RECENT TRENDS IN CATALYST DEVELOPMENT FOR PEMFC/DIRECT METHANOL FUEL CELLS

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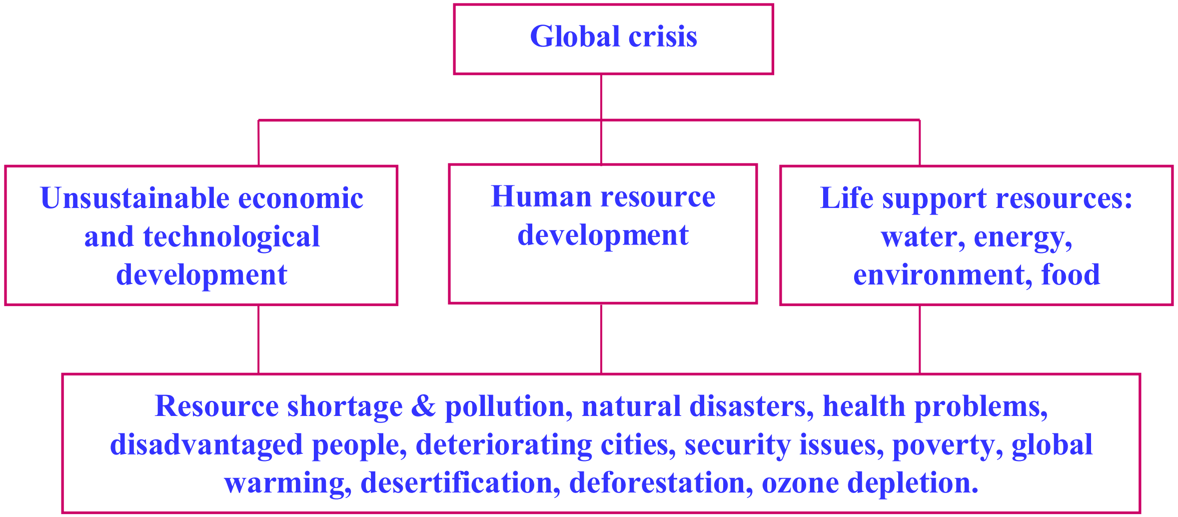
Unsustainable *Vs* Sustainable development



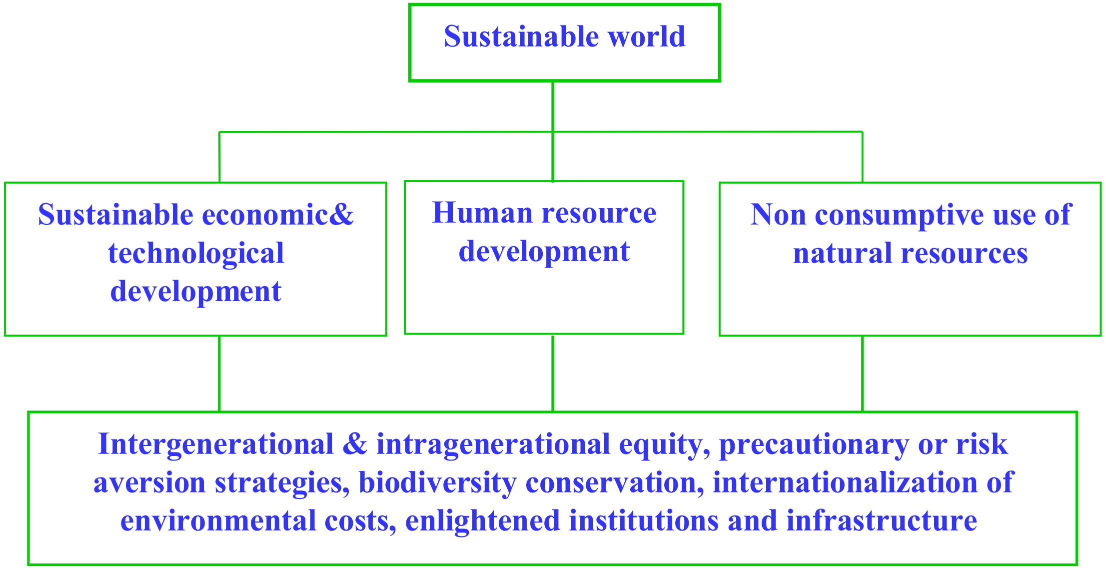
Global crisis

Unsustainable economic and technological development

Human resource development

Life support resources: water, energy, environment, food

Resource shortage & pollution, natural disasters, health problems, disadvantaged people, deteriorating cities, security issues, poverty, global warming, desertification, deforestation, ozone depletion.



Sustainable world

Sustainable economic& technological development

Human resource development

Non consumptive use of natural resources

Intergenerational & intragenerational equity, precautionary or risk aversion strategies, biodiversity conservation, internationalization of environmental costs, enlightened institutions and infrastructure

ALTERNATIVE ENERGY TECHNOLOGIES

- Alternative energy technologies are needed to address the impending energy problem
  - Reduces our dependence on foreign oil
  - Fosters energy security and national security
  - Promotes a cleaner environment

Alternative Energy Technologies

- Fuel cells
- High energy density batteries
- Supercapacitors
- Solar energy
- Wind energy
- Geothermal energy

WHY FUEL CELLS?

Direct Energy Conversion *Vs* Indirect Technology

Thermal Energy → Mechanical Energy

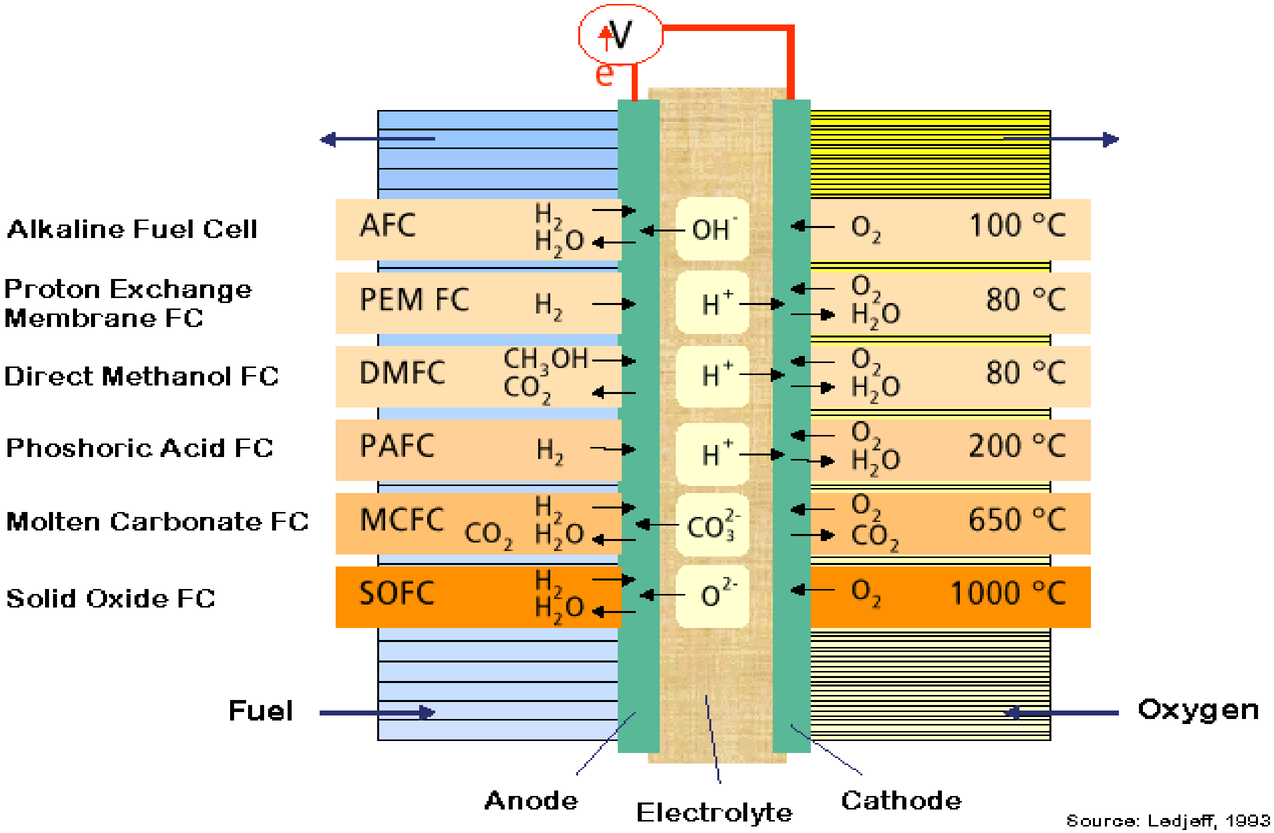
↑ *Fuel Cell* ↓

Chemical Energy of Fuels → Electrical Energy

ADVANTAGES

- ✓ **Efficiency**
- ✓ **Reliability**
- ✓ **Cleanliness**
- ✓ **Unique operating characteristics**
- ✓ **Planning flexibility**
- ✓ **Future development potential**

VARIOUS TYPES OF FUEL CELLS



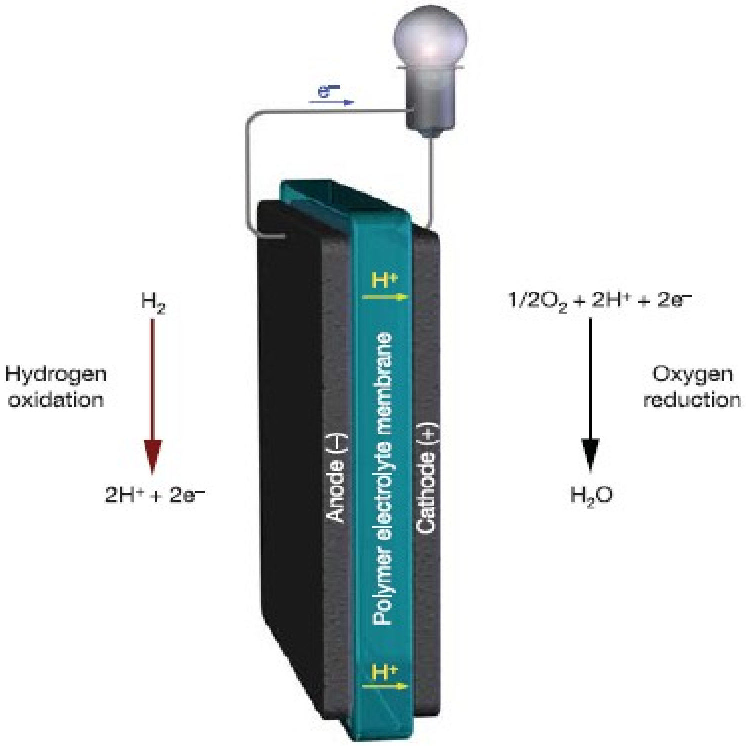
Source: Ledjeff, 1993

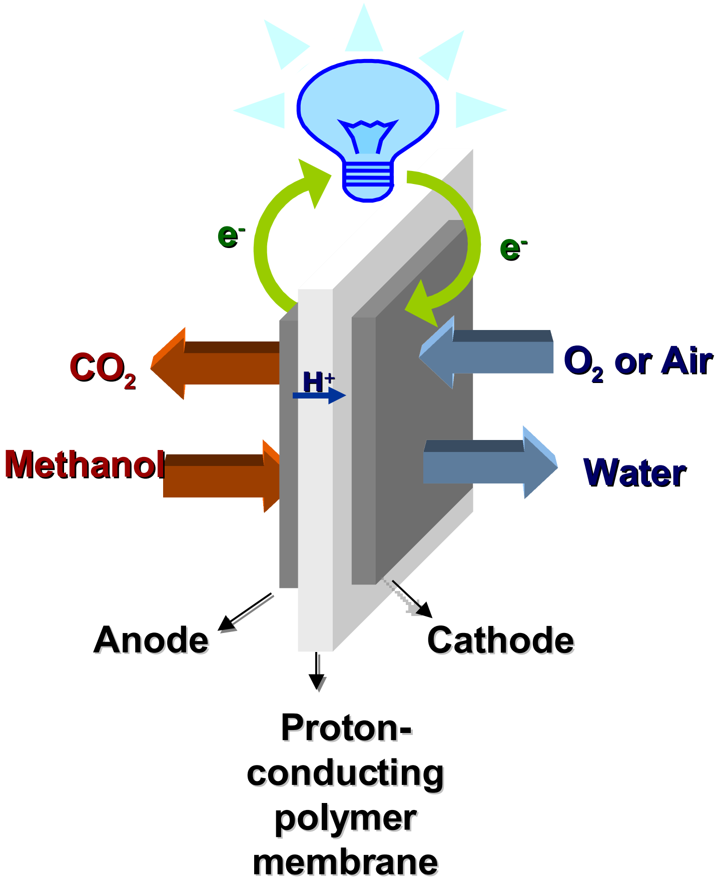
- ✓ **PEMFC:** Leading contender for vehicular applications
- ✓ **DMFC:** Possible portable applications

Chemical and Electrochemical Data on Various Fuels

FUEL	ΔG^0, kcal/mol	E^0_{theor} (V)	E^0_{max} (V)	Energy density (kWh/kg)
Hydrogen	-56.69	1.23	1.15	32.67
Methanol	-166.80	1.21	0.98	6.13
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic acid	-68-20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	-
Propane	-503.20	1.08	0.65	-

Schematics of Operational PEMFC & DMFC





$H_2 = 2H^+ + 2e^-$ 0.00V

$1/2O_2 + 2H^+ + 2e^- = H_2O$ 1.23V

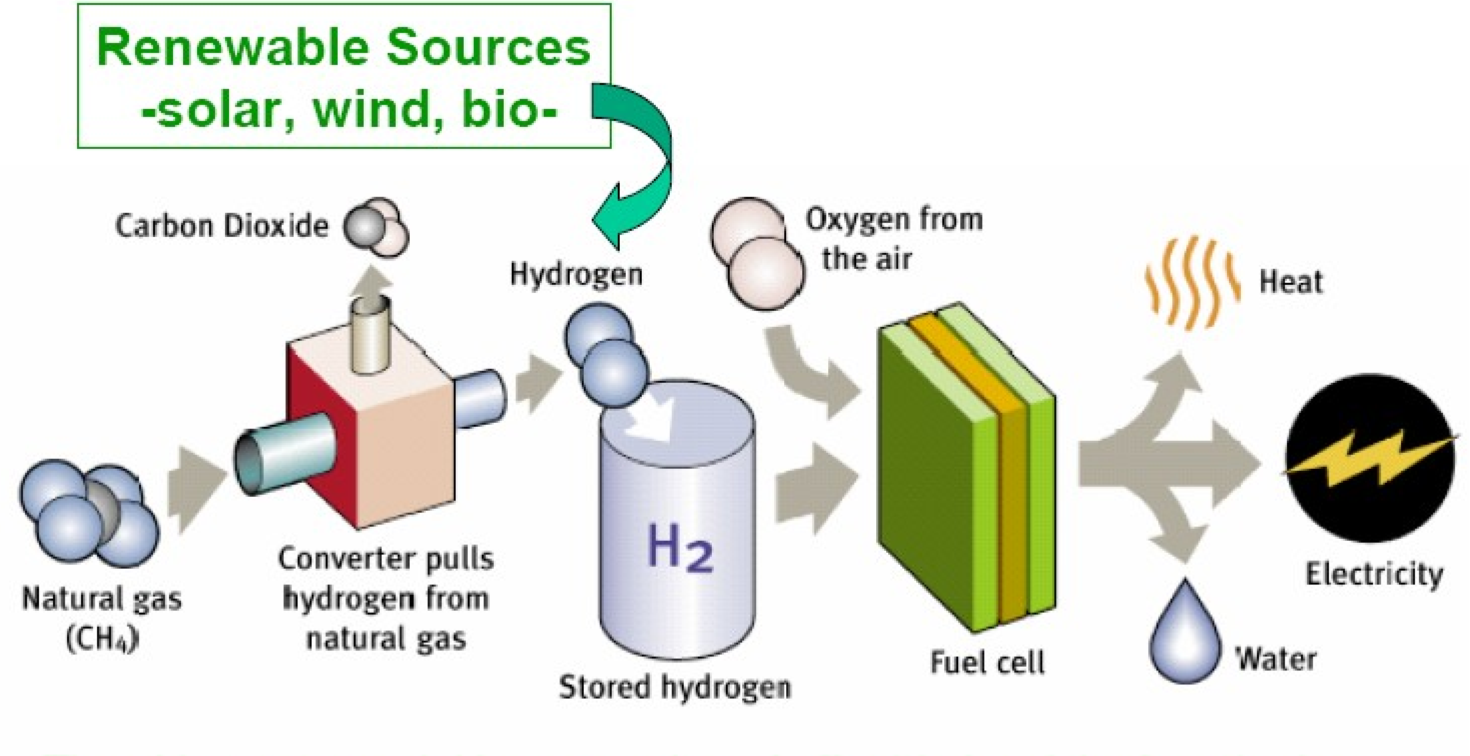
$l/2O_2 + H_2 = H_20$ 1.23V

Anode $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ 0.05 V

Cathode $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ 1.23 V

$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$ 1.18 V

“What is a fuel cell”

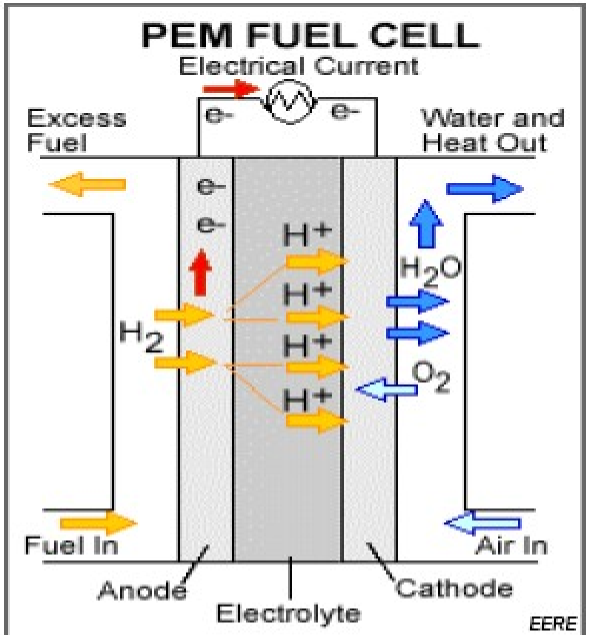


Renewable Sources
-solar, wind, bio-

The ultimate potential is generation of off-grid electricity from hydrogen produced from completely renewable, widely dispersed energy sources.

Grand Challenges & Needed Breakthroughs for Fuel Cells

PEM FC - The Whole Picture



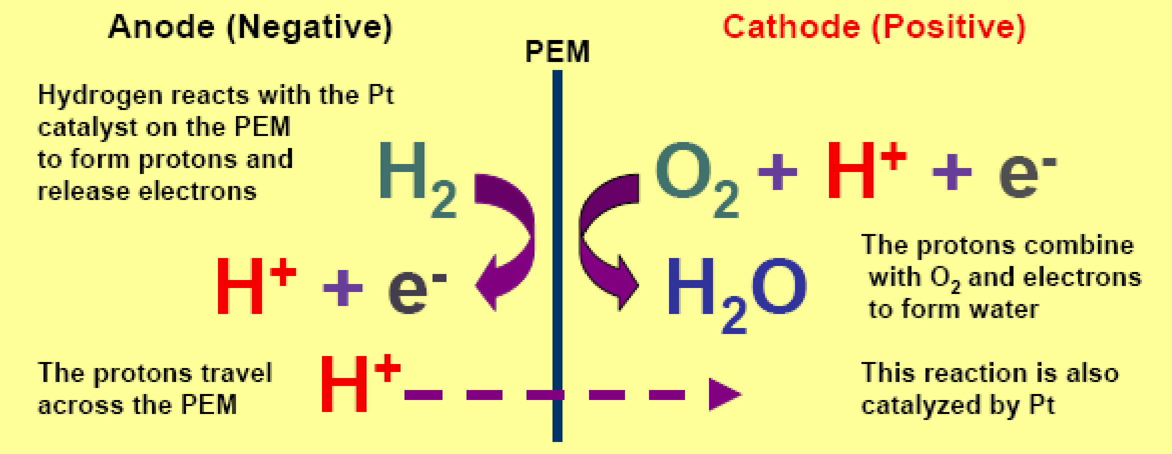
Grand Challenges
- Affordability ($/kW)
- Durability (performance loss ~ time)

Needed Breakthroughs
- Adv. Catalysts
- Adv. PEM Material
- Innovative CCM/MEA mft.

How Does a PEM FC Work?

Anode: $2H_{2(g)}$ -----> $4H^+_{(aq)} + 4e^-$

Cathode: $O_{2(g)} + 4H^+_{(aq)} + 4e^-$ ----> $2H_2O_{(l)}$



Anode (Negative)

PEM

Cathode (Positive)

Hydrogen reacts with the Pt catalyst on the PEM to form protons and release electrons

H_2

$H^+ + e^-$

$O_2 + H^+ + e^-$

H_2O

The protons combine with O_2 and electrons to form water

The protons travel across the PEM

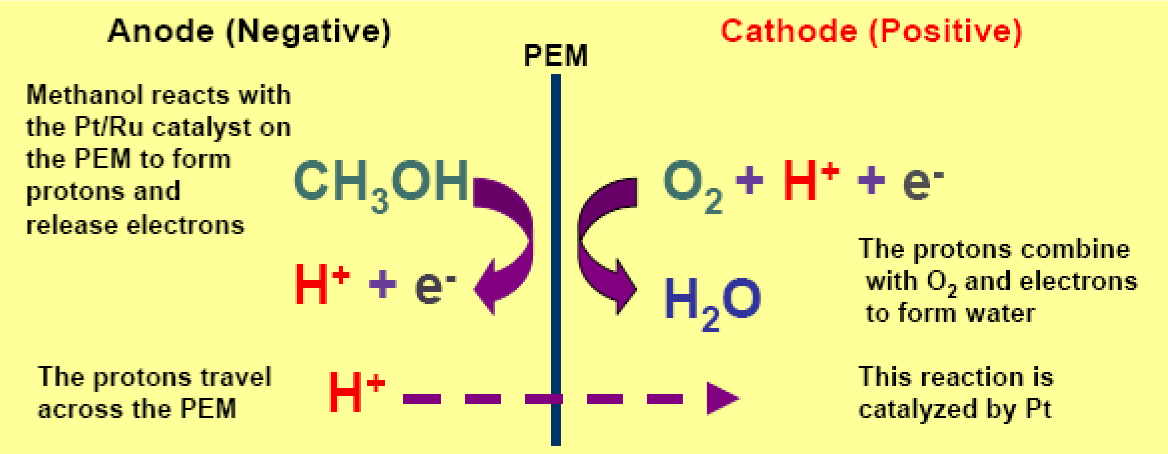
H^+

This reaction is also catalyzed by Pt

Direct Methanol PEM FC

Anode: $CH_3OH_{(aq)} + H_2O_{(l)} \text{ -----> } CO_{2(g)} + 6H^+_{(aq)} + 6e^-$

Cathode: $3/2O_{2(g)} + 6H^+_{(aq)} + 6e^- \text{ ----> } 3H_2O_{(l)}$



Anode (Negative)

PEM

Cathode (Positive)

Methanol reacts with the Pt/Ru catalyst on the PEM to form protons and release electrons

CH_3OH

$H^+ + e^-$

$O_2 + H^+ + e^-$

H_2O

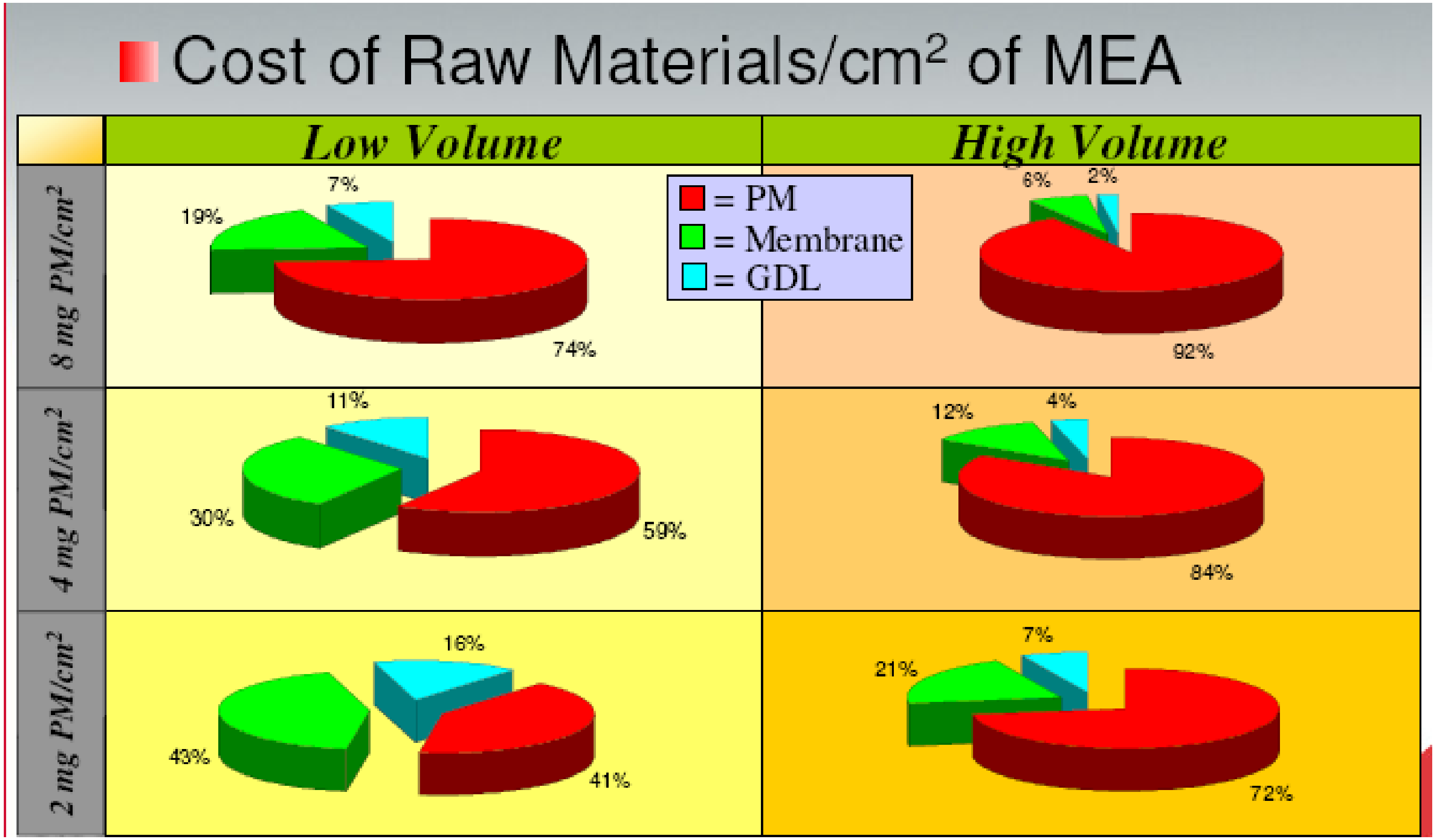
The protons combine with O_2 and electrons to form water

The protons travel across the PEM

H^+

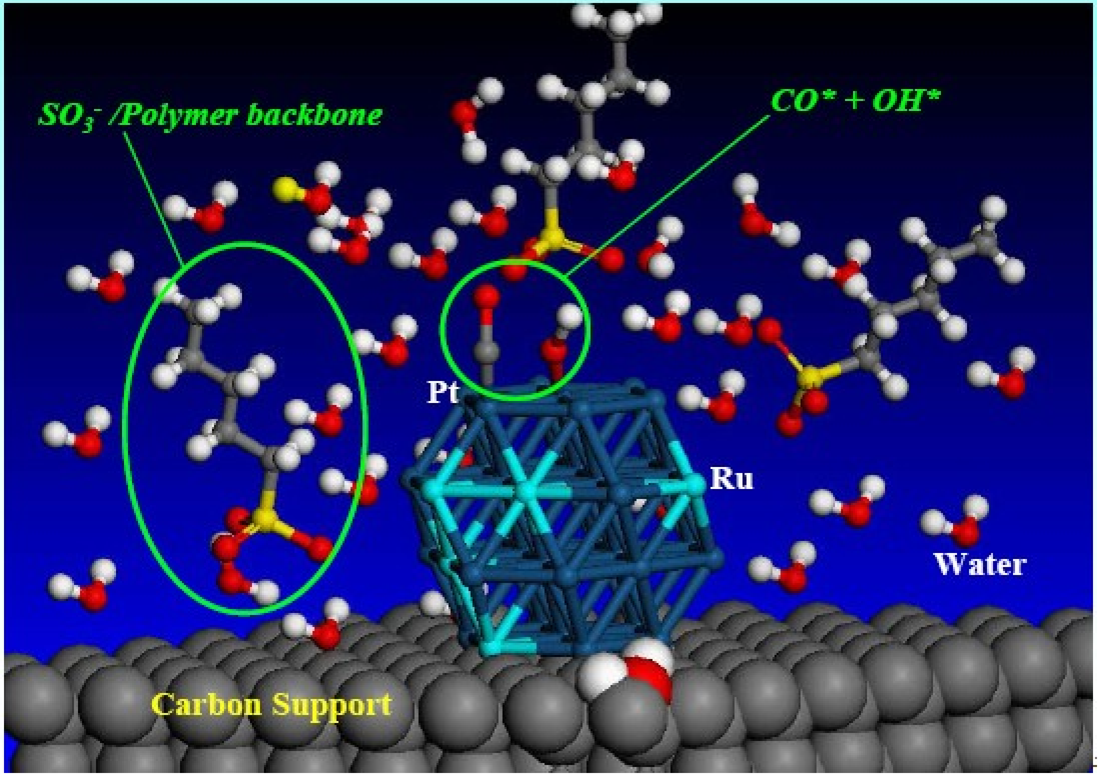
This reaction is catalyzed by Pt

DMFC MEA Raw Materials Cost Analysis

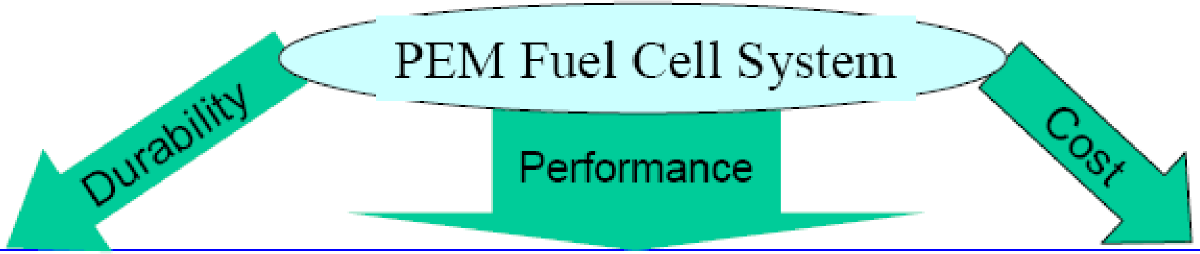


Cost of Raw Materials/cm^2 of MEA

The Chemist's Eye-view



NanoStructured Thin Film Catalysts (NSTFC) for Next Generation PEM Fuel Cells



Critical Characteristics for PEMFC Electrocatalysts

- High Specific Activity (A/cm^2-Pt)
- High ECSA (cm^2-Pt/ cm^2-planar)

High Mass Activity (A/mg-Pt)

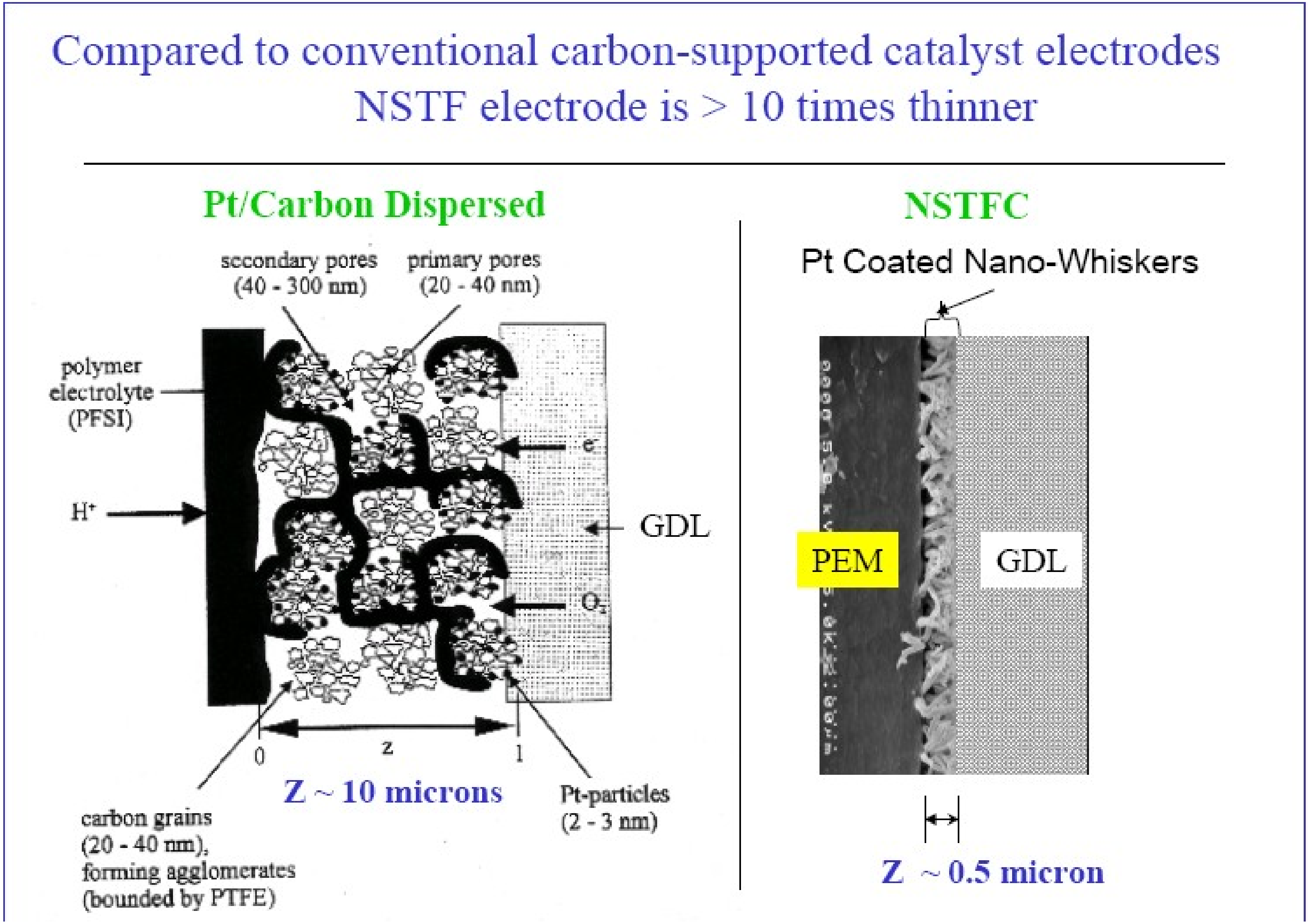
Just one of many important attributes

- High catalyst utilization - at all current densities
- Negligible mass transfer overpotential at high current densities

- High resistance to support oxidation at high potentials, start-stop, fuel starvation
- High resistance to Pt dissolution/agglomeration at high voltages, start-stop, etc.

- Robust, low cost process for fabrication
- Minimal ionic and electronic losses under dry conditions
- Cold start capable (wide RH range) and freeze tolerant

NanoStructured Thin Film Catalyst (NSTFC)



Compared to conventional carbon-supported catalyst electrodes
NSTF electrode is > 10 times thinner

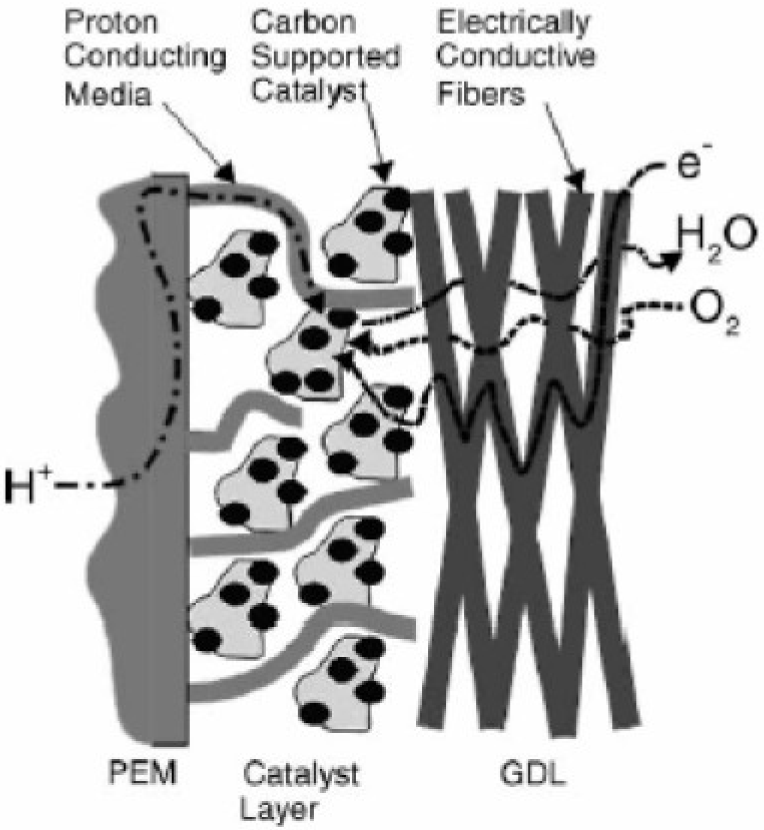
Pt/Carbon Dispersed

Z ~ 10 microns

NSTFC

Z ~ 0.5 micron

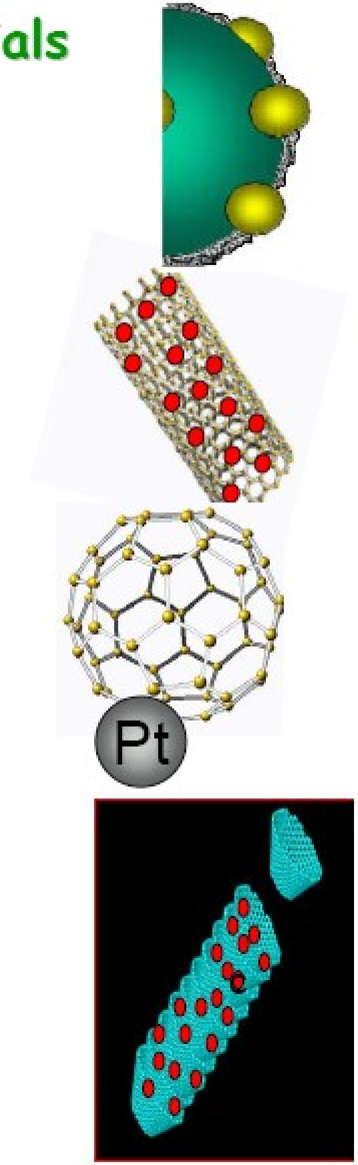
Electrode Design



- Electrode creates 'triple point':
  - Reaction at catalyst site
  - Supply of fuel/oxidant
  - Electron AND proton conductivity
  - Heat and Water removal
- 'Catalyst Coated Membrane' technology dominates:
  - Pt nano-particles plated to high surface area carbon powder
  - Via inks/dispersions deposited onto electrolyte (Wilson, Los Alamos)
- Nano-Tech Approaches:
  - Larger surface areas on electrolyte interface
  - Direct deposition of catalyst using thin film techniques
  - Engineered nano-catalyst in place of present 'ink' based techniques

Ref: S. Litster, G. McLean *PEM Fuel Cell Electrodes. J. Power Sources 2004*

Carbon nanostructures as novel support materials in fuel cells



Advantages of SWCNTs

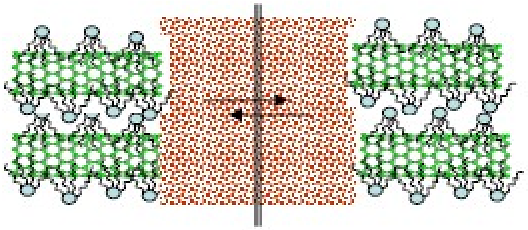
- High surface area
- Good electronic conductivity, excellent chemical and electrochemical stability
- Good mechanical strength

Goal

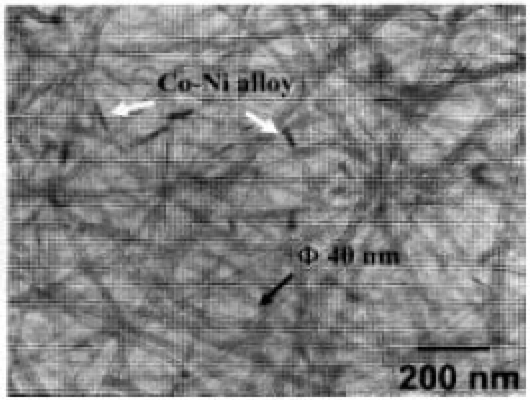
Effective utilization of carbon nanostructures for improving the performance of fuel cells

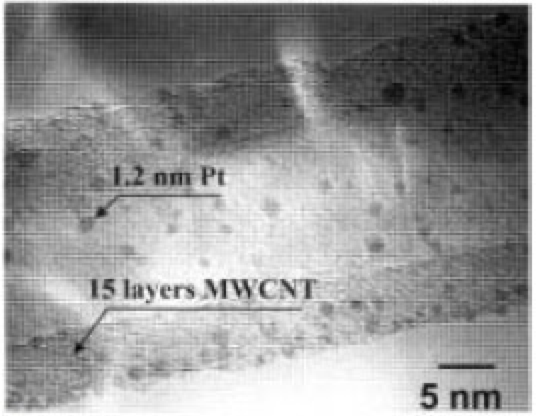
- To develop PEM assembly with CNT supports
- Improve the performance of electrocatalysts
- Minimize the catalyst content while maintaining the high power output
- Standardize the operation of nanotube based Fuel Cells

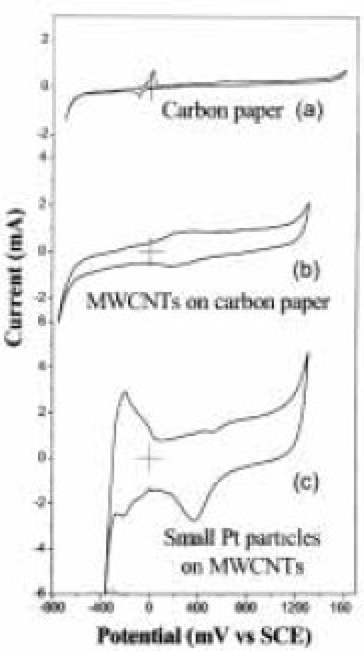
…..towards the miniaturization of fuel cells



Carbon Nanotubes(CNT) – Fuel cell Electrodes

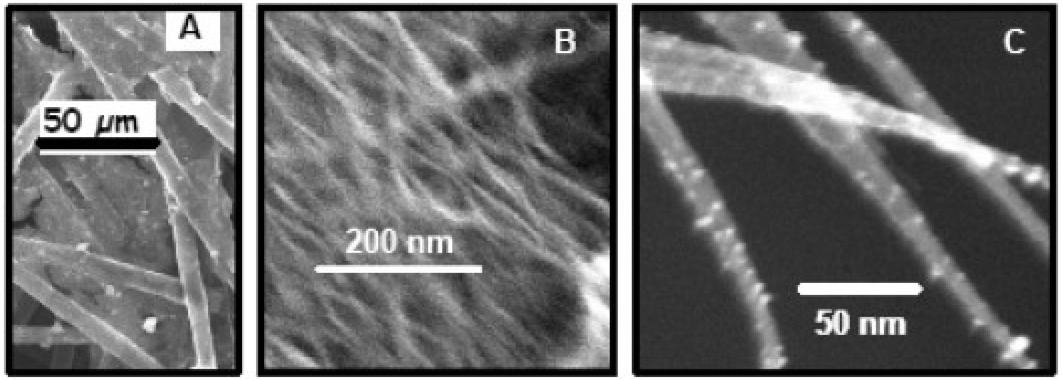




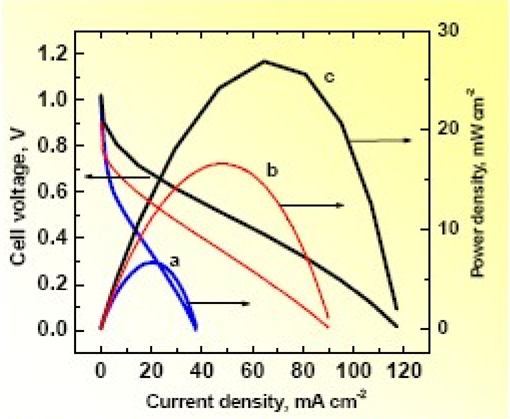


Pt nanoparticle deposited on CNT

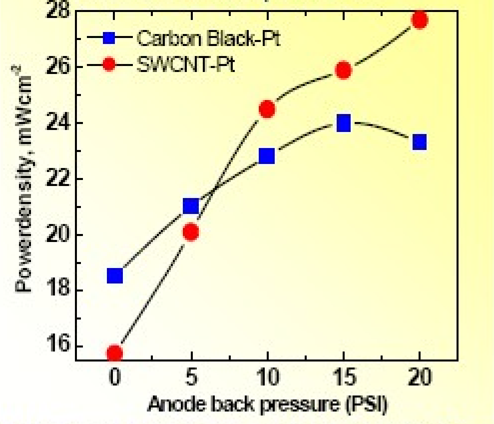
SWCNT based H_2-Fuel Cell



Galvanostatic polarization data



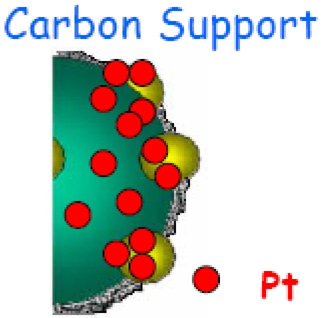
Dependence of power output on anodic back pressure



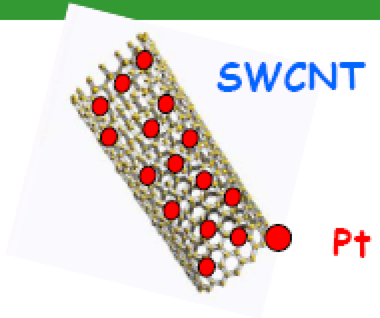
MEA was prepared by electrophoretic deposition of Pt black on varying amount of SWCNTs

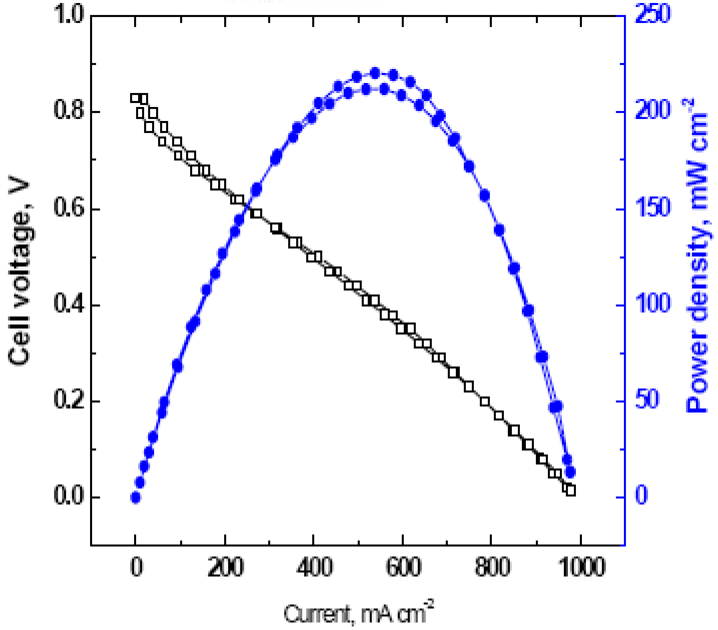
J. Phys. Chem. B, 2004. **108** 19960 – 19966 Langmuir, 2005. **21** 8487 - 8494

Fuel cell performance

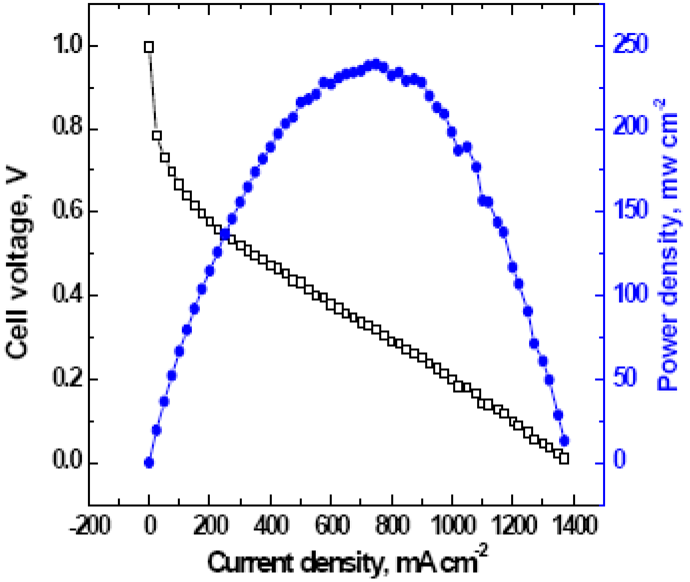


0.2 mgPt/ cm^2 (Pt/C, Nafion 117 as membrane, Test conditions 70 °C





Peak power density, 224 mWcm^{-2}



Peak power density, 240 mWcm^{-2}

WHY METHANOL ?

- ✓ High specific energy density
- ✓ Clean liquid fuel
- ✓ Larger availability at low cost
- ✓ Easy to handle and distribute
- ✓ Made from Natural gas and renewable sources
- ✓ Possible direct methanol operation fuel cell
- ✓ Economically viable option

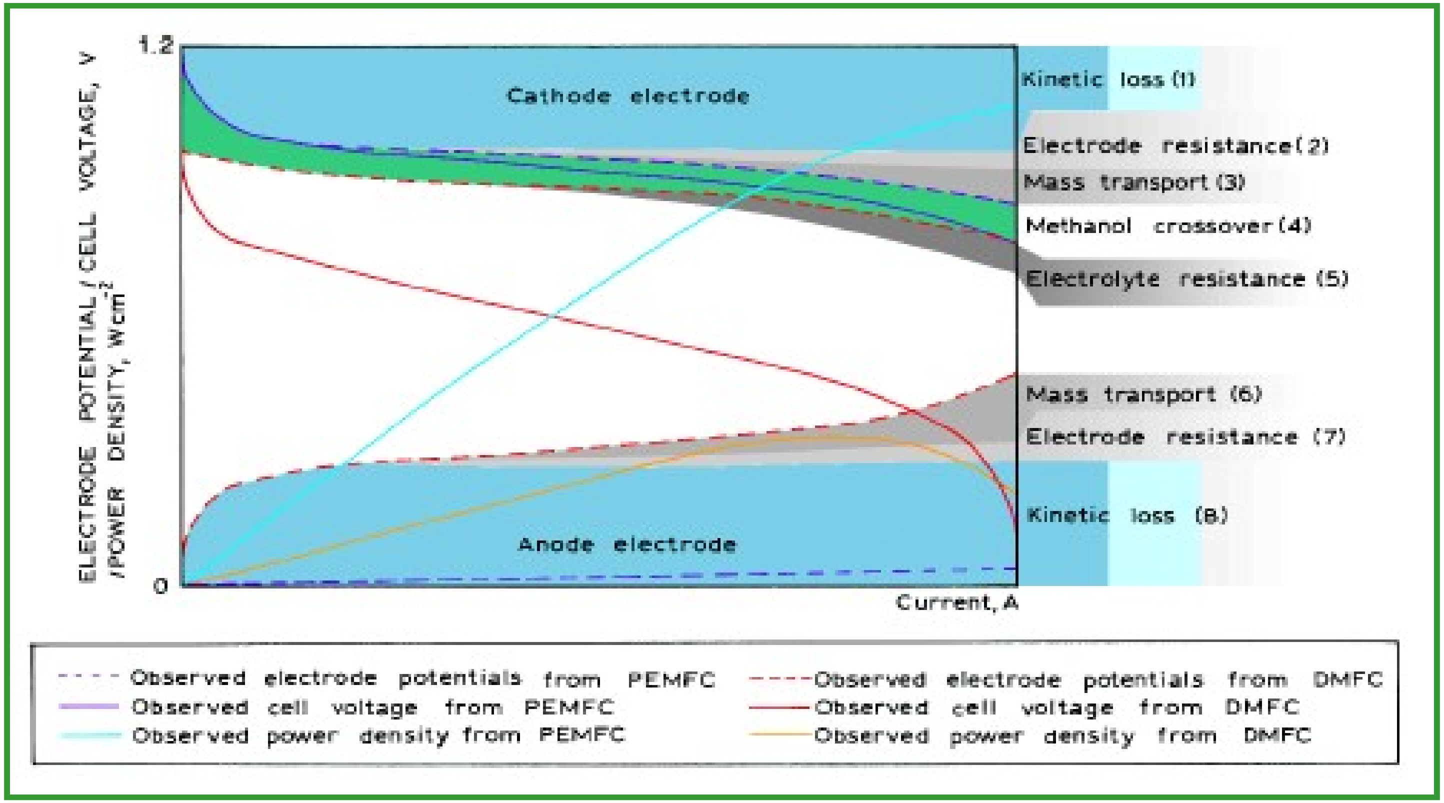
ADVANTAGES OF DMFC

- Elimination of the external Fuel Processor
- Elimination of complex humidification & thermal management systems
- Low costs for DMFC
- Can use existing infrastructure for gasoline

DIFFICULTIES IN DMFC

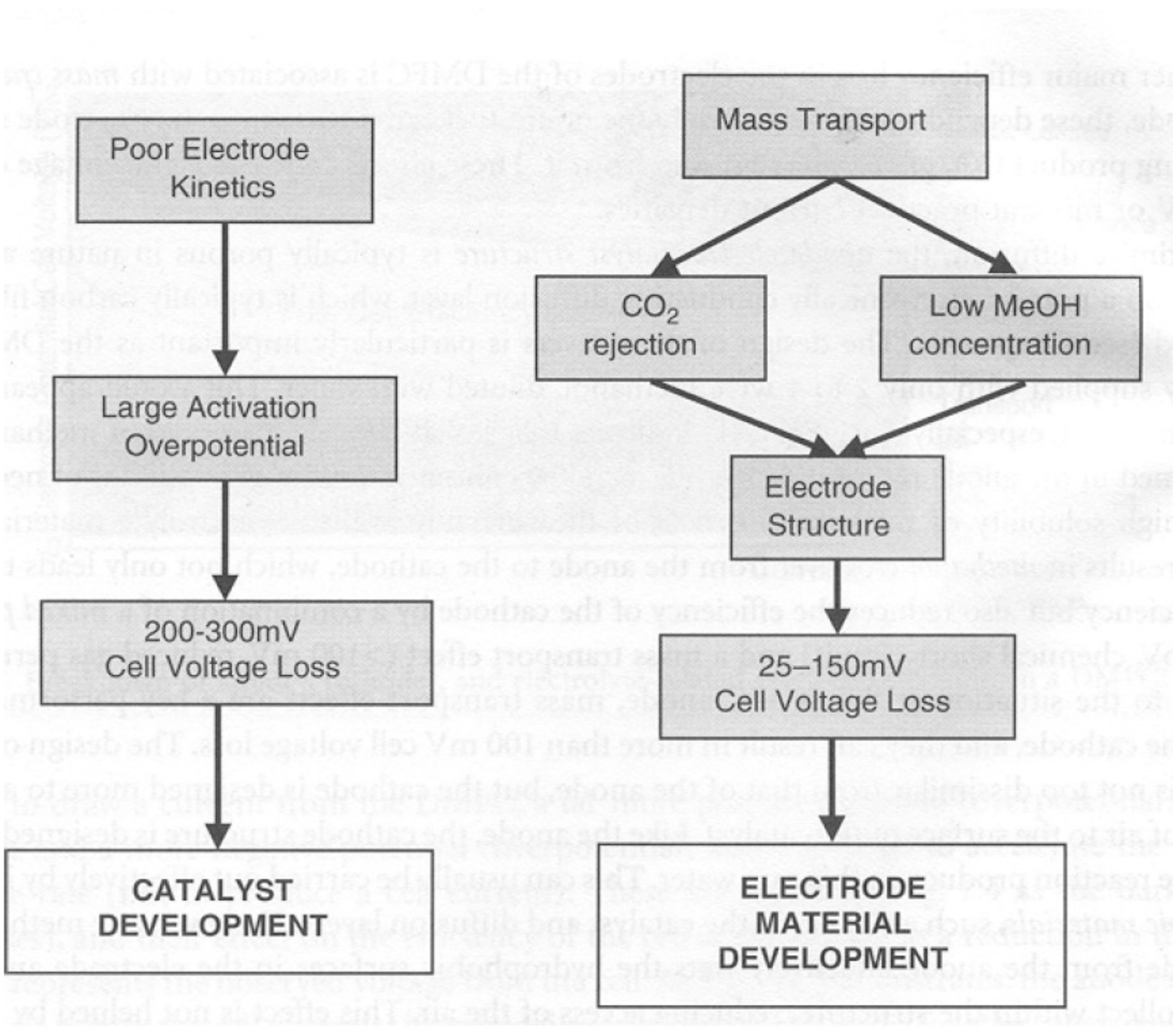
- ➢ Poor electrode kinetics
- ➢ Fuel crossover
- ➢ Electrocatalysts

Comparison of PEMFCs & DMFCs



Performance losses seen in a typical DMFC MEA operating with dilute MeOH & Air at 80ºC, compared to those in a PEMFC

DMFC ANODE



Poor Electrode Kinetics

Large Activation Overpotential

200-300mV Cell Voltage Loss

CATALYST DEVELOPMENT

Mass Transport

CO_2 rejection

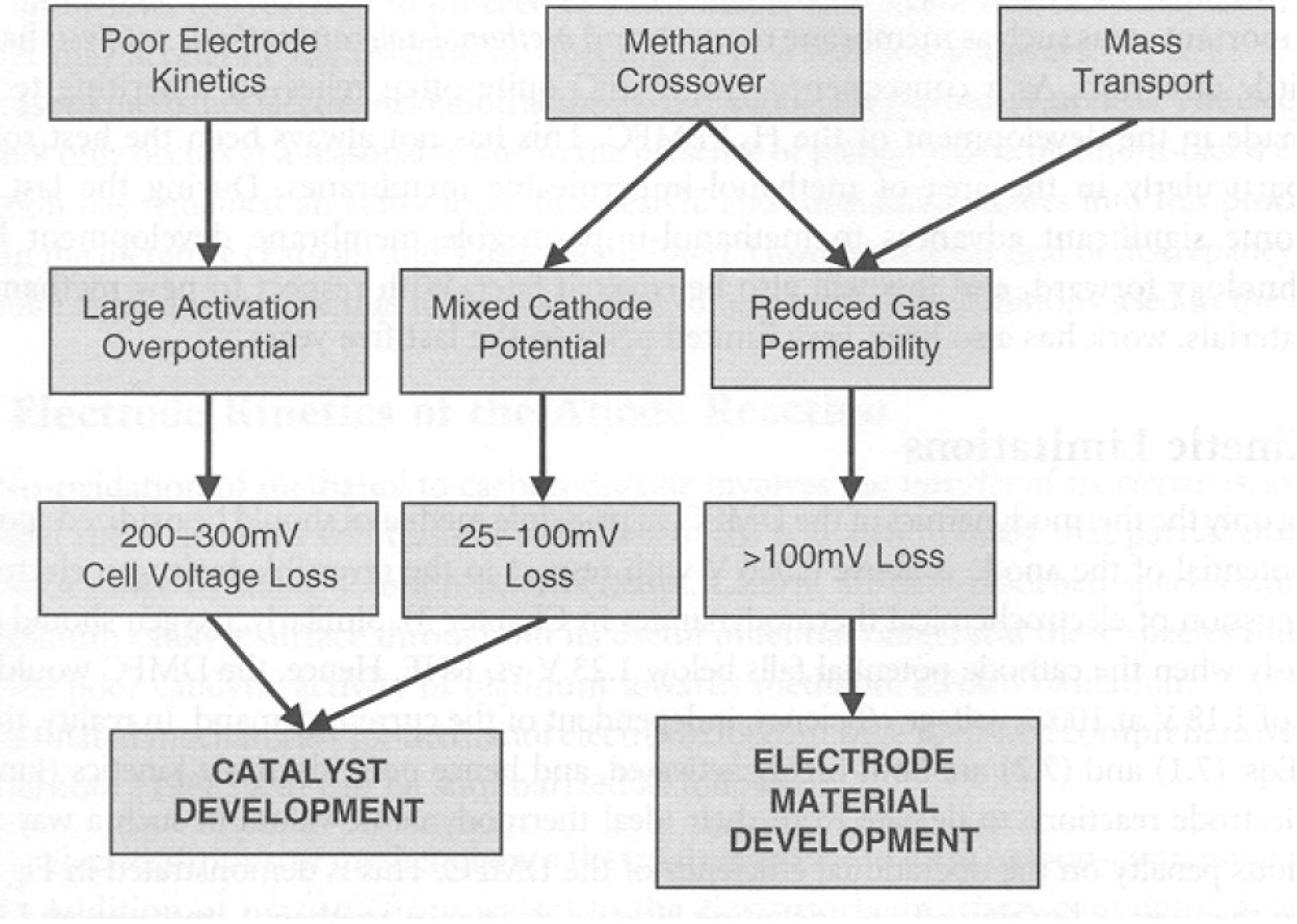
Low MeOH concentration

Electrode Structure

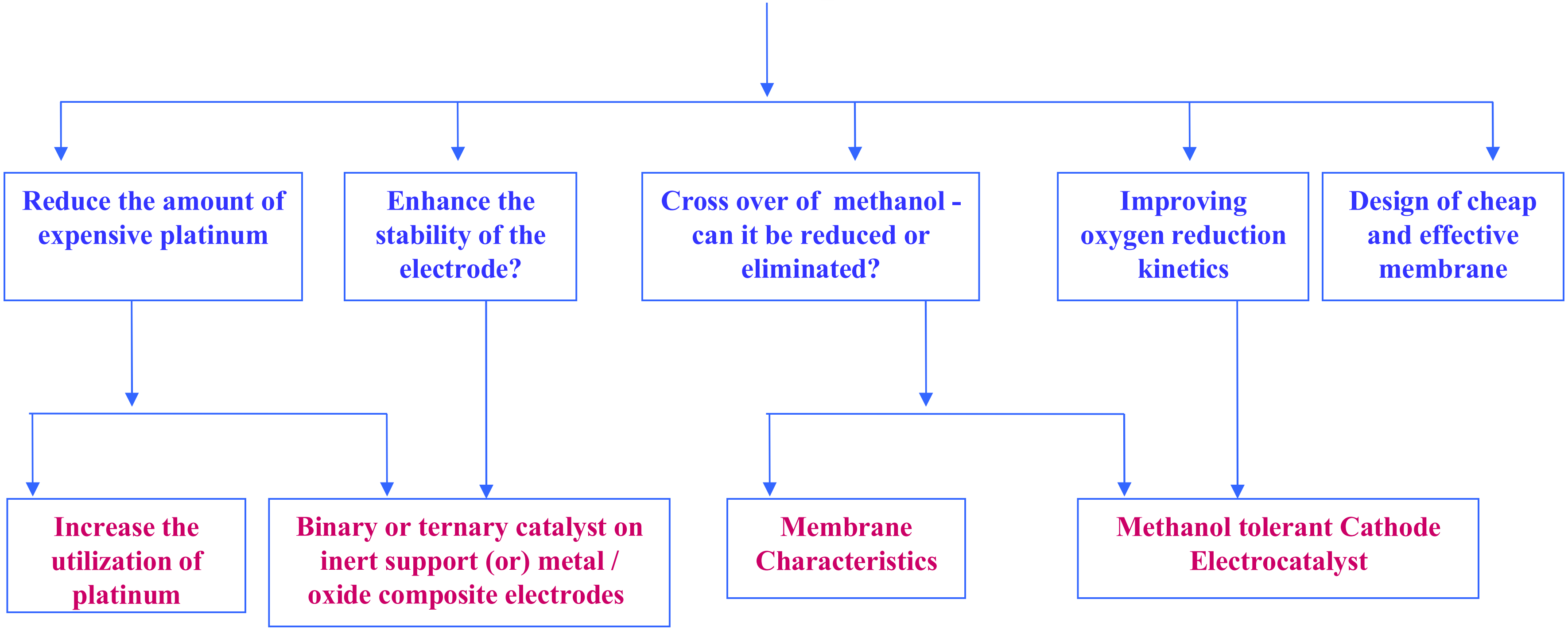
25–150mV Cell Voltage Loss

ELECTRODE MATERIAL DEVELOPMENT

PEMFC/DMFC CATHODE



Material Challenges facing PEMFC/DMFC developers



Reduce the amount of expensive platinum

Enhance the stability of the electrode?

Cross over of methanol - can it be reduced or eliminated?

Improving oxygen reduction kinetics

Design of cheap and effective membrane

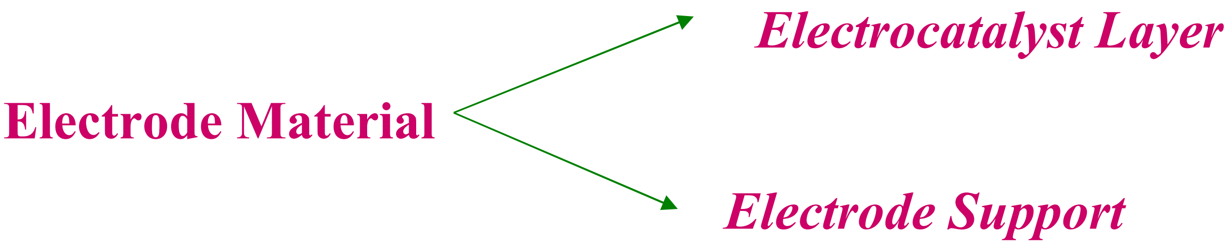
Increase the utilization of platinum

Binary or ternary catalyst on inert support (or) metal / oxide composite electrodes

Membrane Characteristics

Methanol tolerant Cathode Electrocatalyst

OUR FOCUS



Electrode Material

Electrocatalyst Layer

Electrode Support

1. Identification of suitable catalyst

2. Improve/Tailor Carbon material → desired electrochemical properties

→ design a suitable support material

Identification of Suitable Catalyst

- **Listing out & classification of reported catalysts**
- **Why these catalysts?**
- **Limitations in the present ‘best’ available catalyst**
- **Evolving logistics for a novel catalyst (modifying the present system/completely new one)**

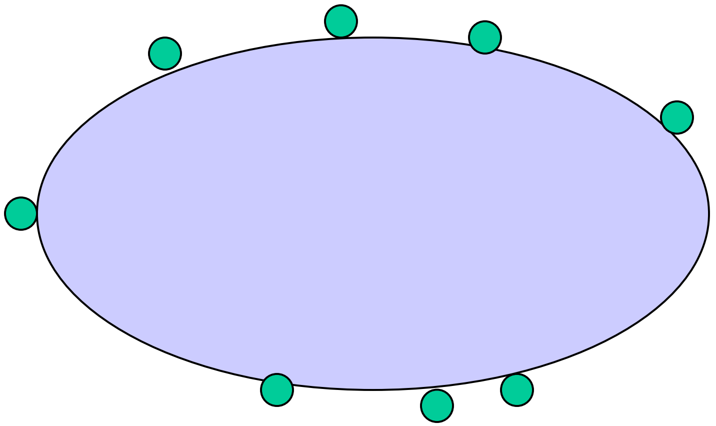
Logistics

- ***Model studies (atomic level interactions)***
- ***Questions not answered in the present system***
- ***Awareness of the limitations with the proposed system followed by trouble shooting possibilities***
- ***Mechanism / Role of a catalyst***

CATALYST DEVELOPMENT FOR PEMFC/DMFC

- **Fundamental understanding of the reaction**
- **Formulation & Design of new catalysts**
- **Noble & Non-noble metal catalysts – Associated Issues**
- **Optimization of catalytic properties of the electrodes**
- **Where to go?**

Why Supported Catalyst?



What is the support?
How to choose better Support ?

Utilization ↑

Stability ↑

Tailoring Support

Support - Why Carbon?

Properties attractive to electrochemical applications…

Chemical properties

- Good corrosion resistance
- Availability in high purity
- Forms intercalation compounds

Electrical properties

- Good conductivity

Mechanical properties

- Dimensionally & mechanically stable
- Low modulus of elasticity
- Light weight & adequate strength
- Availability in variety of physical structures
- Easily fabricated into composite structures

Carbon as Electrode Material

- Anisotropic electronic property
- Surface can adsorb wide range of materials
- Richer & more complex surface chemistry
- Strong covalent bond formation with variety of surface modifiers
- Wide useful potential window

Carbon is unique material

Tailoring carbon for its suitability as support in MOR &ORR – How?

- Knowledge of the interaction & location of the active phase with the support
- Surface groups on the support
- Anchorage sites for metal precursor
- Active centers due to acid-base or red-ox properties
- Possible modification procedures

Preparation of Hydrongen/Methanol Oxidation Catalysts with the Modified Supports in DMFC

Methanol oxidation Mechanism: addition of the secondary metal

1. Bifuntional mechanism

$Pt + CH_3OH \rightarrow Pt\text{-}(CH_3OH)_{ads}$ (1)

$Pt\text{-}(CH_3OH)_{ads} \rightarrow Pt\text{-}(CH_3O)_{ads} + H^+ + e^-$ (2)

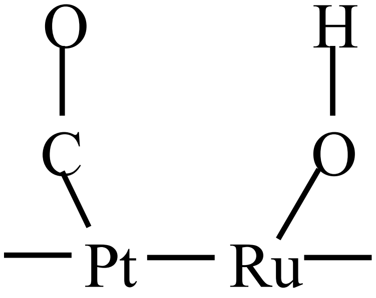
$Pt\text{-}(CH_3O)_{ads} \rightarrow Pt\text{-}(CH_2O)_{ads} + H^+ + e^-$ (3)

$Pt\text{-}(CH_2O)_{ads} \rightarrow Pt\text{-}(CHO)_{ads} + H^+ + e^-$ (4)

$Pt\text{-}(CHO)_{ads} \rightarrow Pt\text{-}(CO)_{ads} + H^+ + e^-$ (5)

$M + H_2O \rightarrow M\text{-}(OH)_{ads} + H^+ + e^-$ (6) slow step

$Pt\text{-}(CO)_{ads} + M\text{-}(OH)_{ads} \rightarrow Pt + M + CO_2 + 2H^+ + 2e^-$ (7) slow step



$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e^-$ (0.7V)

$Ru + H_2O \rightarrow Ru\text{-}OH + H^+ + e^-$ (0.2V)

2. Electronic mechanism

The secondary metal modifies the electronic properties of the catalyst, weakening the chemical bond b/w platinum & the surface intermediate.

Ref) A. Hamnett, Catal. Today, 38, 445 (1997).

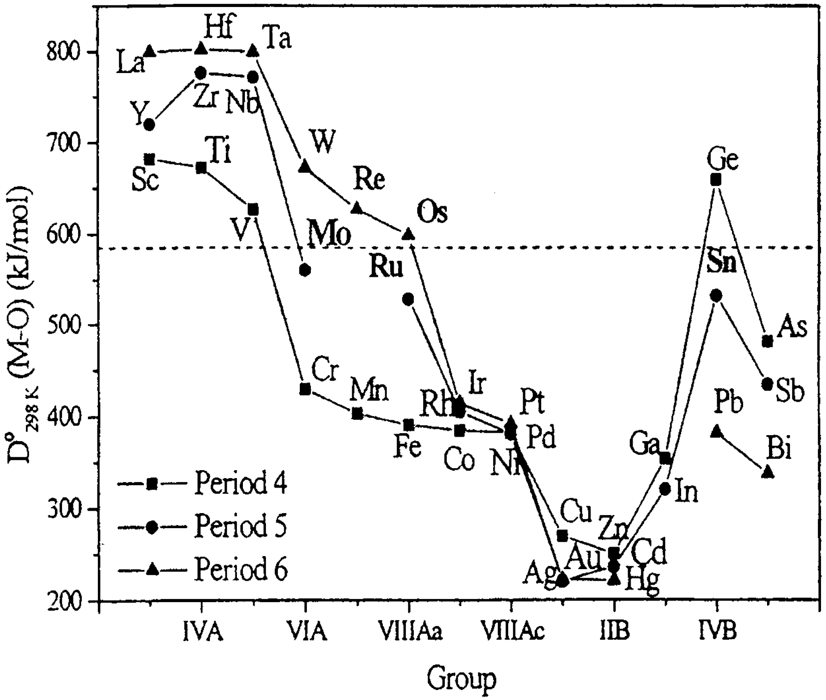
3. Structural mechanism

The Pt(111) face has been shown to have a much higher activity than other faces with respect to methanol oxidation.

Ref) W. Chrzanowski et al., Langmuir, 14, 1967 (1998).

Choice of secondary metal depends on the affinity of metal for oxygen

When the bond strength b/w Pt and C of CO is same with that b/w 2nd metal and oxygen, it is easy to break the bond of Pt and CO and to form CO_2.



dissociation energy b/w the Pt and C

The metal-oxygen bond dissociation energy [D^o_{298K} (M-O)] in diatomic molecules as a function of grouping the period.

Ref) I.T. Bae et al., J. Phys. Chem., 297, 185 (1985).

Recent Research Routes

Active metals

- Binary catalysts: PtRu, PtW, PtNi, PtSn, PtMo, PtPd, PtFe, PtCr, PtNi etc.
- Ternary catalysts: PtRuW, PtRuMo, PtRuV etc.
- Quaternary catalysts: PtRuRhNi, PtRuSnW etc.

Supports

- Carbon black: Acetylene black (SBET=50m^2/g), Vulcan XC-72 (SBET=250m^2/g), KETJEN black (SBET=1000m^2/g) etc.
- Others: CNTs (carbon nanotubes), GNFs (graphite nanofibers), MCMBs (mesocarbon microbeads) etc.

Catalyst preparations

- Physical methods: Spray-drying, co-precipitation, sol-gel, sputtering etc.
- Chemical methods: Thermal decomposition, impregnation, colloid etc.
- Modified colloidal method, spontaneous deposition, implantation method using plasma etc.

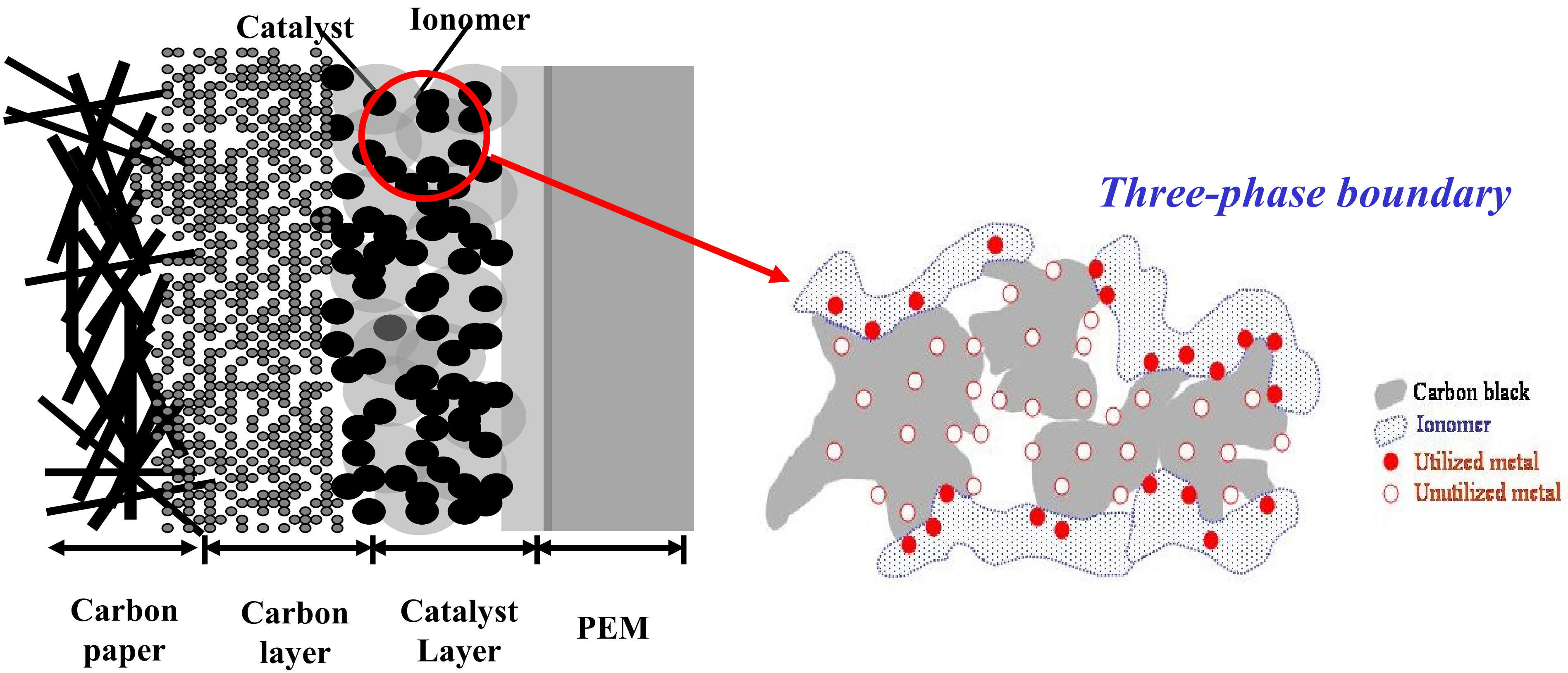
Others

- To increase voids→ addition of void forming, solvent having a high boiling point etc.
- To improve the structure of three-phase boundary of the electrode

Improve the utilization of methanol oxidation catalysts

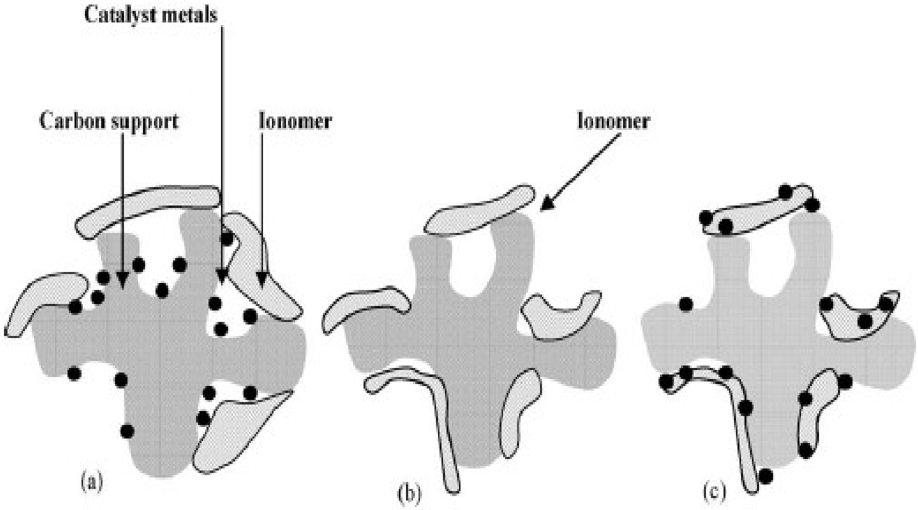
Preparation of ionomer- coated carbon supports

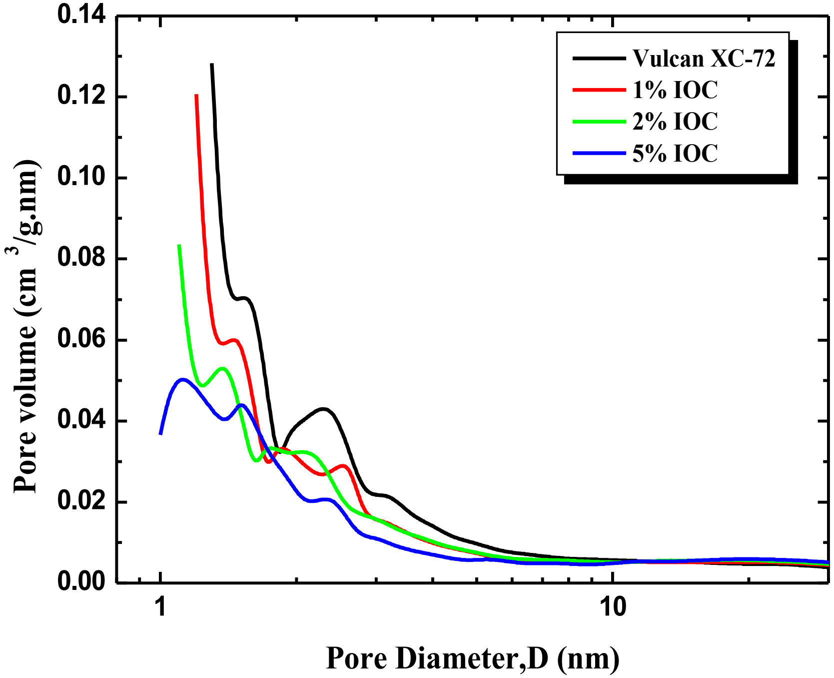
(i) To reduce the micropore volume in carbon black particles
(ii) To extend the area of the three-phase boundary



Three-phase boundary

*Ionomer- coated carbon supports : **Pore-Size Distribution***





(a) Catalyst–ionomer interaction in electrode using plain carbon as a support
(b) ionomer-coated carbon support
(c) catalyst–ionomer interaction on ionomer-coated carbon support.

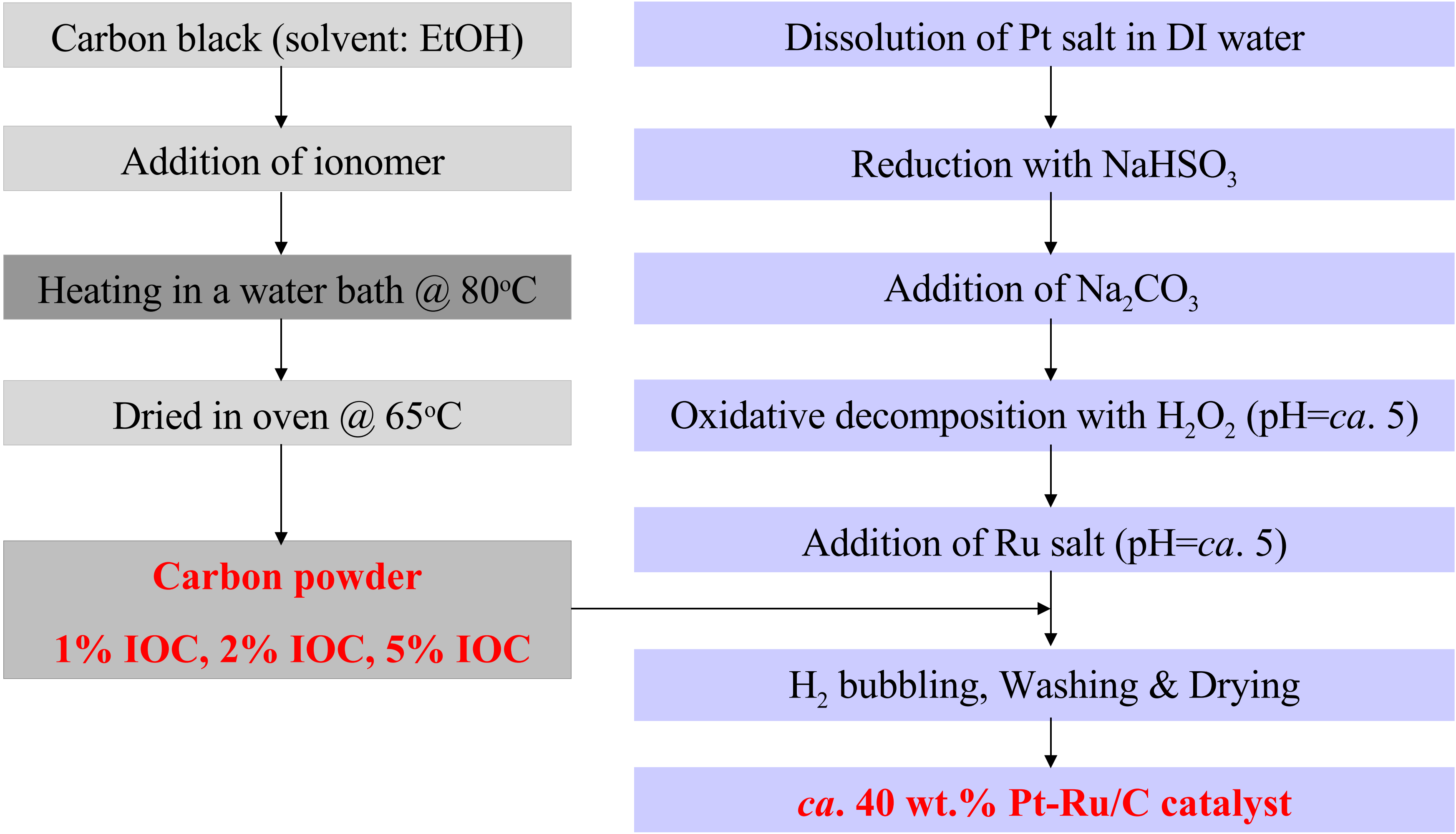
BET surface area

Vulcan XC-72	**(217 m^2/g)**
1% IOC	**(189 m^2/g)**
2% IOC	**(178 m^2/g)**
5% IOC	**(161 m^2/g)**

Catalyst Preparation

Colloidal Method by Watanabe *et al.*

[J. Electroanal. Chem., 229, 395 (1987)]



Carbon black (solvent: EtOH)

Addition of ionomer

Heating in a water bath @ 80°C

Dried in oven @ 65°C

Carbon powder

1% IOC, 2% IOC, 5% IOC

Dissolution of Pt salt in DI water

Reduction with $NaHSO_3$

Addition of Na_2CO_3

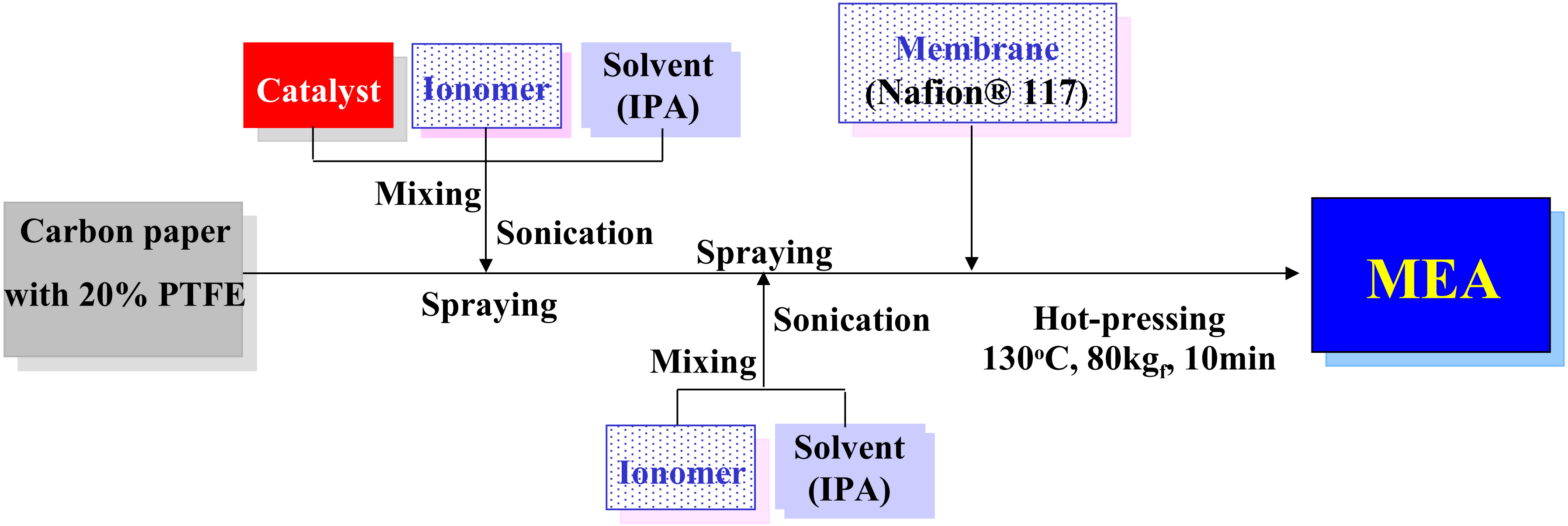
Oxidative decomposition with H_2O_2 (pH=*ca*. 5)

Addition of Ru salt (pH=*ca*. 5)

H_2 bubbling, Washing & Drying

***ca*. 40 wt.% Pt-Ru/C catalyst**

Fabrication of MEA (Electrode area = 10.89 cm^2)



Catalyst

Ionomer

Solvent (IPA)

Mixing

Sonication

Membrane (Nafion® 117)

Carbon paper with 20% PTFE

Spraying

Spraying

Sonication

Mixing

Ionomer

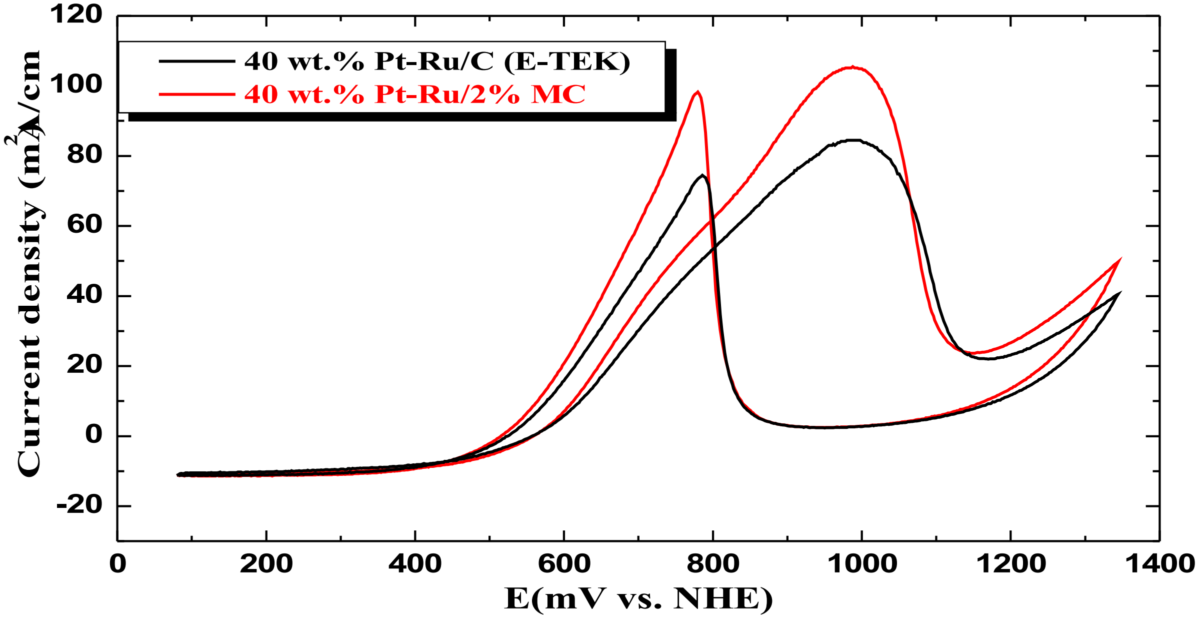
Solvent (IPA)

Hot-pressing
130°C, 80kg$_f$, 10min

MEA

Electrode	Catalyst	Metal Loading	Ionomer/Catalyst
Cathode	46.5 wt.% Pt/C (Tanaka)	3 mg Pt/cm^2	0.3 (inner: 1/4, outer: 3/4)
Anode	*ca*. 40 wt.% Pt-Ru/C (Home-made & E-TEK)	3 mg Pt-Ru/cm^2	0.15, 0.3, and 0.6 (inner: 1/4, outer: 3/4)

Cyclic Voltammetries



Cyclic voltammograms of prepared catalysts for the electrooxidation of methanol in 0.5M H_2SO_4 + 1M CH_3OH with a scan rate of 25mV/s & scan cycle of 30.

Incorporation of ionomer into carbon increased the EAS

CATHODE RESEARCH – MAIN FOCUS

- Selective cathode catalyst and/or
- Methanol-tolerant catalyst for oxygen reduction

ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_r = 1.229$ V

ORR- At Fuel Cell Electrodes- Associated Issues

Acid Electrolyte Conditions

- Reaction takes place at high, positive potentials – hence most metals dissolve
- Only noble metals and some of their alloys

Even with Pt!

- Formation of surface oxide
- Complications - PtO_2 is a catalyst for H_2O_2 reduction
- Involvement of high potentials - sintering

Essentially, Metal dissolution & oxide formation

Catalysts for oxygen electro-reduction

Noble metal catalysts

- Pt & certain Pt alloys
- Amounts allowable (for the air electrode) would not produce currents required for commercial success at the desired cell terminal voltage

Attempts

(i) Improve the activity at high positive potentials

(ii) Develop non-noble metal complex catalysts – macrocyclic organometallic chelates

State of the art cathode catalysts

Methanol tolerant catalyst

Metal phthalocynines, porphyrins, metal oxides,

metal carbides & chalcogenides

ORR activity & methanol tolerant capability, but the life-time still need to improve

V. Trapp et al., J. Chem. Soc., Faraday Trans. 21 (1996), 4311
R.W. Reeve et al., J. Electrochem. Soc. 145 (1998), 3463

H. Tributsch et al.,Appl. Electrochem. 31 (2001), 739

To improve ORR activity

Pt-Alloy catalysts

Pt–Co/C, Pt–Cr/C, Pt–Ni/C, Pt–Fe/C and Pt–Cr–Co/C

E. Antolini. Mater. Chem. Phys. 78 (2003), 563
S. Mukerjee, et al., J. Electrochem. Soc. 142 (1995), 1409

Our Directions

Our Focus

Increasing air utilization in the cathode

Incorporation of oxygen storage materials

Why Ceria?

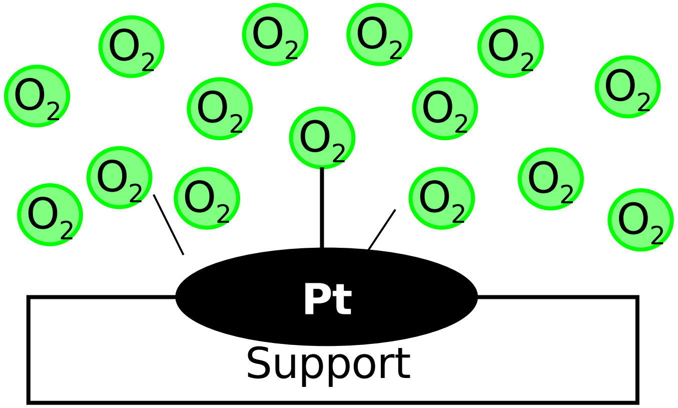
The ability of ceria to store, transport and release oxygen

$$CeO_2 \leftrightarrow CeO_{2-x} + (x/2)\,O_2 \qquad (0 \leq x \leq 0.5)$$

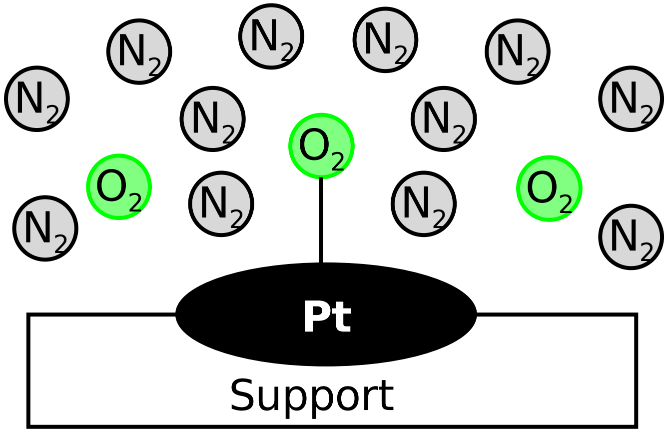
Unique and delicate balance between structural (phase formation), kinetic (rate of shift between reduced and oxidized states ($Ce^{3+} \leftrightarrow Ce^{4+}$) and textural (presence of surface cerium sites) factors

Ceria functions as an oxygen buffer

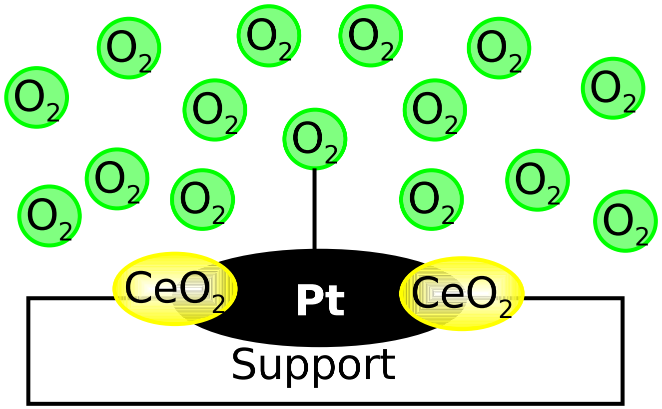
Role of ceria in ORR at air



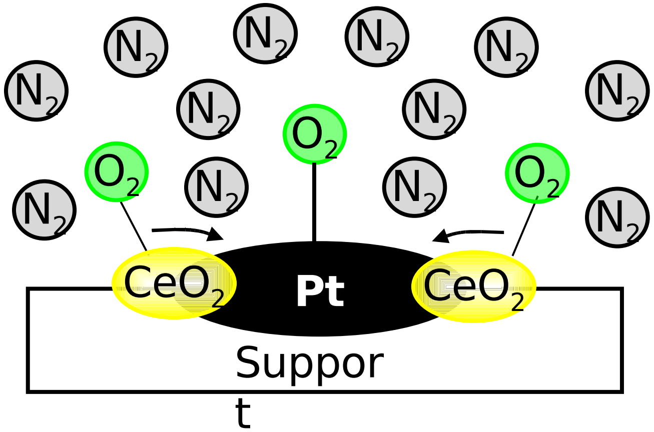
(a) Oxygen



(b) Air

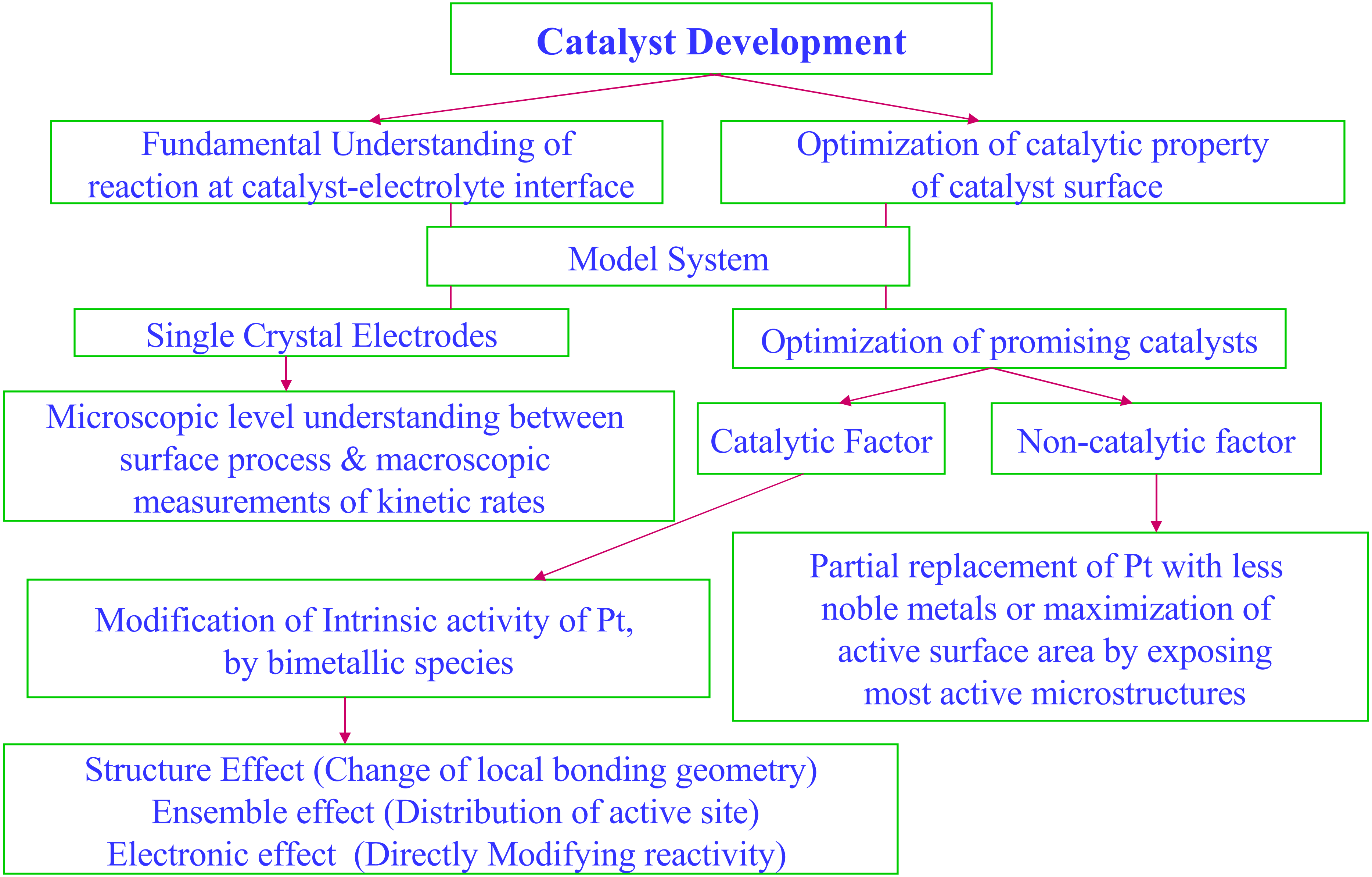


(a) Oxygen



(b) Air

Art & Science of Catalyst Development



Catalyst Development

Fundamental Understanding of reaction at catalyst-electrolyte interface

Optimization of catalytic property of catalyst surface

Model System

Single Crystal Electrodes

Microscopic level understanding between surface process & macroscopic measurements of kinetic rates

Optimization of promising catalysts

Catalytic Factor

Non-catalytic factor

Modification of Intrinsic activity of Pt, by bimetallic species

Partial replacement of Pt with less noble metals or maximization of active surface area by exposing most active microstructures

Structure Effect (Change of local bonding geometry)
Ensemble effect (Distribution of active site)
Electronic effect (Directly Modifying reactivity)

Fuel Cell Technology : R&D - Multidirectional!

- *Multi-component* (CH_3OH, H_2O, CO_2, O_2, etc.)
- *Multi-phase* (liquid, gas, solid)
- *Multi-scale* (nano, micro, macro)
- *Multi-coupled* (fluid flow, heat/mass transfer, electrochemical reactions)
- *Multi- discipline* (electrochemistry, material, mechanical engineering, etc.)

Stylized Stages of Technological Development

Stage	Mechanism	Cost	Commercial Market Share	Status
Invention	Seeking & Stumbling upon new ideas, breakthroughs, basic research	High	0%	↑ Radical ↓
Innovation	Applied research, development, demonstration (R&D projects)	High, focused on promising ideas	0%	
Niche Market	Investments in field projects, learning by doing	High, but declining with standardization of productions	0-5%	↑ Incremental ↓
Pervasive diffusion	Standardization and mass production, economies of scale, network building	Rapidly declining	Rapidly rising (5-50%)	
Saturation	More efficient competitor's arrival, redefinition of performance requirements	Low, sometimes declining	Maximum (up to 100%)	↑ Mature ↓
Senescence	Domination by superior competitor	Low, sometimes declining	Declining	

Fuel Cells – Bird's Eye View!

Fuel cells are efficient, silent, reliable and clean!

Hurdles for Commercialization – Material Selection!

- Present FC prototypes often use materials selected more than 25 years ago.
- Commercialization aspects, including cost and durability have revealed inadequacies in some of these materials
- Pt is the most active material - To reduce the cost nanoparticles of Pt on carbon → reduce loading from 2 → 0.5mg cm^{-2} without impacting on performance & life time.
- Less expensive nanocatalysts have to be identified to replace expensive Pt catalysts.
- Development of fluorine free, less expensive membrane materials – high conductivity, low swelling, low gas & methanol permeability & stability
- With advanced alternative materials, considerable R&D would be essential to optimize & manufacture new MEAs
- In PEMFCs, hydrogen production/storage/ transportation, & infrastructure issues in addition to manufacturing cost, durability, need to be addressed for the technology to be fully viable.

Thank you all for your kind attention

Non Noble metal catalysts as electrodes for Methanol fuel cells

B. Viswanthan

Department of Chemistry, Indian Institute of Technology,
Madras, Chennai 600 036, India

Non - noble metal catalysts

Overall objective:

☞ **Reduce catalyst cost for direct methanol fuel cells**

Present objective:

☞ **Develop anode catalysts with enhanced activity.**

☞ **Identifying alternates to precious metal catalysts**

☞ **Developing noble and non noble metal combinations to reduce precious metal loading and enhance activity**

☐ *Literature*

Non-noble Metal electrodes adopted as anode for methanol oxidation

☞ **Metallic glasses such as Fe, Co, Ni, Zr and Pd in alkaline medium**

Pd+Zr glass - 50 mA/cm^2 (apparent) at 0.3 V vs RHE

Cu+Zr glass - 40 mA/cm^2 at +0.2 V vs RHE

Cu+Ti glass - 10 mA/cm^2 at +0.5 V vs RHE

- significant activity but stability problem

K. Machida and M. Enyo, Bull. Chem. Soc., Jpn. 58 (1985) 2043

☞ **Methanol oxidation on NiZr in acid solution**

-reaction proceeds at surface O^{2-} ions neighboring a Ni^{3+} ion of a thicker passivating film; electron transfer from the surface to the electrode occurs diffusively by the nickel atoms of the film

J. B. Goodenough et al J. Power Sources ., J.Power sources 45 (1993) 291

☞ **Tungsten carbide, Molybdenum carbide** [8]

K. Machida and M. Enyo, J. Electrochem. Soc., 137 (1990) 871

☞ **$SmCoO_3$ and Pt containing perovskites in PEM mode**

J. H. Whites and A. F. Samells, J. Electrochem., Soc. 140 (1993) 2167

☞ **NiO exhibit activity in alkaline medium at high potentials**

I. A. El-Shafei, J. Electroanal. Chem., 447 (1998) 81 & , 471 (1999) 89.

☞ **NiO exhibit activity in alkaline medium at high potentials**

B. El-Shafei, J. Electroanal. Chem., 447 (1998) 81 & , 471 (1999) 89.

☞ **oxides of Ni-Cu**

- exhibits low overvoltages at 303 K for methanol oxidation.

- good corrosion resitance towards electrolyte medium

T. shobha et al *J. Solid State Electrochem., 137 (2003) 871*

☞ ***Ni–Pd alloy***

T. shobha et al *Material chemistry and physics., 80 (2003) 656*

Points to consider

❶Methanol adsorption follows very closely to the desorption of H_2 on Pt leaving bare metal sites

▶The maximum methanol adsorption will take place in the double layer region.

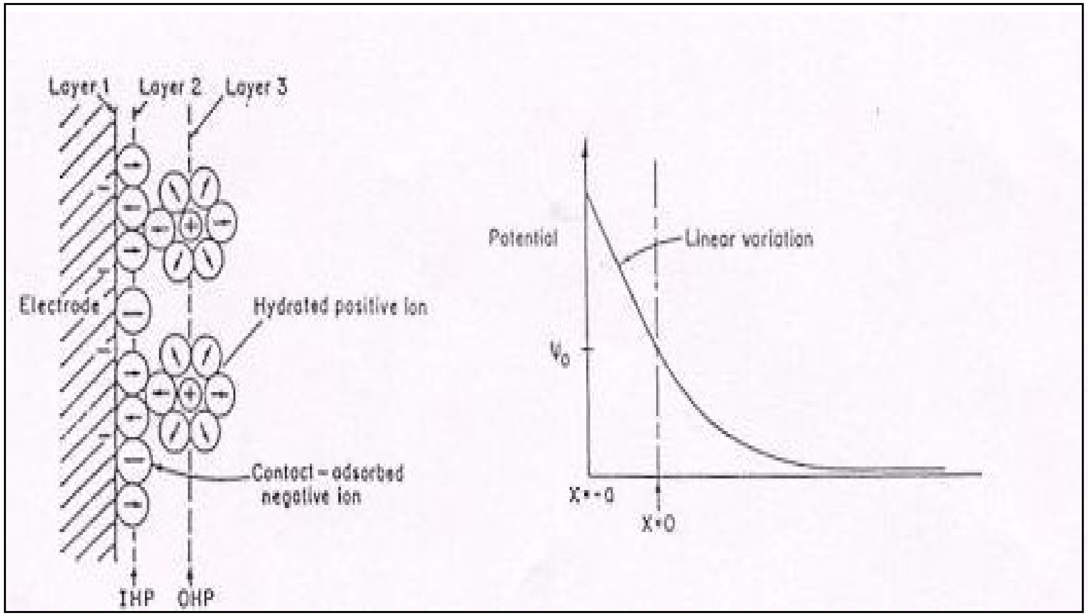
Gasteiger, J. Phys. Chem. 97 (1993) 12020

▶Most of the transition metals other than Pt & Rh, the desorption of H_2 is concomitant with the adsorption of oxygen like surface species thus inhibiting methanol adsorption.

窍 Alternate material Oxide electrodes - a possible choice

Semiconductor Electrochemical Concepts adopted

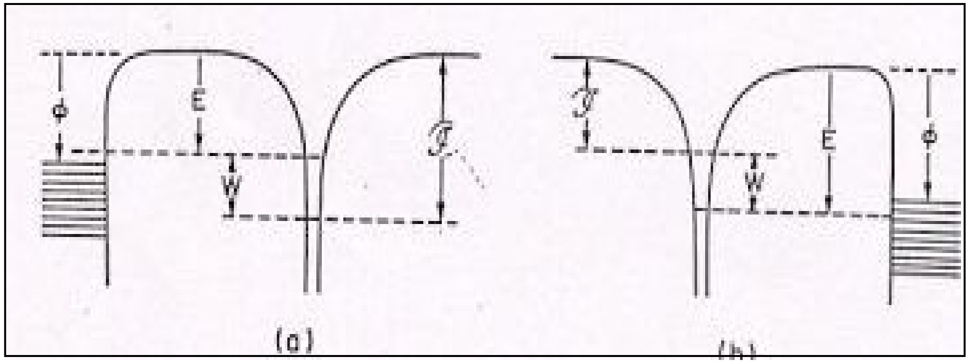
Metal/Electrolyte Interface



$$1/C_{dl} = 1/C_H + 1/C_{GC}$$

- The density of states is 10^{22} $cm^{-3}V^{-1}$
- The space charge of the metal is all squeezed onto the surface.
- Field gradient is absent in the bulk of metal.

Electron transfer at Metal electrode/electrolyte interface

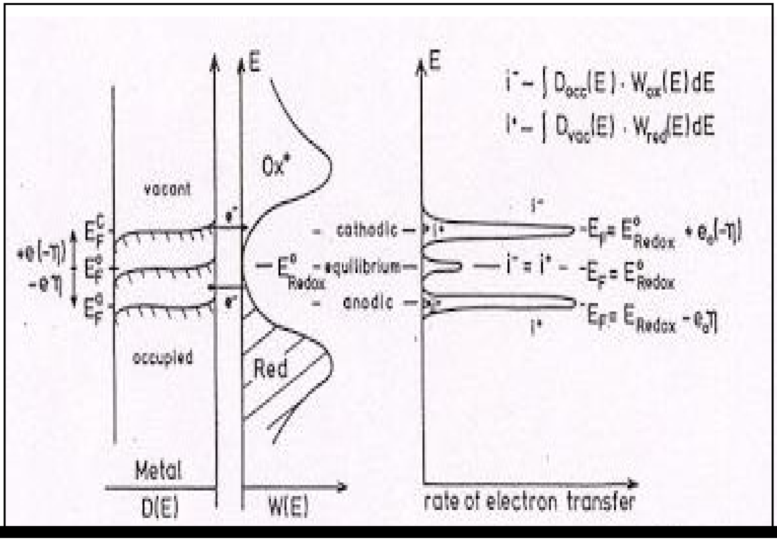


- **Gurney's model :** **Electron passes from**

  Oxidation → Filled donor state of redox species to the Fermi level of the metal

  Reduction → Fermi level of the metal to the empty acceptor states of an oxidant

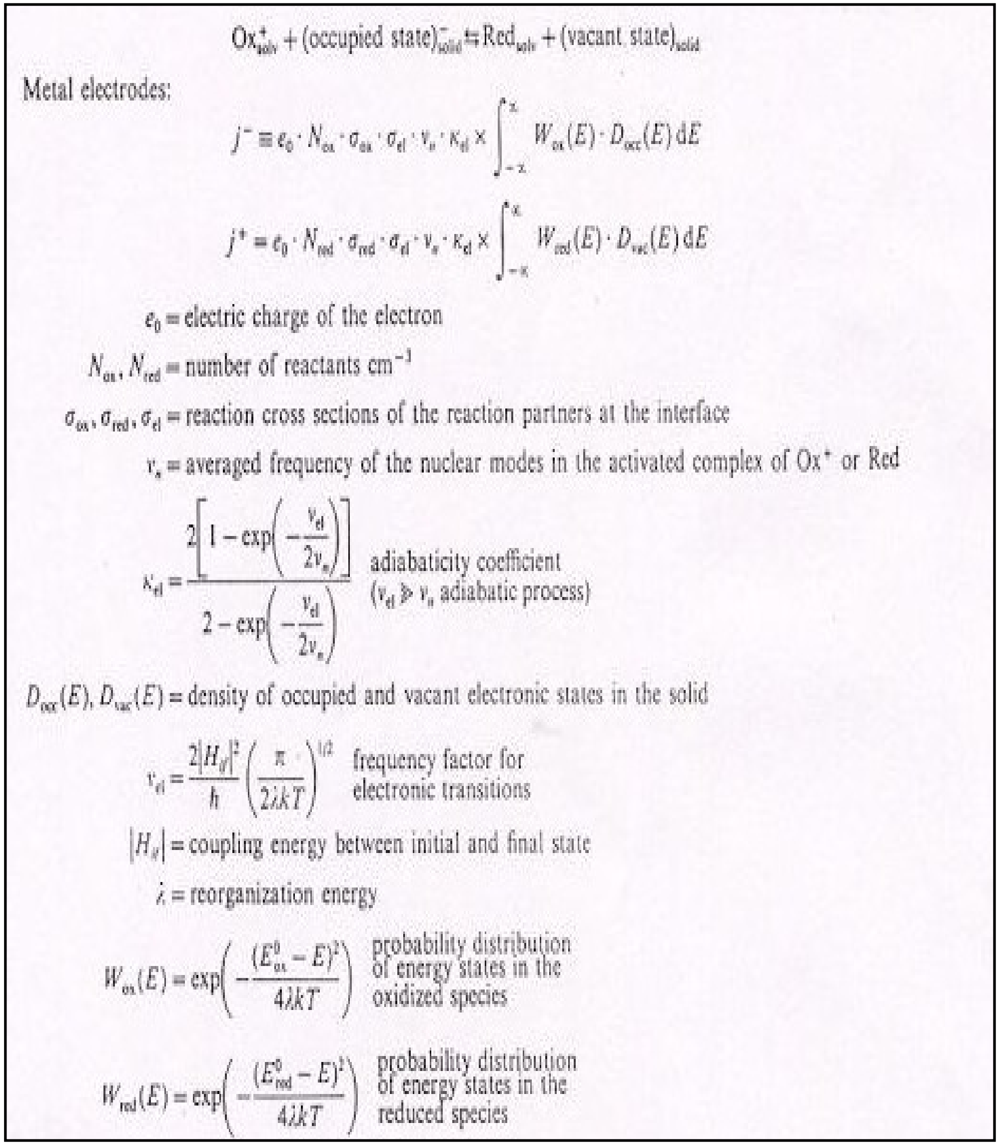
- ***Electron transfer rate at Metal/electrolyte interface***



- **The electron transfer occurs in an energy range close to the Fermi level**

- **not too far from equilibrium condition – does not to go to high overvoltages**

Rate equation at Metal electrodes



$$\mathrm{Ox}^{+}_{\mathrm{solv}} + (\text{occupied state})^{-}_{\mathrm{solid}} \leftrightarrows \mathrm{Red}_{\mathrm{solv}} + (\text{vacant state})_{\mathrm{solid}}$$

Metal electrodes:

$$j^{-} \equiv e_0 \cdot N_{\mathrm{ox}} \cdot \sigma_{\mathrm{ox}} \cdot \sigma_{\mathrm{el}} \cdot \nu_n \cdot \kappa_{\mathrm{el}} \times \int_{-\infty}^{\infty} W_{\mathrm{ox}}(E) \cdot D_{\mathrm{occ}}(E)\,\mathrm{d}E$$

$$j^{+} \equiv e_0 \cdot N_{\mathrm{red}} \cdot \sigma_{\mathrm{red}} \cdot \sigma_{\mathrm{el}} \cdot \nu_n \cdot \kappa_{\mathrm{el}} \times \int_{-\infty}^{\infty} W_{\mathrm{red}}(E) \cdot D_{\mathrm{vac}}(E)\,\mathrm{d}E$$

e_0 = electric charge of the electron

$N_{\mathrm{ox}}, N_{\mathrm{red}}$ = number of reactants cm^{-3}

$\sigma_{\mathrm{ox}}, \sigma_{\mathrm{red}}, \sigma_{\mathrm{el}}$ = reaction cross sections of the reaction partners at the interface

ν_n = averaged frequency of the nuclear modes in the activated complex of Ox^{+} or Red

$$\kappa_{\mathrm{el}} = \frac{2\left[1 - \exp\left(-\frac{\nu_{\mathrm{el}}}{2\nu_n}\right)\right]}{2 - \exp\left(-\frac{\nu_{\mathrm{el}}}{2\nu_n}\right)}$$ adiabaticity coefficient ($\nu_{\mathrm{el}} \gg \nu_n$ adiabatic process)

$D_{\mathrm{occ}}(E), D_{\mathrm{vac}}(E)$ = density of occupied and vacant electronic states in the solid

$$\nu_{\mathrm{el}} = \frac{2|H_{if}|^2}{h}\left(\frac{\pi}{2\lambda kT}\right)^{1/2}$$ frequency factor for electronic transitions

$|H_{if}|$ = coupling energy between initial and final state

λ = reorganization energy

$$W_{\mathrm{ox}}(E) = \exp\left(-\frac{(E^0_{\mathrm{ox}} - E)^2}{4\lambda kT}\right)$$ probability distribution of energy states in the oxidized species

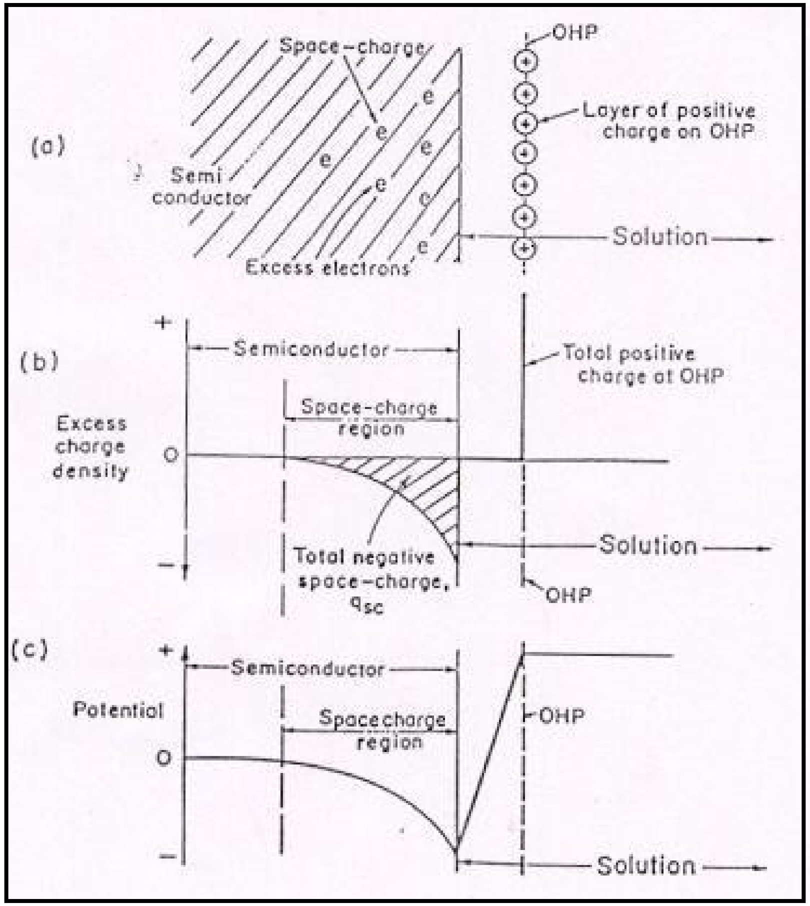
$$W_{\mathrm{red}}(E) = \exp\left(-\frac{(E^0_{\mathrm{red}} - E)^2}{4\lambda kT}\right)$$ probability distribution of energy states in the reduced species

- **The integrals represents the currents for metal electrodes**

→ probability distribution of energy states in the Ox^{+} or Red species.

→ density of occupied or vacant electronic states in the solid

Semiconductor/Electrolyte Interface



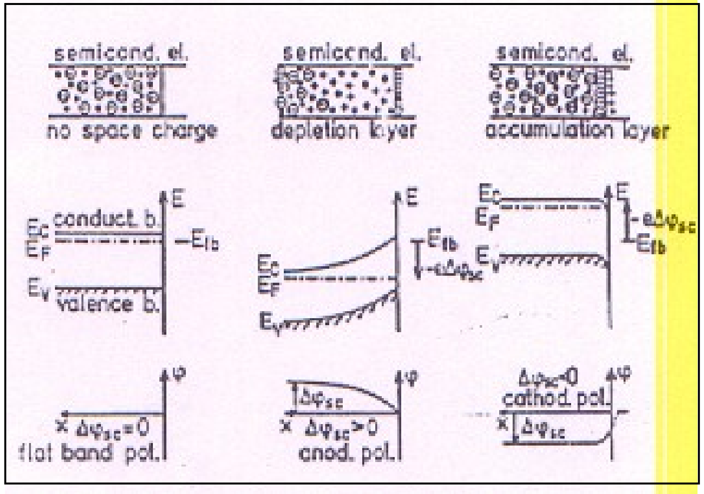
$$1/C_{dl} = 1/C_{SC} + 1/C_{H} + 1/C_{GC}$$

- The potential due to atmosphere of holes and electrons is given by

$$\chi = (8\pi\eta^{o}e_{o}^{2}/\varepsilon kT)^{1/2}$$

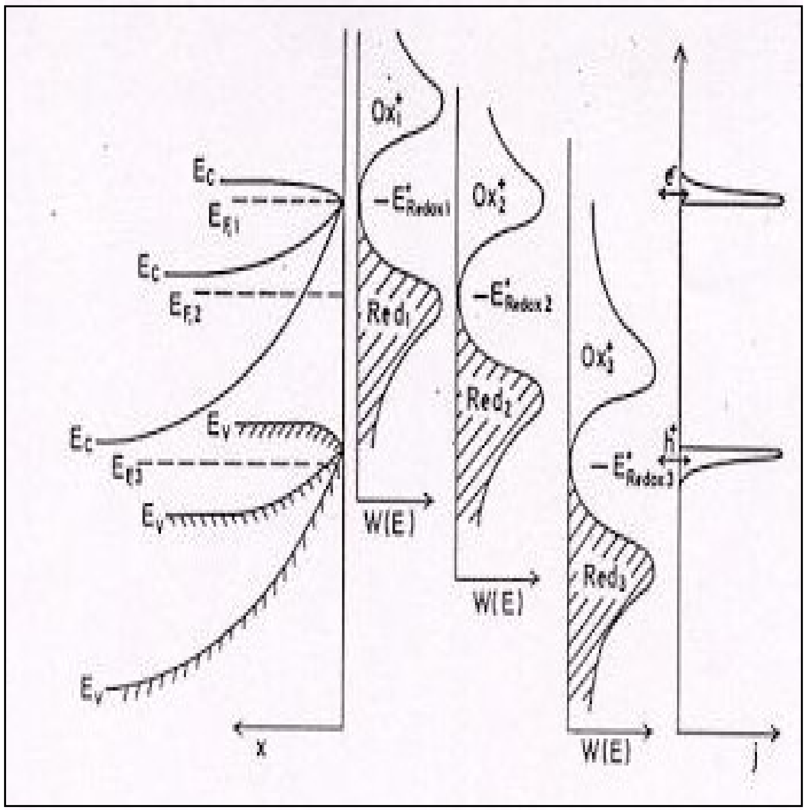
$\chi^{-1} \rightarrow$ Thickness of the Garrett-Brattain space charge inside a semiconductor.

Effect of potential on the Energy levels of the Semiconductor



- **The energy bands near the surface of the Semiconductor are disturbed by the existence of the field.**
- **The bending of the bands up or down depends on the sign of the ionic charge populating the OHP.**
- **Field penetration exists inside the Semiconductor.**
- **Field gradient depends on**
  - **(i) Density of states**
  - **(ii) Surface states**
  - **(iii) Adsorption capacity**

Electron transfer at Semiconductor electrode/electrolyte interface



Redox system 1 → E^o_{redox} close to CB edge

Accumulation layer

High rate of e^- exchange
can be expected

Redox system 2 → Depletion layer

Electron transition to
Ox^+ species nor from
reduced species reach the
conduction band energy.

Redox system 3 → The barrier height for
electron is even higher

(close to E_g energy)

E^o_{redox} close to VB edge

e^- exchange is possible
with VB edge.

Reference: H. Gerischer, Electrochimica Acta, 35 (1990) 1677.

Electron transfer at the Semiconductor/electrolyte interface:

Current *via* the conduction band

$$j_c = k_c^+ \cdot N_c \cdot N_{red} - k_c^- \cdot n_s \,.\, N_{ox}$$

$$n_s = n_o \cdot \exp(e_o \Delta\varphi_{SC}/kT)$$

where n_s is surface concentration of electrons

Current *via* the valence band

$$j_v = k_v^+ \cdot p_s \cdot N_{ox} - k_v^- \cdot N_v \,.\, N_{ox}$$

$$p_s = p_o \cdot \exp(e_o \Delta\varphi_{SC}/kT)$$

where p_s is surface concentration of holes

- Equilibrium between the Semiconductor electrode and a redox system/depolarizer in solution can result in a situation where the Fermi level is located in the band gap of the semiconductor.

- Considerable electron transfer can occur only if the redox potential of the redox system is located close to the band edges of a semiconductor.

- The rate of electron transfer across the semiconductor/depolarizer depends only the surface concentration of the charge carriers (density of states).

H. Gerischer, Electrochimica Acta, 35 (1990) 1677

A. M. Kuznetsov and J. Ulstrup, Electrochimica Acta, 45 (2000) 2339

Fermi level and Density of states

- The position of the Fermi level determines the chemisorption properties of the surface and controls the equilibrium population of the various species created by the adsorbed species.

- By suitable doping of oxides with small amounts of foreign atoms alters the Fermi level which reflects the availability of carrier concentration (density of states) at the surface.

  → accelerated by the rise of F.L – availability of electrons – n-class or acceptor reaction

  → accelerated by lowering of F.L – availability of holes – p-class or donor reactions.

- States without intervention of foreign atoms – broken bonds on the surface.

Selection criteria for Multicomponent system

1. **Field gradient**

   Insulators (10^5 V/cm)

   Semiconductors

   Metals (10^7-10^8 V/cm)

2. **Adsorption capacity depends on the nature of**

   active site

   depolarizer

3. **Potential range of application**

4. **Identifying the possible candidates**

☞ **Perovskites, Pyrochlores and Spinels - satisfies the above condition to some extent**

Rare Earth Cuprates
as
Anode Electrocatalysts

Why $La_{2-x}M_xCu_{1-y}M'_{1-y}CuO_4$?

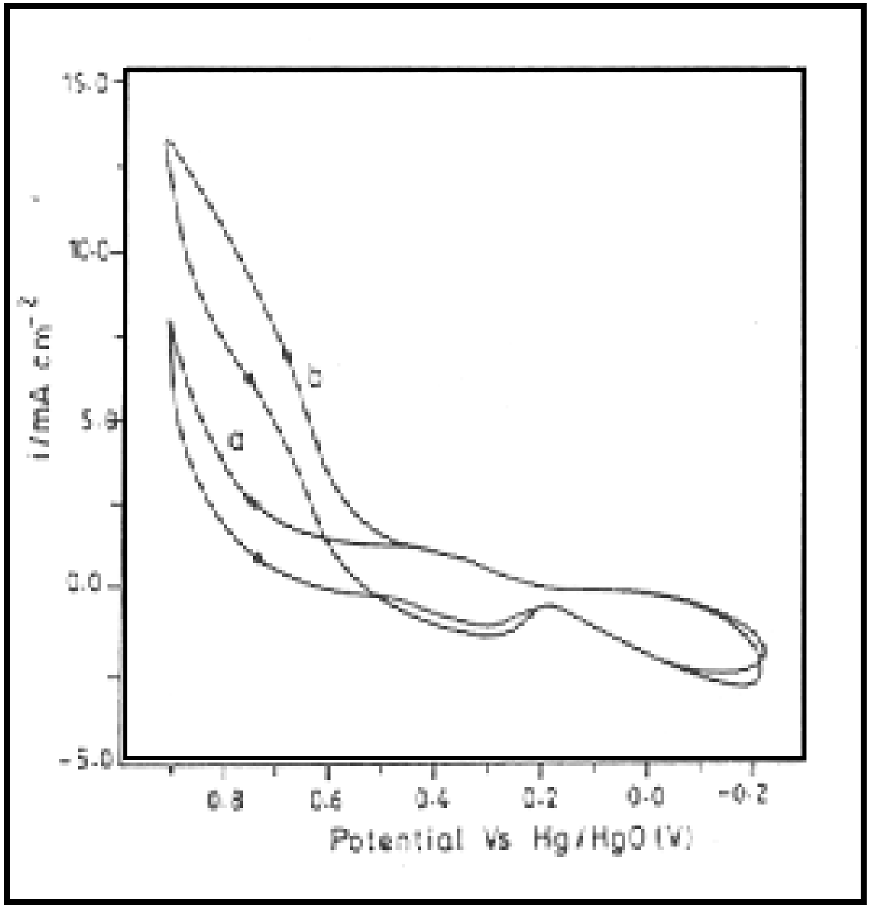
☞Oxide surface is coordinatively unsaturated hence covered with water molecules in aqueous solution

☞ In order for the depolariser (methanol) to adsorb, the M-OH bond strength should be weak.

☞ M-OH bond strength weak → copper containing rare earth perovskite

J. O'M. Bockris and T. Otagawa, J. Electrochem. Soc., 131 (1984) 290.

Electrochemical studies on bulk Sr substituted Lanthanum cuprates



- Anodic peak between +0.26 V - +0.5 V

  ⇒ Cu(2+) →Cu(3+)

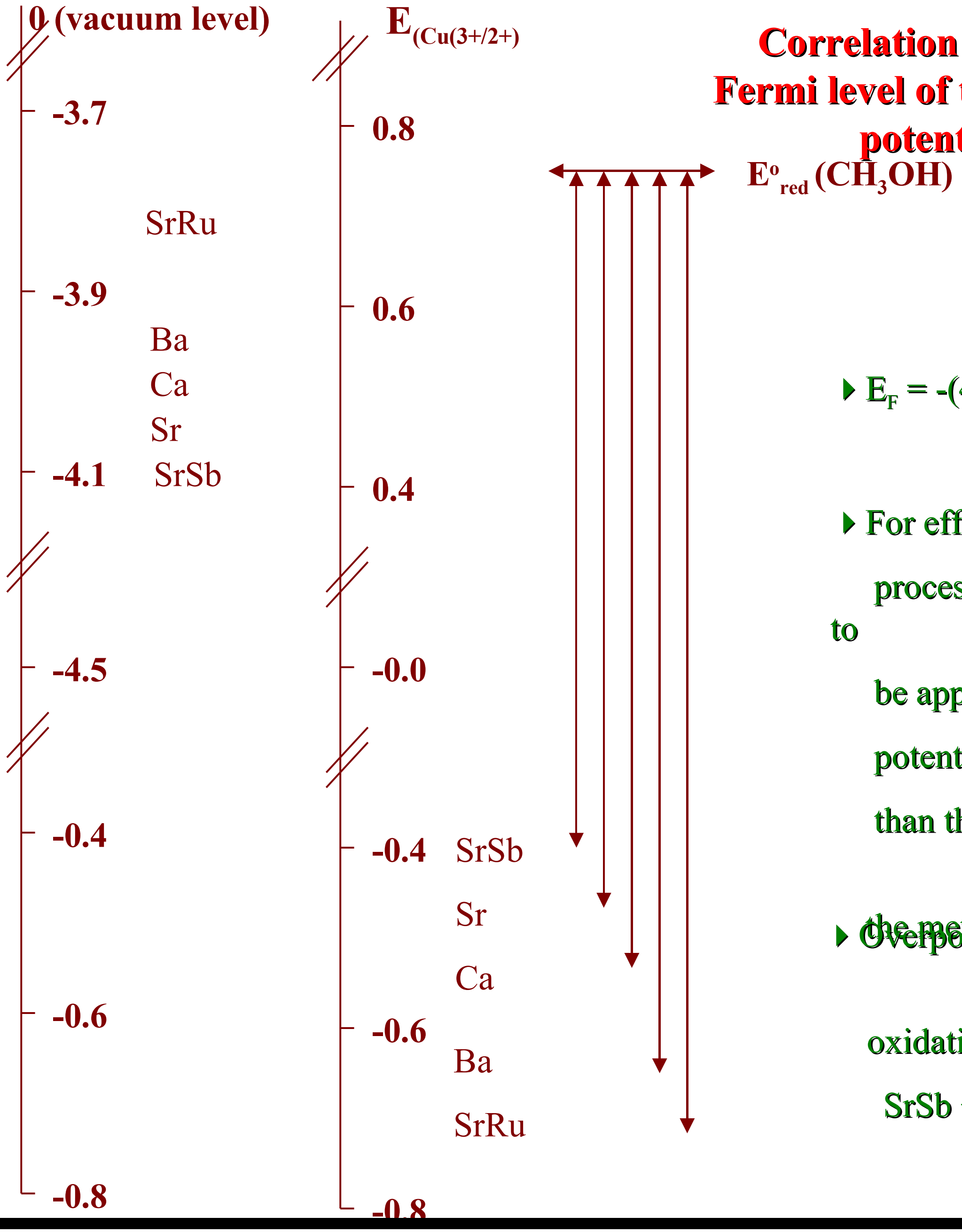
- Methanol oxidation starts at ~0.46 V vs Hg/HgO

- Methanol oxidation to CO_2 was confirmed by charging measurements and carbonate estimation.

V.Raghuveer, K.R. Thampi, N. Xanthapolous, H.J. Mathieu and B. Viswanathan, Solid State Ionics 140 (2001) 263

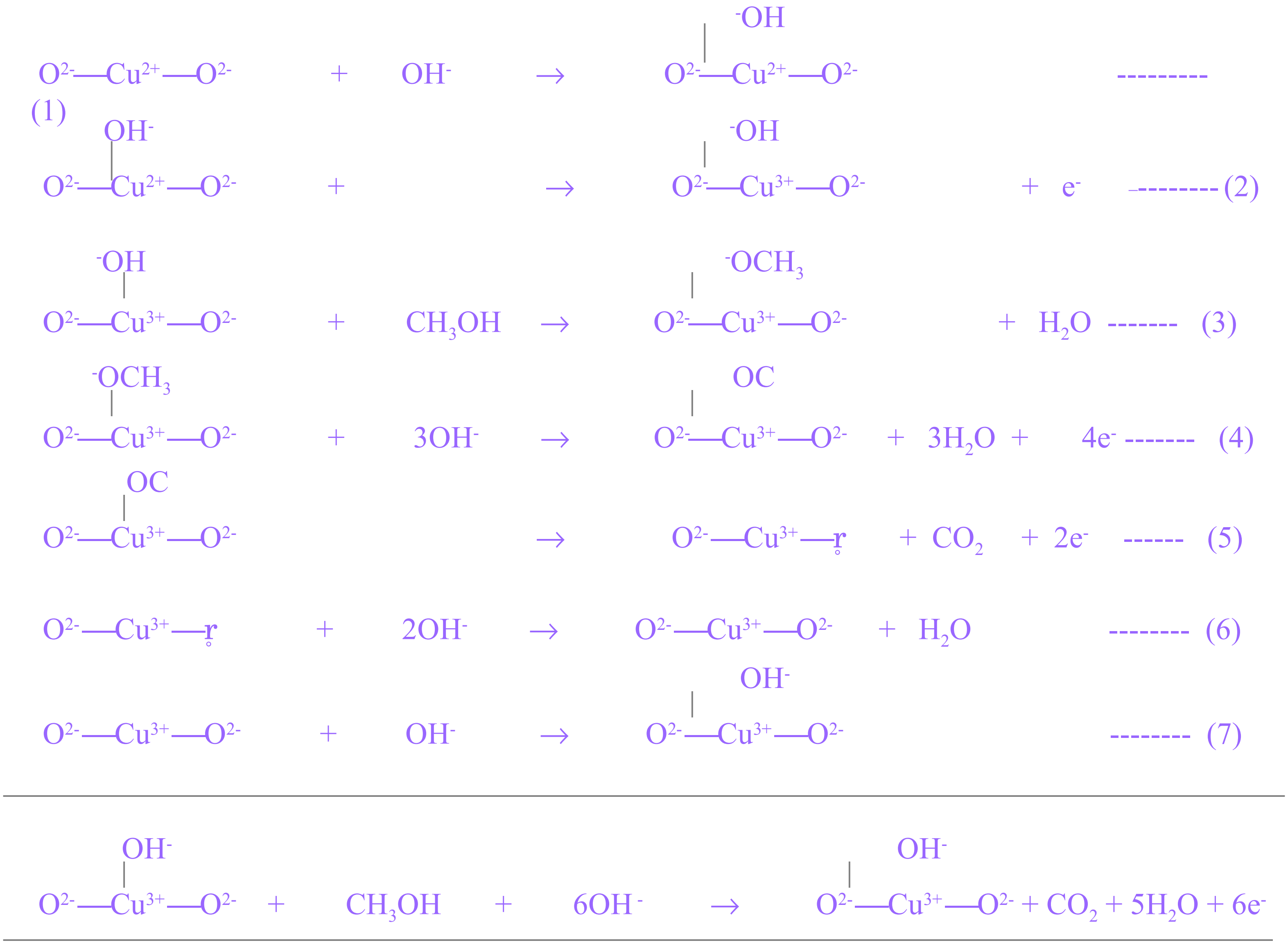
Cyclic Voltammogram of bulk cuprate in (a) 3 M KOH and (b) 1 M CH_3OH at a scan rate of 25 mVs^{-1}

Correlation of Redox potential & Fermi level of the electrode with redox potential of methanol



- $E_F = -(4.5eV + eE_{redox})$
- For effective charge transfer process to occur – potential has to be applied to bring the redox potential of the electrode higher than that of the redox potential of the methanol
- Overpotential required for methanol oxidation onset follows the order SrSb < Sr < Ca < Ba < SrRu

Speculative Mechanism of Methanol Oxidation on the Oxide Surface



$$\mathrm{O^{2-}—Cu^{2+}—O^{2-} \;+\; OH^{-} \;\rightarrow\; O^{2-}—\overset{\overset{{}^{-}OH}{|}}{Cu^{2+}}—O^{2-}}$$ --------- (1)

$$\mathrm{O^{2-}—\overset{\overset{OH^{-}}{|}}{Cu^{2+}}—O^{2-} \;+\; \rightarrow\; O^{2-}—\overset{\overset{{}^{-}OH}{|}}{Cu^{3+}}—O^{2-} \;+\; e^{-}}$$ ---------(2)

$$\mathrm{O^{2-}—\overset{\overset{{}^{-}OH}{|}}{Cu^{3+}}—O^{2-} \;+\; CH_3OH \;\rightarrow\; O^{2-}—\overset{\overset{{}^{-}OCH_3}{|}}{Cu^{3+}}—O^{2-} \;+\; H_2O}$$ ------- (3)

$$\mathrm{O^{2-}—\overset{\overset{{}^{-}OCH_3}{|}}{Cu^{3+}}—O^{2-} \;+\; 3OH^{-} \;\rightarrow\; O^{2-}—\overset{\overset{OC}{|}}{Cu^{3+}}—O^{2-} \;+\; 3H_2O \;+\; 4e^{-}}$$ ------- (4)

$$\mathrm{O^{2-}—\overset{\overset{OC}{|}}{Cu^{3+}}—O^{2-} \;\rightarrow\; O^{2-}—Cu^{3+}—\underset{\circ}{r} \;+\; CO_2 \;+\; 2e^{-}}$$ ------ (5)

$$\mathrm{O^{2-}—Cu^{3+}—\underset{\circ}{r} \;+\; 2OH^{-} \;\rightarrow\; O^{2-}—Cu^{3+}—O^{2-} \;+\; H_2O}$$ -------- (6)

$$\mathrm{O^{2-}—Cu^{3+}—O^{2-} \;+\; OH^{-} \;\rightarrow\; O^{2-}—\overset{\overset{OH^{-}}{|}}{Cu^{3+}}—O^{2-}}$$ -------- (7)

$$\mathrm{O^{2-}—\overset{\overset{OH^{-}}{|}}{Cu^{3+}}—O^{2-} \;+\; CH_3OH \;+\; 6OH^{-} \;\rightarrow\; O^{2-}—\overset{\overset{OH^{-}}{|}}{Cu^{3+}}—O^{2-} + CO_2 + 5H_2O + 6e^{-}}$$

Sr Substituted Lanthanum Cuprates as Electrode For Methanol Oxidation and Its Comparison with Platinum

Electrocatalysts*	Tolerance factor	Specific Conductivity (Ω^1cm^{-1})	Cu(2+)	Cu(3+)	δ	Methanol Oxidation Onset Potential (V)	Activity I (mAcm^{-2}) at +0.7 V	Rate of deactivation MAmin^{-1}
La_2CuO_4	0.9034	0.28	1.0	0.0	0.0	0.46	5(10)	0.42 (12.3)
$La_{1.9}Sr_{0.1}CuO_4$	0.9107	18.27	0.921	0.079	0.011	0.46	8(16)	0.36 (14)
$La_{1.8}Sr_{0.2}CuO_4$	0.9170	67.56	0.856	0.144	0.028	0.46	14(28)	-
$La_{1.7}Sr_{0.3}CuO_4$	0.9119	16.97	0.938	0.062	0.098	0.46	0.68(1.4)	0.03 (173)
$La_{1.6}Sr_{0.4}CuO_4$	0.9101	10.3	0.975	0.026	0.186	0.46	0.5(1)	0.05 (104)
$La_{1.9}Ca_{0.1}CuO_4$	0.9058	24.11	0.965	0.035	0.033	0.51	3.3	-
$La_{1.9}Ba_{0.1}CuO_4$	0.9101	17.98	0.972	0.028	0.036	0.78	1.8	-
$La_{1.9}Sr_{0.1}Cu_{0.9}Sb_{0.1}O_4$	0.9098	-	-	-	-	0.34	5.0	-
$La_{1.9}Sr_{0.1}Cu_{0.9}Ru_{0.1}O_4$	0.9112	-	-	-	-	0.76	1.0	-
$Nd_{1.8}Sr_{0.2}CuO_4$	0.8806	-	-	-	-	0.35	13.0	-
$Nd_{1.8}Sr_{0.2}Cu_{0.8}Sb_{0.2}O_4$	0.8909	-	-	-	-	0.30	12.0	-
Bulk Pt	NA	M	NA	NA	NA	-0.6^{μ}	35	16.56
Pt/C	NA	M	NA	NA	NA	-0.6^{μ}	106	5.2 (1)

- CCeramic method, Disk type electrode, Experimental Condition : 3M KOH and 1M CH_3OH

. ∓ at +0.08 V *vs* Hg/HgO