-black electrode-catalysts + Nafion ionomer + Activated carbon powder + PTFE dispersion

↓

Mix by ultrasonic agitation

↓

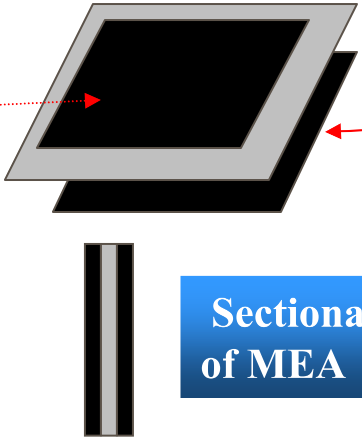
Paint on diffusion layer

↓

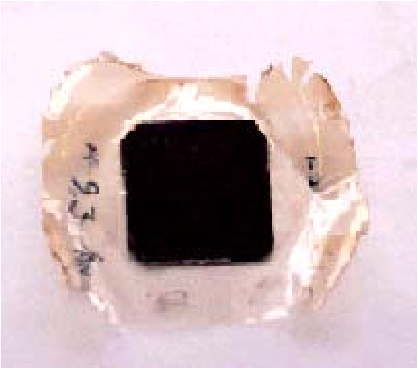
Dry diffusion layer with electrode catalysts

↓

Cathode

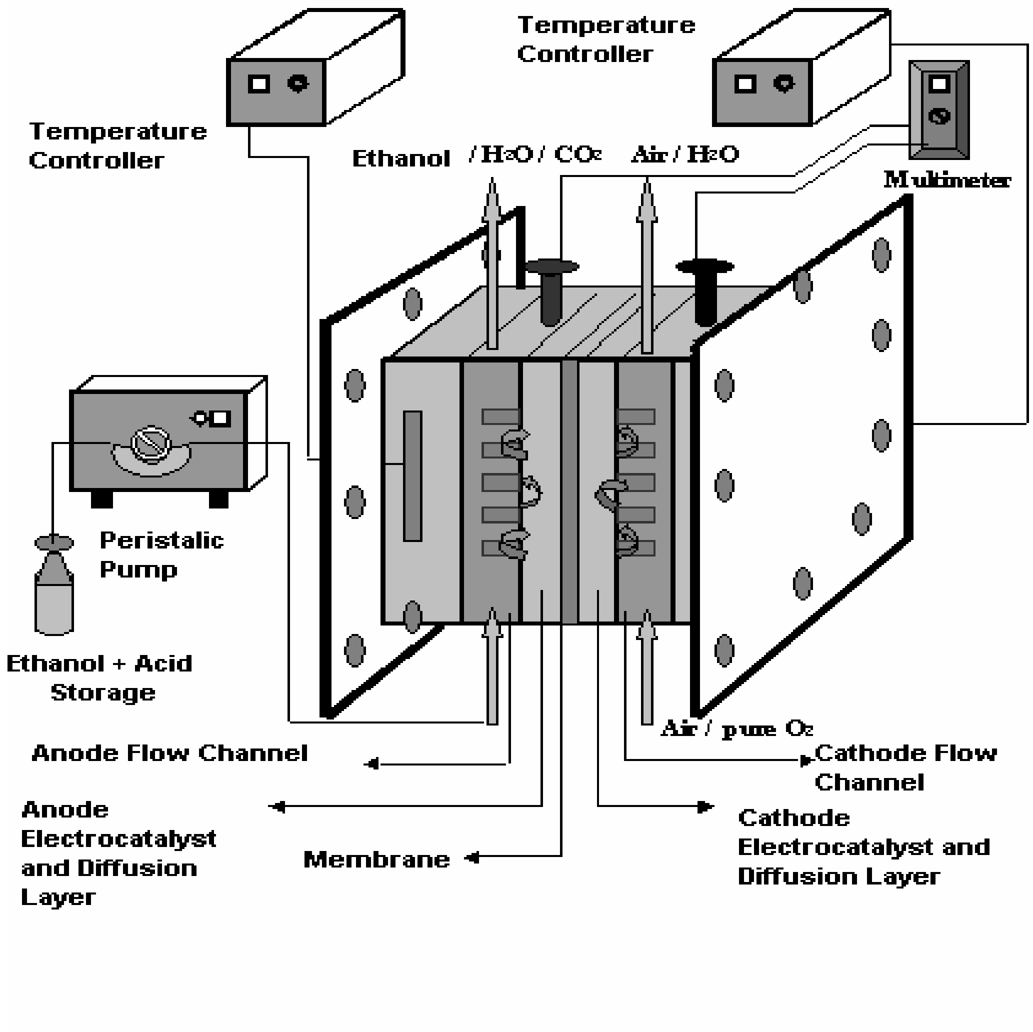


Sectional and Plan View of MEA



Photograph of MEA

Schematic Diagram of Direct Ethanol Fuel Cell



Direct Ethanol Fuel Cell Experimental Setup

O_2 cylinder

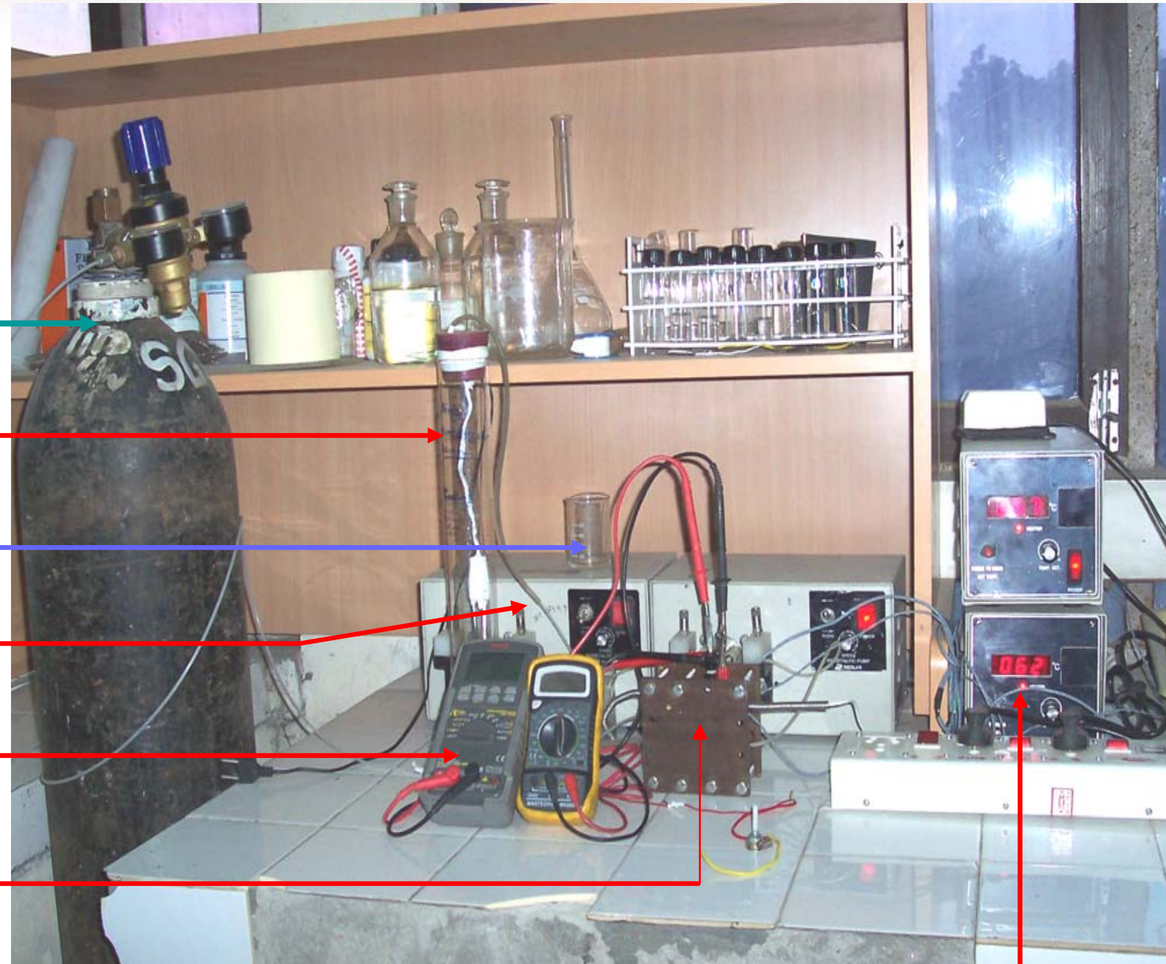
O_2 Humidification column

Ethanol + acid storage

Peristaltic pump

Multimeter

Fuel Cell

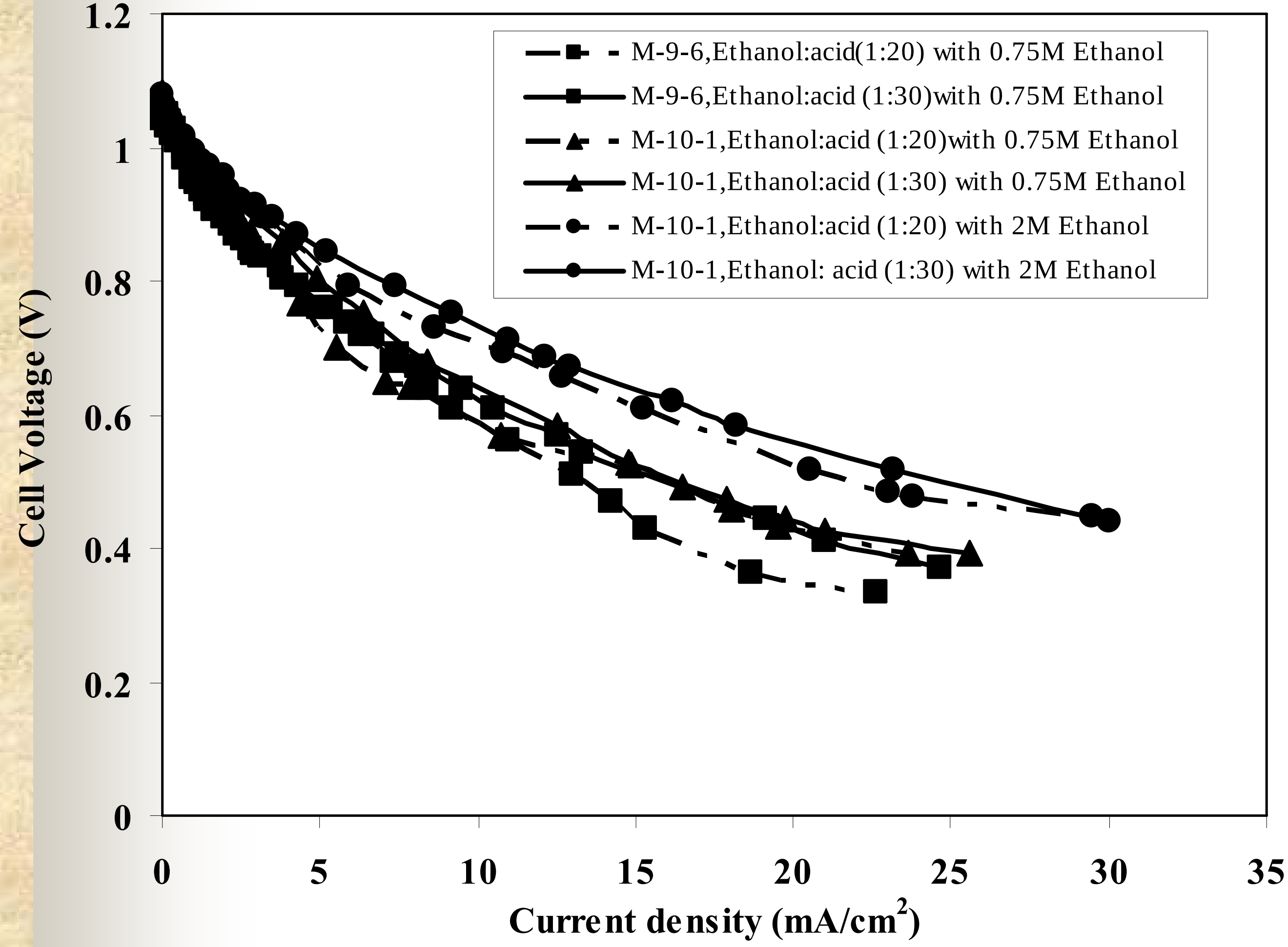


Temperature controller

Comparison of Polarization Curves: Cathode Catalysts Loading

Fuel: 0.75 M and 2M ethanol + 0.5 M sulfuric acid

Anode Temp. : 90^{O}C and Cathode Temp. : 60^{O}C.



Electrode-catalysts loading:

Anode:

M-9-6: 1 mg/cm^2

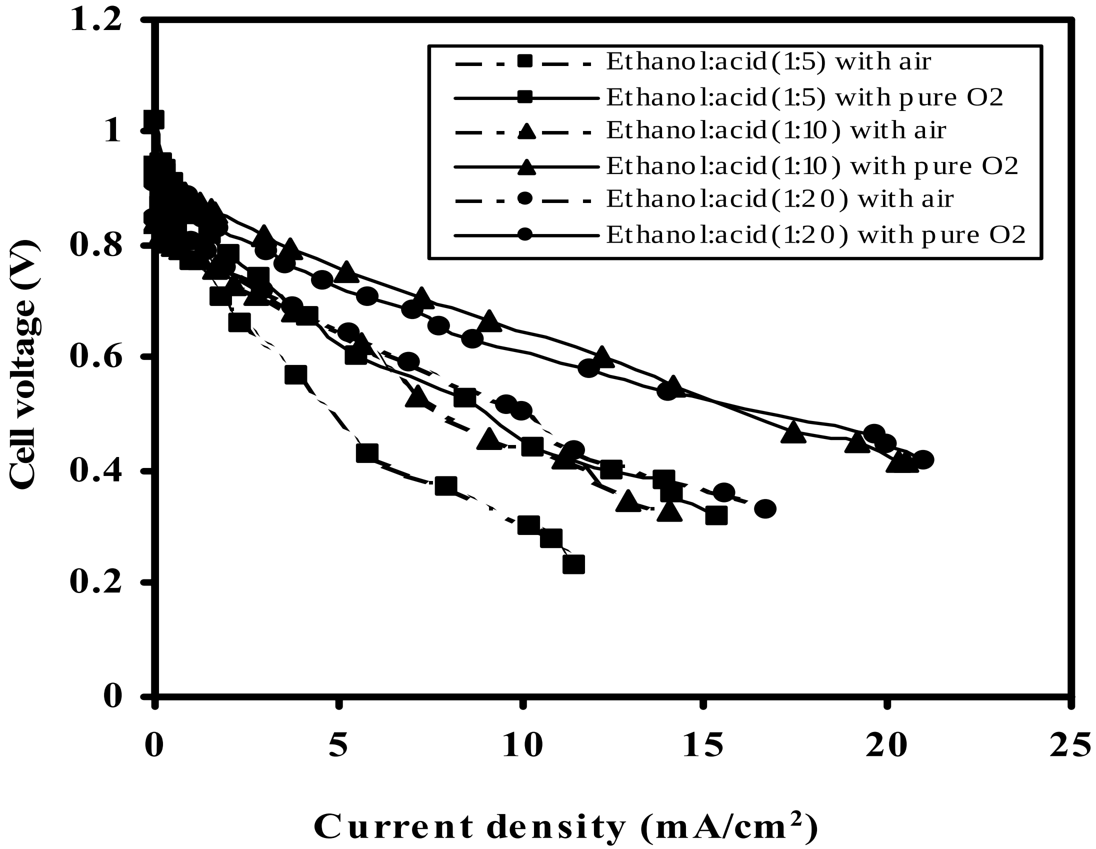
M-10-1: 0.6 mg/cm^2

Cathode:

M-9-6: 0.5 mg/cm^2

M-10-1: 0.6 mg/cm^2

Comparison of Polarization Curves : Air and Oxygen at Cathode



Electrode-catalysts loading:

Anode: 0.6 mg/cm^2

Cathode: 0.5 mg/cm^2

PEMFC/DAFC Challenges

- **<u>Membrane</u>**: high temp operation, high proton conductivity, no electron conductivity, low fuel cross-over, thermal, mechanical and chemical stability, low cost ➡ **Polyfuel**

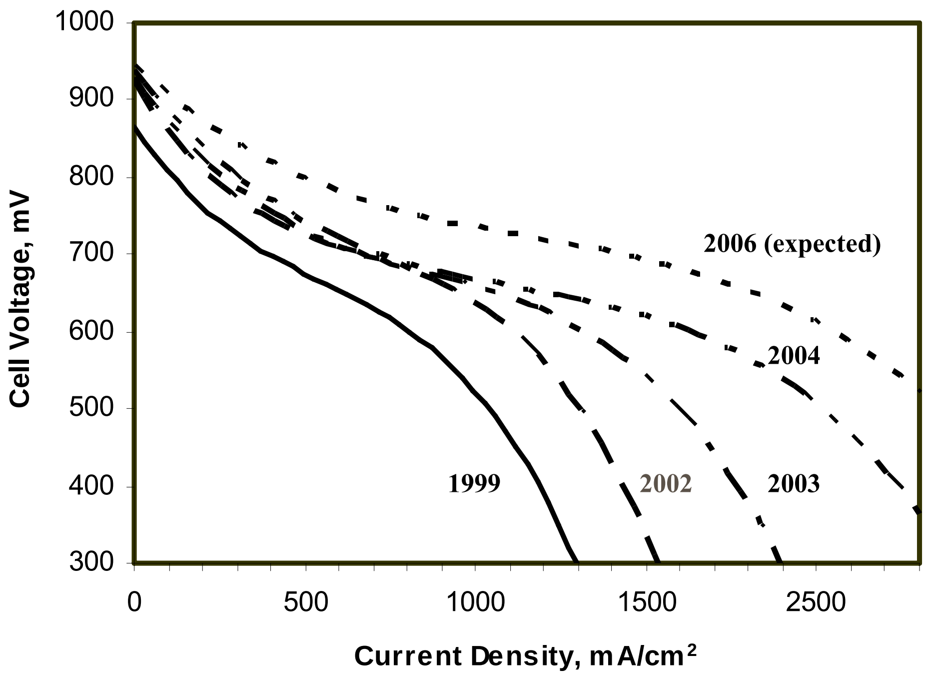
Ashley, S., On the road to fuel cell cars, Scientific American, March 2005, 50-57, (2005)

- **<u>GDL</u>**: uniform distribution of fuel/oxidant on to electrode, excellent electron conductivity, heat conductivity, catalyst support, reasonably stiff and flexural strength, low cost

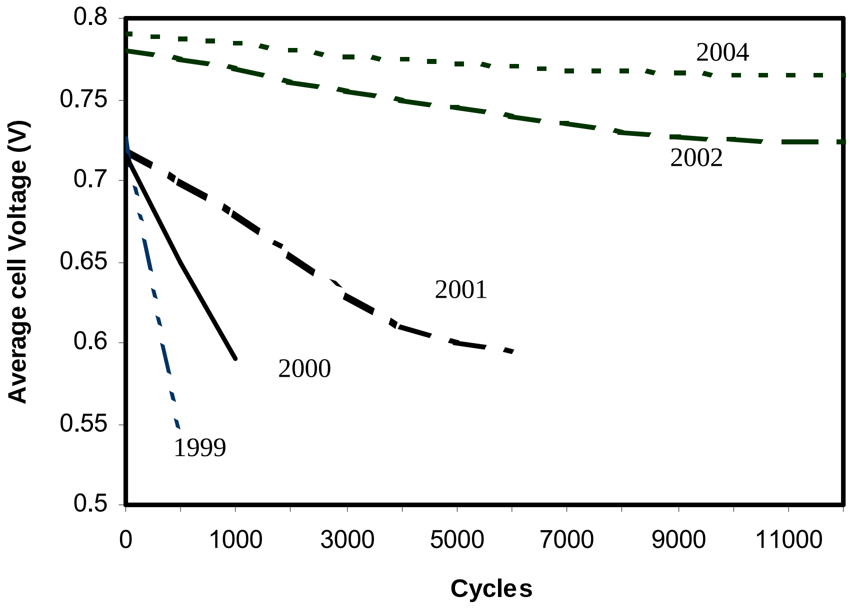
  ➡ ***Indigenous development***

- **<u>Bipolar Plate</u>**: thinner plate and low density material, excellent electron conductor, fuel, oxidant and by product transport (corrosion resistant), high heat conductivity, high flexural strength, low cost (graphite/SS)
- **<u>Catalyst</u>**: low loading, new catalyst – no deactivation, CO tol. C-C bond cleavage at low temp.
- **<u>Stack Eng.</u>**: Improved BOP, thermal and water management

PEMFC Efficiency: Roadmap



Improvement in cell stack performance year wise



Improvement of cyclic endurance year wise

DAFC Challenges

Anode Kinetics – Methanol, Ethanol, Higher Alcohols oxidation (C-C bond cleavage at low temp.)

CuNiPt and CuNiPtRu alloys (Gupta et al. 2004; Tarasevich et al. 2005)

- DA PEM FC
  - Fuel Cross Over through PEM
  - GDL
- DA AFC
  - CO_2 poisoning – flowing electrolyte
  - Anion Exchange Membrane Development (Varcoe at al. 2005)

Gupta, S.S., Mahapatra, S.S, and Datta, J., A potential anode material for the direct alcohol fuel cell, *J. Power Sources*, 131, 169-174 (2004)

Tarasevich, M. R., Karichev, Z. R., Bogdanovskaya, V. A. Kinetics of ethanol electrooxidation at RuNi catalysts, Electrochem. Commun. 7 141-146 (2005)

Varcoe, J. R., Slade, C. T., Prospect for alkaline anion exchange membrane in low temperature fuel cells, Fuel Cells **5**(2) 187-200, (2005)

Fuel Cell for Portable Electronic Equipments

No.	Parameters	Requirements Proposed	Present Status
a.	Type	DAFC	
b.	Power rating, w	50 – 500	5 – 12
c.	Ambient temperature, ^{O}C	-30 to +45	2 to + 40
d.	Operating temperature, ^{O}C	100 – 150	50 – 70
e.	Start up time, s	5-10	60-120
f	Operating pressure, bar	1 – 3	1 – 1.5
g	System power density watts/ liter	2000	77 – 120
h	Efficiency at rated capacity, %	50	35 – 40
i	Min fuel recharging interval (hrs)	10-12	
j	Cell stock performance current density, mA/cm^2 at 50% no-load voltage (b)	350	130
k	Fuel Cell stack cost, US$/kW	120-150 (c)	300-600 depending on the capacity and no. of unit produced

S. Basu (Ed.), Recent Trends in Fuel Cell Science and Technology, Springer / Anamaya (2007)

Title: Recent Trends in Fuel Cell Science and Technology
Au (Ed): Suddhasatwa Basu Department of Chemical Engineering, IIT Delhi
Publisher: Springer (outside India) and Anamaya (In India) (2007)
Price: Rs 1400.00 (in India) / US$ 76.00 (outside India)
Pages 375; ISBN 0 387 35537 5 (the book is available now)

Content

Acknowledgment:

Ph.D. Dr. P. Pandit, Dr A. Verma, Hiralal P., Amit Gupta, S. Biswas, S. Sahoo

M.Tech. P. Malpani, Vinay Chowdhary, S. Das, C. Sarkar, Ashok jain Amit Jha, Hemant K, D Tikadar, S. Chari, Emmanuel, Saurav Gupta, K. V. Singh, V. Singla, Jugal K Gupta, Vipul Gupta, A. K. Jha, Deep Gaurav

B.Tech. Udit, Rachana Agrawal, Joshua Luthra, Kshitij Jain, Veeramani, Kapil Dhingra, Divya Kumar, Chetan Arora, Vibha Kalra, Anshul Sharma, Paresh Goyal, Anshuman, Jyoti, Nitin Kundra

Funding: DST, MNES, HLRC, IITD Thrust

To see a World in a Grain of Sand
And a Heaven in a Wild Flower,
Hold Infinity in the palm of your hand,
And Eternity in an hour.

- *William Blake*

Thank you!

Comparisons

- Performance

	Current Den.(at 0.7V) mA/cm^2	Power at 0.7 V w/cm^2	Pressure psig	Temp ^{o}C
AFC	450	0.315	atm H_2-air	75
	115	0.081	same	40
PEMFC	250	0.175	same	60
	125	0.088	same	70

- Cost

Astris (LC200-16)	240 W	AFC	2400 USD
H-Power (PowerPEM-PS250)	250 W	PEMFC	5700 USD
DAIS-Analytic (DAC-200)	200 W	PEMFC	8500 USD

Kordesch, K., et al.'Revival of AFC hybrid system for electric vehicles' Proc. Fuel Cell Sem., Palm Springs 1998

Literature Review on Direct Alcohol Alkaline FC

Fuel/ oxidant	System information			Operating temp. (ºC)	Current density (mA cm⁻²)	OCV (V)	References
	Anode	Cathode	Electrolye				
MeOH/ air	Pt	Carbon	10M KOH	25	2	0.9	Vielstich (1965)
MeOH/ air	Pt/Pd	Ag	11 M KOH	25	---	1.0	Perry (1976)
MeOH/ not specified	Fe(III)-treated graphite	Ag(I)-treated graphite	6 M KOH	25	18	0.85	Verma et al. (2000)
MeOH/ air	Pt/C	Pt/C	AEM	60	69.3	0.75	Yu et al. (2004)
$NaBH_4$/ air	Au/Pt	Not specified	AEM	25	152	1.1	Amendola et al. (1999)
$NaBH_4$/ H_2O_2	LaCeNd PrNiAl MnCo	Pt/C	Pretreated Nafion-117	70	500	1.25	Choudhury et al. (2003)

❖ **A typical cell voltage of 700 mA cm^{-2} at 0.6 V is treated as a good PEMFC operation**

Conclusions

Fuel cell

- Performance of the fuel cell increases up to 3 M KOH and further increase in KOH concentration decreases performance
- Fuel cell performance is found maximum at 2 M fuel concentration
- The maximum power densities for methanol, ethanol and sodium borohydride are 150 W m^{-2} (260 A m^{-2}), 160 W m^{-2} (300 A m^{-2}) and 215 W m^{-2} (330 A m^{-2}) respectively.
- Performance of the fuel cell decreases by 250 μV/hr (approx.)

FC Modeling

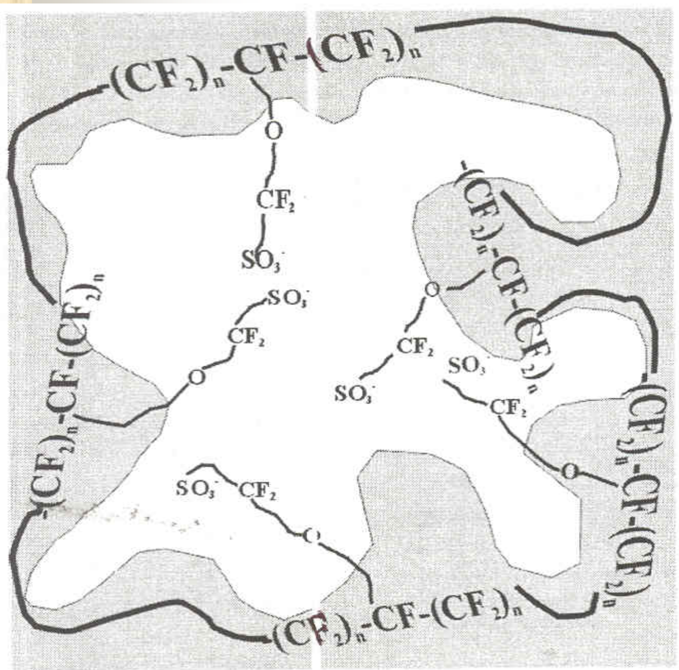
- Mathematical model fairly predicts the experimental data for variation in electrolyte and fuel concentrations, temperature
- Validates the reaction mechanisms used to derive the model

Experimental: DAFC

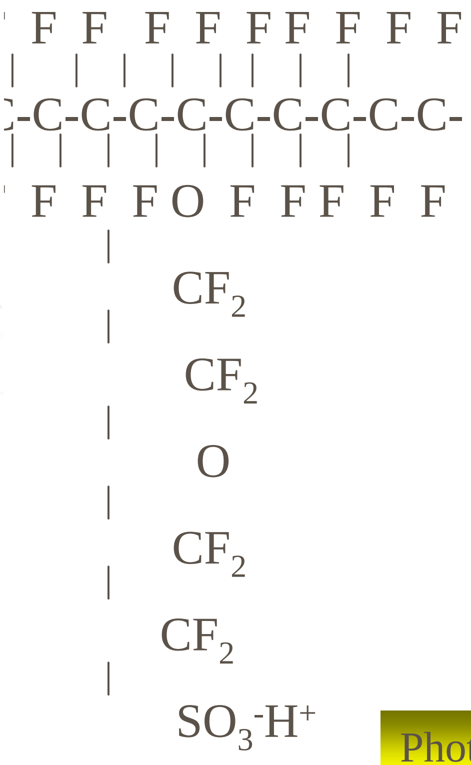
➢Membrane preparation

Membrane material: Perfluorosulfonic acid PTFE copolymer (Nafion dispersion, SE-5112, Dupont USA)

Structure of Nafion membrane :



The structure of Nafion showing the three different regions: the hydrophobic PTFE backbone, the hydrophilic ionic zone, and the intermediate region.



Photographs of cast Nafion membrane

Summary of Results

O_2 supply at cathode ; Ethanol: acid(1:30)

Electrodes	Anode Feed (Ethanol)	OCV (V)	SCCD (mA/cm^2)	MPD (mW/cm^2)	Temperatures (^{O}C)
M-9-6	0.75M	1.044	24.66	9.15	Anode: 90 Cathode: 60
Anode:1 mg/cm^2 Cathode:0.5 mg/cm^2	2M	1.102	28	11.50	Anode: 90 Cathode: 60
M-10-1	0.75M	1.083	25.55	10.01	Anode: 90 Cathode: 60
Anode:0.6 mg/cm^2 Cathode:0.6 mg/cm^2	2M	1.072	30	13.2	Anode: 90 Cathoe:60
	2M	1.081	30.5	14.58	Anode:90 Cathode: 90

OCV: Open circuit voltage; **SCCD**: Short circuit current density; **MPD**: Maximum power density.

Conclusions

- DEFC gives higher voltage (O.C.V= 1.102V) and current density at higher cathode temperature.
- O.C.V and current density increases with the increase of acid conc. in ethanol.
- Oxygen supply at cathode gives higher power density.
- Minute increase in cathode electrode-catalysts loading enhances the performance of DEFC.