Development of Electro-catalysts for Fuel Cell Applications



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What is a Fuel Cell ?

Direct Energy Conversion Vs. Indirect Technology



2

Choice of fuel and oxidant

Chemical and Electrochemical data on various fuels

FUEL	∆G ⁰ kcal/mol	E ⁰ theoretical (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	-

Oxidant ---- gaseous oxygen/air

(In general, the oxygen needed by a fuel cell is supplied in the form of air)

Different '	Types of	f	Fuel	Cells		
Fuel (Cells					
	Low Temperature		Medium Temperature		High Temperature	
	Fuel Cells		Fuel Cells		Fuel Cells	
	PEMFC	DMFC	AFC	PAFC	SOFC	MCFC
Characteristic	(Proton Exchange Membrane Fuel Cells)	(Direct Methanol Fuel Cells)	(Alkaline Fuel Cells)	(Phosphoric Acid Fuel Cells)	(Solid Oxide Fuel Cells)	Molten Carbonate Fuel Cells)
Operating temp (°C)	60 - 80	60 - 80	100 –150	180 - 220	750 - 1050	650
Fuel	H ₂ (pure or reformed)	CH ₃ OH	H ₂	H ₂ (reformed)	H ₂ and CO reformed & CH ₄	H ₂ and CO reformed & CH ₄
Charge carrier in the electrolyte	H+	H+	OH-	\mathbf{H}^+	CO ₃ ²⁻	O ²⁻
Poison	CO>10 ppm	Adsorbed intermediates (CO)	CO , CO ₂	CO>1% H ₂ S>50 ppm	H ₂ S>1ppm	H ₂ S>0.5 ppm
Applications	Transporta	ition, Portable	Space	e, Military	Power ger Cogene	neration, ration ⁴

Schematics of Operational PEMFC & DMFC



$\mathbf{H}_2 = 2\mathbf{H}^+ + 2\mathbf{e}^-$	0.00V	Anode	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	0.05 V
$1/2O_2 + 2H^+ + 2e^- = H_2O$	1.23V	Cathode	$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	1.23 V
$I/2O_2 + H_2 = H_20$	1.23V		$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$	1.18 V

WHY METHANOL ?

- ✓ High specific energy density
- ✓ Clean liquid fuel
- ✓ Larger availability at low cost
- \checkmark 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



OUR FOCUS



1. Identification of suitable catalyst

- **2.** Improve/Tailor Carbon material → desired electrochemical properties
 - \rightarrow 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 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?

Preparation of Methanol Oxidation Catalysts with the Modified Supports in DMFC

Methanol oxidation Mechanism: addition of the secondary metal

1. Bifuntional mechanism

$Pt + CH_3OH \rightarrow Pt - (CH_3OH)_{ads}$	(1)
$Pt-(CH_3OH)_{ads} \rightarrow Pt-(CH_3O)_{ads} + H^+ + e^-$	(2)
$Pt-(CH_3O)_{ads} \rightarrow Pt-(CH_2O)_{ads} + H^+ + e^-$	(3)
$Pt-(CH_2O)_{ads} \rightarrow Pt-(CHO)_{ads} + H^+ + e^-$	(4)
$Pt-(CHO)_{ads} \rightarrow Pt-(CO)_{ads} + H^+ + e^-$	(5)
$M + H_2O \rightarrow M-(OH)_{ads} + H^+ + e^-$	(6) slow step
$Pt-(CO)_{ads} + M-(OH)_{ads} \rightarrow Pt + M + CO_2 + 2H^+ + 2e^-$	(7) slow step



Pt + H₂O → Pt-OH + H⁺ + e⁻ (0.7V) Ru + H₂O → Ru-OH + H⁺ + e⁻ (0.2V)

2. Electronic mechanism

The secondary metal modifies the electronic properties of the catalyst \rightarrow

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 .



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, 18*52(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=50m²/g), Vulcan XC-72 (SBET=250m²/g), KETJEN black (SBET=1000m²/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 method, implantation method using plasma etc.

Others

- To increase voids \rightarrow addition of void forming, solvent having a high boiling point etg.3
- 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



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 ionomercoated carbon support.

BET surface area

Vulcan XC-72 (217 m²/g)

1% IOC	$(189 \text{ m}^2/\text{g})$
2% IOC	(178 m ² /g)
5% IOC	$(161 \text{ m}^2/\text{g})$

15

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 and scan cycle of 30.

Incorporation of ionomer into carbon increased the EAS

Performances of Single Cell



Comparison - At 90°C, 2.0M CH₃OH 5cc/min, humidified O₂ 250sccm. Cathode, 46.5wt.% Pt/C (Tanaka, catalyst loading 3.0mg Pt/cm²); membrane, Nafion-117 (Dupont).

A slightest of addition of ionomer in carbon support improve the catalyst utilization significantly

CATHODE RESEARCH – MAIN FOCUS

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

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

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 PtO₂ is a catalyst for H₂O₂ 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

<u>Attempts</u>

(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

Directions

Focus

Increasing air utilization in the cathode

Incorporation of oxygen storage materials

Why Ceria?

The ability of ceria to store, transport and release oxygen

 $CeO_2 \leftrightarrow CeO_{2-x} + (x/2)O_2 \quad (0 \le x \le 0.5)$

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 22

Optimization of CeO₂ loading



Single cell performance of various loading of CeO₂ on 40 wt% Pt/C using oxygen and air 250 sccm.

Incorporation of nanophase ceria (CeO₂) into the cathode catalyst Pt/C increased the local oxygen concentration at air atmosphere leading to enhanced single-cell performance of DMFC.

Effects of flow rate



Single cell performance using oxygen 80 sccm

Single cell performance using air 1250 sccm

Effects of oxygen partial pressure

Current density at constant voltage (Total flow rate: 250 cc/min fixed)



The effect of ceria was more prominent with air as the cathode reactant and with pure oxygen ceria acted as a mere impurity decreasing the DMFC performance.

Art & Science of Catalyst Development



Fuel Cells : R&D - Multidirectional!

- **Multi-component** (CH₃OH, H₂O, CO₂, O₂, 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.)

Limitations

Sluggish methanol oxidation (anode) kinetics:

- 6 electron transfer
- formation of CO as an intermediate in the multi-step methanol oxidation mechanism poisoning of catalyst

Sluggish oxygen reduction (cathode) kinetics:

- 4 electron transfer
- formation of H_2O_2 as an intermediate in the multi-step oxygen reduction mechanism poisoning of catalyst
- Cost of electrocatalysts
- **>** Large methanol crossover through the membrane:
 - Linked to the electro osmotic drag
 - had detrimental effect on fuel efficiency
 - may poison the cathode
 - creates mass transport problems at cathode layer by wetting hydrophobic gas channels, leading to increased flooding



Replacement of Pt by non-noble metal based electrodes
29

Why supported catalyst?



Role of electro-catalyst supports

- High surface area
- High dispersion of noble metal particles to reduce noble metal loadings
- ***** Avoid the agglomeration of the metal particles in operation,
- Good stability of electrocatalysts
- Improved the activity of electro-catalysts through the interaction between metal and support
- Lower the resistance of mass transportation
- Always superior to respective unsupported supported systems
- Shorten the time of DMFC commercialization

Why carbon materials are used as an electrocatalyst support ?

*** Electrochemical properties**

- Wide electrochemical potential window

* Chemical properties

- Good corrosion resistance

***** Electrical properties

- Good conductivity

***** Mechanical properties

- Dimensional & mechanical stability
- Light weight & adequate strength

Nitrogen functionalization in carbon support

Current – potential curve for sulfur functionalized (S), nitrogen functionalized (N) and un-functionalized (U) carbon supports



S.C. Roy et al., J. Electrochem. Soc., 144 (1997) 2323

Carbon nanotube as an electrode support in fuel cells

- Mesoporosity (2-50 nm)
- Improved mass transfer
- Better dispersion
- Surface functional groups
- High accessible surface area
- High purity \rightarrow avoids self-poisoning
- Good electronic conductivity



Nitrogen functionalization in carbon nanotubes

- Pt bound strongly to nitrogen sites so higher dispersion, sintering doesn't takes place
- Addition of nitrogen increases the conductivity of the material by raising the Fermi level towards the conduction band
- The presence of nitrogen generates catalytic site and this catalytic site is responsible for increased activity of methanol oxidation.



Interactions between the noble metal and the support may lead to increase catalyst performance

Synthesis of carbon nanotubes

Arc discharge

Laser Ablation

Chemical vapor deposition

>Difficulties: Controlling parameters, less purity, less yield and expensive

Template synthesis

- Carbon nanotubes are prepared from the pores of alumina membrane.

Advantages:

Simpleness,

Proper alignment possible,

A new and effective way to control the diameter of the nanotube.








SEM images of alumina membrane: (a-b) Surface View and (c-d) Cross-sectional View

Preparation of pure CNTs using polyphenylacetylene (PPA) as precursor



Synthesis of WO₃ and Pt-WO₃ Loaded Carbon Nanotube, CNT_{ppa}



39

Synthesis of Pt and Pt-Ru Loaded Carbon Nanotube, CNT_{ppa}





(a) SEM image of CNT's projecting perpendicularly from the surface of sample holder (obtained by the carbonisation of PPA on alumina membrane)





(b-c) HR-TEM of CNT: (b) showing part of CNT which are slightly deformed, due to HF treatment (c) Cylindrical, hollow carbon nanotube with diameter almost equal to the 41 template used (200 nm)



HR-TEM of CNT_{ppa}

 \rightarrow showing the open end of the tube which can be utilized to fill the particles also amorphous carbon seen on the wall of the CNT



(a) Pt filled CNT (1.2 nm)



(b-C) Pt-Ru filled CNT (1.6 nm)





(d) Pt-WO₃ filled CNT (⁴³₁₀ nm)



(a) X-ray photoelectron spectra of Pt 4f in Pt loaded CNT. X-ray photoelectron spectra of (b) Pt 4f in Pt-Ru loaded CNT and (c) Ru 3d in Pt-Ru loaded CNT (also shown C1s of Pt-Ru loaded CNT in (c)). (d) X-ray photoelectron spectra of W 4f in WO₃ loaded CNT. X-ray photoelectron spectra of (e) Pt 4f in Pt-WO₃ loaded CNT and (f) W 4f in Pt-WO₃ loaded CNT.

→ showed the presence of Pt and Ru in the metallic state and W in 44 +VI oxidation state.

Electrode Fabrication

Catalyst + 5 wt% Nafion in 200 µl distilled water

↓ Ultrasonicated for 15 min

↓ 20 µl pipetted onto Glassy carbon (GC, 0.07 cm²)

 \downarrow dried at 110 °C for 5 min

GC/CNT_{ppa}-Nafion (metal loaded or unloaded)



Cyclic Voltammograms of (a)GC/CNT_{ppa}-Pt-WO₃ Nafion in 1 M H₂SO₄(absence of CH₃OH) (b)GC/CNT_{ppa}-Pt-WO₃₋Nafion in 1 M H₂SO₄/1 MCH₃OH run at 50 mV/s
46



Cyclic Voltammograms of (c) GC/CNT_{ppa}-Pt-Ru- Nafion and (d) GC/CNT_{ppa}-Pt-Nafion in 1 M $H_2SO_4/1$ MCH₃OH run at 50 mV/s

Comparison of Electro-Catalytic Activity of Methanol Oxidation on Supported CNT_{ppa} -Based Electrodes

		activity ^a				
		forward sv	forward sweep		reverse sweep	
electrode	onset E (V)	I (mAcm ⁻²)	E (V)	I (mAcm ⁻²)	E (V)	
GC/CNT/Pt-WO ₃	0.10	$ 80.0^{b} 57.4 $	0.54 0.80	67.8 ^b	0.53	
GC/CNT/Pt-Ru	0.16	67.1 ^b 46.4	0.60 0.80	58.5 ^b	0.55	
GC/CNT/Pt	0.20	13.3^{b} 8.3	0.66 0.80	10.0^{b}	0.6	

^{*a*}Activity evaluated from cyclic voltammogram run in 1 M H₂SO₄/1 M CH₃OH scanned between -0.2 and +0.8 V vs Ag/AgCl at 50 mV/s.

^bPeak current density (mA/cm²).

Activity order:

GC/CNT/Pt-WO₃-Nafion > GC/CNT/Pt-Ru-Nafion > GC/CNT/Pt-Nafion





The stability of the electrode for methanol oxidation polarized at +0.6 V follows the order GC/CNT/Pt-Ru-Nafion > GC/CNT/Pt-WO₃ > GC/CNT/Pt-Nafion, and for the electrodes polarized at +0.4 V, the order is GC/CNT/Pt-WO₃-Nafion > GC/CNT/Pt-Nafion.

The differences in the stability possibly suggest the better tolerance of the adsorbed species of methanol oxidation for the GC/CNT/Pt-WO₃-Nafion electrode (when it is polarized at +0.4 V).

Synthesis of nitrogen containing carbon nanotube, CNT_{ppy} and metal (Pt and Pt-Ru) Loaded CNT_{ppy}



50

Synthesis of WO₃ and Pt-WO₃ Loaded Carbon Nanotube, CNT_{ppy}



51





SEM of carbon material obtained by carbonisation of polypyrrole for 3 h at (a) 973 K and (b) 1023 K



SEM of carbon material obtained by carbonisation of polypyrrole at 1073 K for (a) 3 h, (b) 4 h and (c) 5 h.







HR-TEM images of carbon nanaotubes (a-c) obtained by the carbonisation of polypyrrole at 1173 K, 4 hr



HR-TEM of Carbo nanotubes obtained by the carbonisation of Polypyrrole (a-b) 1173 K, 3 hr and (c-d) 1173 K, 6 hr



HR-TEM images of loaded carbon nanotubes obtained by the carbonization of polypyrrole at 1173 K for 4 h (a) Pt loaded CNT (b) and (c) Pt-Ru loaded CNT and (d) Pt-WO₃ loaded CNT



XPS of (a) Pt 4f in Pt–Ru loaded CNT (b) Ru 3d in Pt–Ru loaded CNT (also shown C1s of Pt–Ru loaded CNT in (b)), (c) Pt 4f in Pt–WO₃ loaded CNT, and (d) W 4f in Pt–WO₃ loaded CNT

→ showed the presence of Pt and Ru in the metallic state and W in +VI oxidation state.

56

Electrode Fabrication

Catalyst + 5 wt% Nafion in 200 µl distilled water

↓ Ultrasonicated for 15 min

↓ 20 µl pipetted onto Glassy carbon (GC, 0.07 cm²)

 \downarrow dried at 110 °C for 5 min

GC/CNT_{ppy}-Nafion (metal loaded or unloaded)



Cyclic voltammograms of a) GC/CNT-Nafion, b)GC/Vulcan XC72 R carbon-Nafion c) Graphite, d) Glassy Carbon electrodes run in 1M H₂SO₄ at 25 mV/s and at 298 K



Cyclic voltammogram of (a) GC/CNT–Pt–Nafion in 1 M H₂SO₄ (absence of methanol), (b) GC/CNT–Pt–WO₃–Nafion, and (c) GC/CNT–Pt–Nafion electrodes in 1 M H₂SO₄/1 M CH₃O₄ run at 50 mV/s between -0.2 and +0.8 V vs. Ag/AgCl. The nitrogen content in the nanotube was 8%

Performance of composite electrodes based on carbon nanotubes in comparison with commercial catalysts for methanol oxidation

Electrode	E _{pa} (V) Ag/AgCl	Activity I _{pa} (mA/cm ²)	Normalised Activiy
GC/CNT-WO ₃ -Pt-Naf	+0.70	98.5	42.82
GC/CNT-Pt-Naf	+0.67	14.0	6.1
GC/ETek20%Pt/C-Naf	+0.70	2.3	1.0
GC/Etek20%Pt-Ru/C- Naf	+0.50	11.7	5.1

*Activity was evaluated from cyclic voltammogram run in 1M $\rm H_2SO_4/1M$ $\rm CH_3OH$ at 25 mV/s



Chronoamperometric response of

- (a) GC/CNT-Pt-WO₃-Nafion,
- (b) (b) GC/E-TEK 20% Pt-Ru/Vulcan carbon-Nafion,
- (c) (c) GC/CNt–Pt–Nafion,
- (d) (d) GC/E-TEK 20% Pt/Vulcan Carbon-Nafion, and

(e) Bulk Pt electrodes polarised at +0.6 V vs. Ag/AgCl in 1 M $H_2SO_4/1$ M CH_3OH for 2 h.



- (a) GC/CNT-Pt-WO₃-Nafion and
 (b) GC/CNT-Pt-Ru-Nafion electrodes
- (c) polarised at +0.4 V vs. Ag/AgCl in
- (d) $1 \text{ M H}_2\text{SO}_4/1 \text{ M CH}_3\text{OH}$ for 2 h.

The activity and stability (evaluated from chronoamperometric response) of the electrodes for methanol oxidation follows the order: GC/CNT-Pt-WO₃-Nafion > GC/E-TEK 20% Pt-Ru/Vulcan Carbon-Nafion > GC/CNT-Pt-Nafion > GC/E-TEK 20% Pt/Vulcan carbon-Nafion > Bulk Pt.

Comparison of catalytic activity for methanol oxidation between CNT_{ppa} **and CNT**_{ppy} **as Supports**

S No	Electrode	Activity ^a (mA/cm ²)
1.	GC/CNT _{ppa} -Pt-WO ₃ -Naf	76.5
	GC/CNT _{ppy} -Pt-WO ₃ -Naf	98.5
2	GC/CNT _{ppa} -Pt-Ru-Naf	60.0
	GC/CNT _{ppy} -Pt-Ru-Naf	80.4
3	GC/CNT _{ppa} -Pt-Naf	12.3
	GC/CNT _{ppa} -Pt-Naf	14.0

^aThe catalytic activity was evaluated from the maximum current obtained in the forward scan from cyclic voltammogram which was run in 1 M H_2SO_4 and 1 M CH_3OH at 50 mV/s between -0.2 V and +0.8 V vs Ag/AgCl.

Correlation of catalytic activity with percentage of Nitrogen in the carbon nanotube

% Nitrogen	Activity (mA/cm ²)
3	80.5
3-8	98.5
10	75.5

Synthesis of nitrogen containing carbon nanotubes



Synthesis of CNT from poly(paraphenylene)



Electron microscopy images of CNT_{PPP}



T. Maiyalagan, B.Viswanathan, Indian. J. Chem. Sec A , 45 (2006) 3711

Raman spectrum and AFM image

Raman spectrum





AFM image

AFM image for the part of a long^onanotube on a silicon substitate

Electrochemical studies



Cyclic voltammograms in 1 M H_2SO_4 at (a) Glassy carbon coated carbon nanotube electrode (b) Glassy carbon coated vulcan electrode (c) Glassy carbon 68

Pt/C (E-TEK)





Cyclic Voltammograms of (c) GC/CNT_{ppp}-Pt-Nafion in 1 M H₂SO₄/1 MCH₃OH run at 50 mV/s

Microscopy images of CNT_{PVP}

AFM

SEM







Data type Z range 60

4.43 μm 0 Height 600.0 nm

Data type Friction Z range 0.3914 V

4.43 µm Friction 0.3914 ∨









T. Maiyalagan, B.Viswanathan, Mater. Chem. Phys, 93 (2005) 291



Cyclic voltammograms of (a) GC/CNTpvp-Pt-Nafion in 1 M H₂SO₄/1 M CH₃OH run at 50 mV/s

T. Maiyalagan, B. Viswanathan, U.V. Varadaraju, *Electrochem. Commun.* 7 (2005) 905

SEM: N-CNT



TEM: Pt/N-CNT









Cyclic voltammograms (e) GC/CNTppy-Pt-Nafion in 1 M H₂SO₄/1 M CH₃OH run at 50 mV/s
SEM images of CNT_{PVI}



Elemental analysis (CHN)

Polymer (Calculated)			CNT (Experimental)			
Sample	% C	% N	% H	% C	% N	% H
CNT _{PPP}	93.0	0.0	4.9	92.3	0.0	1.8
CNT _{PVP}	64.8	12.6	8.2	87.0	6.6	0.8
CNT _{PPY}	66.7	21.2	6.1	78.2	10.3	0.6
CNT _{PVI}	63.8	29.8	6.4	75.5	18.9	0.6

Electro-catalytic activity

Electrode	Nitrogen content	Activity Ip (mA/cm ²)
Pt	-	0.076
GC/ETek 20% Pt/C Naf	-	1.3
GC/CNT-Pt PPP-Naf	0.0	12.4
GC/CNT-Pt PVP -Naf	6.63	16.2
GC/CNT-Pt PPY -Naf	10.5	21.4
GC/CNT-Pt PVI-Naf	16.7	18.6
Electro-catalytic activity of the Pt/N electrodes in comparison with comm catalysts for methanol oxidation	-CNT ercial 20 18 16 14	

% Nitrogen content

Specific activity for methanol oxidation Vs nitrogen content of the catalysts

Chronoamperometric response of the electrodes



Higher surface area and nitrogen presence - better dispersion –better catalytic activity

* Pt/C (E-TEK) < Pt/CNT_{PPP} < Pt /CNT_{PVP} < Pt /CNT_{PVI} < Pt /CNT_{PVI} < Pt

Nitrogen presence – increasing the hydrophilic nature of the catalyst

Among the N-CNT electrodes studied, 10 % Nitrogen containing CNT shows highest catalytic activity

Exploitation of template synthesized conducting polymeric nanotubules and nanocones as supports of Pt for methanol oxidation

Why Conducting polymers ?

- ☞ Good electronic/ionic conductivity
- ☞ Better stability
- Three-dimensional structures and high porosity of the polymeric matrices leads to high dispersion
- High dispersion of metallic particles inside these polymers gives electrodes with higher surface areas and enhanced electrocatalytic activity
- ☞ Easy Fabrication
- ☞ Minimum transport limitations

Conducting Polymer matrices used as supports



Template assisted electrochemical synthesis of conducting polymer nanotubes



Electrodes based on template-synthesized polyaniline support





Cyclic Voltammograms for the polymerisation of aniline (0.1M) in $1 \text{ M H}_2\text{SO}_4$ at 50 mV/s on CC/Naf/Al₂O₃





SEM images of (a) template synthesized PANI nanotubes and (b) Pt incorporated PANI nanotubes



SEM images of (a) conventionally synthesized polyaniline and (b) Pt particles on the conventionally synthesized polyaniline



HR-TEM image of Pt incorporated polyaniline nanotubules



Electron diffraction image of the Pt particles



CVs of Pt incorporated template-based PANI electrode in (a) 1 M $\rm H_2SO_4$ and (b)1 M $\rm H_2SO_4/1$ M

CH₃OH; Scan rate - 50 mV/sec



CVs of Pt incorporated conventionally prepared PANI electrode in 1M H₂SO₄/1 M CH₃OH; Scan rate - 50 mV/sec



Variation of electrocatalytic activity of methanol oxidation with Pt loading on nanotubule and conventional PANI electrodes

Comparison of methanol oxidation activity of template- and conventionally synthesized Pt loaded PANI electrodes

			Activity			
S.No	Electrode	Onset Potential	Forward sweep		Reverse sweep	
		(V)	Ι	E	Ι	E
			(mA cm ⁻²)	(V)	(mA cm ⁻²)	(V)
1	CC/Naf/PANI _{Temp} -Pt	0.20	49.6	+0.8		
2	CC/Naf/PANI _{Conv} -Pt	0.25	14.8	+0.67	10.52	+0.52



 $Chronoamperometric responses of CC/Naf/PANI_{Temp} - Pt, commercial Pt/C and CC/Naf/PANI_{Conv} - Pt electrode in 1 M H_2SO_4 / 1 M CH_3OH polarized at +0.6 V for 2h$

		Activ		
S No	Electrode	Polarizatio	Activity (%) decrease	
		Initial current density (mAcm ⁻²)	Final current density (mAcm ⁻²)	After 2 h
1	CC/Naf/PANI _{Temp} –Pt	74.3	59.4	18
2	CC/Naf/PANI _{Conv} -Pt	20.0	13.4	33

*Activity was evaluated by polarizing the electrode at 0.6 V vs Ag/AgCl in 1M $\rm H_2SO_4/$ 1 M CH_3OH for 2 h

Electrodes based on template-synthesized polypyrrole support







SEM images of template-synthesized polypyrrole nanotubes



HR-TEM image of CC/Naf/PPY_{Temp}-Pt and *inset* shows the electron diffraction pattern of Pt nanoparticles



(d) SEM image of CC/Naf/PPY_{conv} and *inset* shows SEM image of CC/Naf/PPY_{conv}/Pt



CVs of CC/Naf/PPY_{Temp}-Pt in 1 M H₂SO₄/ 1M CH₃OH; scan rate - 50 mV/s



Variation of electrocatalytic activity of methanol oxidation with Pt loading on nanotubule and conventional PPY electrodes

Comparison of methanol oxidation activity of template- and conventionally synthesized Pt loaded PPY electrodes

			Activity				
S.No	Electrode	Onset Potential	Forward	Forward sweep R		erse sweep	
		(V)	I	E (V)	I	E (V)	
				(•)		(*)	
1	CC/Naf/PPY _{Temp} –Pt	+0.1	191	+ 0.80			
2	CC/Naf/PPY _{Conv} -Pt	+0.2	39.2	+0.70	25.1	+0.55	



 $Chronoamperometric \ responses \ of \ CC/Naf/PPY_{Temp} -Pt \ and \ CC/Naf/PPY_{Conv} -Pt \ electrodes \ in \ 1 \ M \ H_2SO_4 \ / \ 1 \ M \ CH_3OH \ polarized \ at \ +0.6 \ V \ for \ 2 \ h$

		Activ			
		Polarization	Activity		
S.No	Electrode	Initial current density (mAcm ⁻²)	Final current density (mAcm ⁻²)	(%) decrease after 2 h	
1	CC/Naf/PPY _{Temp} –Pt	230.7	192.4	14	
2	CC/Naf/PPY _{Conv} –Pt	50	25	50	

*Activity was evaluated by polarizing the electrode at +0.6 V vs Ag/AgCl in 1M $\rm H_2SO_4/$ 1 M CH_3OH for 2 h

Electrodes based on template-synthesized poly(3-ethyl)thiophene (PMT) support





HR-TEM Images of (a-c) template-synthesized poly(3-methyl)thiophene (PMT) nanocones



HR-TEM image of template-synthesized Pt incorporated PMT nanocones and *inset* shows the electron diffraction image of Pt particles



SEM image of template-free PMT (c) and HR-TEM image of Pt incorporated templatefree PMT (d)



CVs of Pt incorporated template-based PMT electrode (CC/Naf/PMT_{Temp}-Pt; Pt loading of 60 μ g/cm²) in (a) 1 M H₂SO₄ and (b)1 M H₂SO₄/1 M CH₃OH; Scan rate-50 mV/sec



CVs of Pt incorporated conventionally prepared PMT electrode (CC/Naf/PMT_{Temp}-Pt; 99 Pt loading of 80 μ g/cm²) in 1M H₂SO₄/1 M CH₃OH; Scan rate-50 mV/sec



Variation of current density with Pt loading at +0.4, +0.6, and +0.8V vs. Ag/AgCl for Pt incorporated templated PMT nanocone electrodes



Variation of current density with Pt loading at +0.4, +0.6, and +0.8V vs. Ag/AgCl for Pt loaded on template-free PMT nanocone (conventional) electrodes

Comparison of methanol oxidation activity of template- and conventionally synthesized Pt loaded PMT electrodes

			Activity			
S.No	Electrode	Onset Potential	Forward sweep		Reverse sweep	
		(V)	Ι	E	Ι	E
			(mA cm ⁻²)	(V)	(mA cm ⁻²)	(V)
1	CC/Naf/PMT _{Temp} –Pt	+0.01	356.0	+0.8		
2	CC/Naf/PMT _{Conv} –Pt	+0.20	35.0	+0.65	25.0	0.45



Chronoamperometric responses of CC/Naf/PMT $_{\rm Temp}$ –Pt, commercial Pt/C and CC/Naf/PMT $_{\rm Conv}$ –Pt electrodes in 1 M $\rm H_2SO_4$ / 1 M CH_3OH polarized at +0.6 V for 2h

		Activ	Activity		
C N.		Polarizatio			
5. 1N0	Electrode	Initial current density (mAcm ⁻²)	Final current density (mAcm ⁻²)	(%) decrease (after 2 h)	
1	CC/Naf/PMT _{Temp} –Pt	359.0	305.7	14	
2	CC/Naf/PMT _{Conv} –Pt	33.3	16.6	50	

* Activity was evaluated by polarizing the electrode at 0.6 V vs Ag/AgCl in 1M $\rm H_2SO_4/$ 1 M CH_3OH for 2 h

Data obtained from cyclic voltammogram for various conducting polymer based electrodes in comparison with platinum supported on Glassy Carbon (GC) for methanol oxidation $(1M CH_3OH, 1M H_2SO_4 \text{ at } 50 \text{ mV/s})$

Electrode	Metal Loading (g/cm ²)	Activity Factor	Activity (Wt. basis)
CC/ Naf / PPY-Pt CC/ Naf / PANI-Pt CC/ Naf / PMT-Pt	100 90 110	36.1 (45.5 mA) 9.9 (12.5 mA) 57.1 (71.9 mA)	9.28 2.65 13.3
GC/ Pt*	25.7	1 (1.26 mA)	1.0

* Kost et al., 1988

Evaluation of the present Development with data from Literature

Electrode	Metal(s)	Activity Factor	Weight basis	Reference
CC-Naf-PMT* GC/PMT Graphite	Pt Pt-Sn Pt-Sn	10.3 (239.3) 1 (23.3) 1.72 (40.0)	11.20 1.00	 Swathirajan et al., 1992 Swathirajan et al., 1992
CC-Naf-PANI	Pt	6.25 (62.5)	34.72	
PANI/Au	Pt	1.3 (13.0)	9.42	Laborde et al., 1994
GC/PANI	Pt-Ru	1.0 (10)	1.00	Laborde et al., 1994a
CC-Naf-Ppy*	Pt	151.6(~1)	1.50	
GC/PPY	Pt	1.0 (150)	1.00	Yang et al., 1997
L			1	1

Development of non-noble metal based electrodes for oxygen reduction

Reaction pathways for oxygen reduction reaction



Path A – direct pathway, involves four-electron reduction $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$; $E^o = 1.229 V$

Path B – indirect pathway, involves two-electron reduction followed by further two-electron reduction $O_2 + 2 H^+ + 2 e^- \rightarrow H_2O_2$; $E^o = 0.695 V$ $H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$; $E^o = 1.77 V$

Halina S. Wroblowa, Yen-Chi-Pan and Gerardo Razumney, J. Electroanal. Chem., 69 (1979) 195

Essential criteria for choosing an electrocatalyst for oxygen reduction

- High oxygen adsorption capacity
- Structural stability during oxygen adsorption and reduction
- Stability in electrolyte medium
- Ability to decompose H_2O_2
- High conductivity
- ✤ Tolerance to CH₃OH (in DMFC)
- Low cost
★ Most promising Electrocatalyst – 40 wt% Pt/C

Difficulties with Pt

* Slow ORR due to the formation of -OH species at +0.8 V

 $O_2 + 2 Pt \rightarrow Pt_2O_2$ $Pt_2O_2 + H^+ + e^- \rightarrow Pt_2-O_2H$ $Pt_2-O_2H \rightarrow Pt-OH + Pt-O$ $Pt-OH + Pt-O + H^+ + e^- \rightarrow Pt-OH + Pt-OH$ $Pt-OH + Pt-OH + 2 H^+ + 2 e^- \rightarrow 2 Pt + 2 H_2O$



Cyclic voltammograms of the Pt electrode in helium-deaerated (—) and O_2 sat. (- - -) H_2SO_4

* Development of mixed potential (in DMFC)

* Scarce and expensive

Charles C. Liang and Andre L. Juliard, J. Electroanal. Chem., 9 (1965) 390 109

Non-noble metal Electrocatalysts

***** Transition metal oxides

- perovskites, spinels, pyrochlores

***** Transition metal sulphides

- $Ru_x Se_{y,} Mo_x Ru_y S_z$

***** Transition metal macrocycles

- porphyrins, phthalocyanines, tetraaza-annulenes
- pyrolyzed macrocycles supported on carbon

Active site for oxygen reduction $-MN_4C_x$ (M = Fe, Co)

Why MN₄C_x?

- ***** High Oxygen adsorption capacity
- ***** Structural stability during Oxygen adsorption and reduction
- ***** Stability in Electrolyte medium
- ***** Ability to decompose H₂O₂
- ***** High conductivity
- ***** Tolerance to CH₃OH
- ***** Low cost

Where does the Electron come from and Where does it go ?

* Oxygen reduction takes place by the transfer of electron from HOMO of MN_4 to the anti-bonding π^* of O_2 molecule



Molecular Orbital diagram of O_2 molecule

Methodology

- * Single point energy DFT calculations by Gaussian98
- ★ B3LYP LANL2DZ Basis set
- * MOLDEN for visualization of orbitals
- **Model systems** : $MN_4(M = Fe, Co)$ and O_2



Fe-N distance: 2.00 Å Co-N distance: 2.01 Å \angle N-M-N : 109°47' $\mathbf{0} \equiv \mathbf{0}$

O-O distance : 1.26 Å

Percentage atomic orbital contributions to HOMO and LUMO of MN₄ and O₂

Model	E (eV)	M = Fe, Co			Ν	
system		S	р	d	S	р
F eN	<i>HOMO: -</i> 7.56	0.0	0.0	30.8	0.0	69.1
FeN ₄	<i>LUMO: -</i> 7.00	0.0	0.0	0.0	0.0	100.0
CoN ₄	<i>HOMO: -</i> 7.78	2.3	0.0	21.1	1.1	75.4
	<i>LUMO: -</i> 7.01	0.0	1.6	3.2	1.6	93.4

Model	E (eV)	0		Ο	
system		S	р	S	р
O ₂	<i>HOMO:</i> -8.18 (π* level)	0.0	50.0	0.0	50.0
	<i>LUMO:</i> +6.41	28.3	21.6	28.3	21.6 ¹¹⁴

Synthesis of Iron Tetraphenylporphyrin (FeTPP)

40 ml anhydrous pyridine + 5 ml triethylamine + 0.5 ml TBP

 \downarrow 10⁻² mol FeCl₂

 \downarrow 5 x 10⁻³ mol H₂TPP

refluxed under Ar for 2 hr

↓ filtered and dried at 75 °C

Elemental analysis

expected C: 79.05 wt%, H: 4.22 wt%, N: 8.38 wt%, Fe: 8.35 wt% *found* C: 78.12 wt%, H: 4.31 wt%, N: 8.57 wt%, Fe: 8.49 swt%

FeTPP

Preparation FeTPP/CDX975

0.17 g FeTPP + 60 ml anhydrous Pyridine

- ↓ 0.54 g CDX 975
- refluxed overnight under Ar
- \downarrow filtered and washed with H₂O
- ↓ dried at 75 °C

FeTPP/CDX975

- The prepared catalyst was grounded into fine powder and heat treated at different temperatures ranging from 100 - 900 °C in Ar atm for 2 hr



found C: 62.88 wt%, H: 2.54 wt%, N: 19.87 wt%, Fe: 9.71 wt%

Preparation FePc/CDX975

0.12 g FePc + 60 ml anhydrous Pyridine

- ↓ 0.5 g CDX 975
- refluxed for 8 hr under Ar
- \downarrow filtered and washed with H₂O
- dried at 75 °C

FePc/CDX975

- The prepared catalyst was grounded into fine powder and heat treated at different temperatures ranging from 100 - 900 °C in Ar atm for 2 hr

16 mg catalyst + 0.4 ml of H_2O + 0.4 ml of 5 % Nafion

Ultrasonicated for 10 min

10 µl pipetted onto the GC disk Dried in air at 75°C

Electrochemical Conditions

Electrolyte: $0.5 \text{ M H}_2 \text{SO}_4$ Working electrode: $\begin{array}{c} \text{Catalyst deposited} \\ \text{GC Disk} \end{array}$ Reference electrode: Ag/AgCl, sat KCl (+0.197 V)Counter electrode: PtScan rate: 10 mV/sec







Heat treatment temp (°C)	Wt % of 'Fe' by redox titration method	Wt % of 'N' by Kjeldahl method	Oxygen reduction activity at 0.503 V vs. Ag/AgCl, sat KCl (mA/cm ²)
untreated	1.96	2.3	0.0
100	NM	2.2	0.0
200	NM	2.14	0.0
300	NM	2.1	0.08
400	NM	1.87	1.1
500	NM	1.74	1.8
600	1.97	1.7	3.81
700	NM	1.65	2.72
800	NM	1.3	1.6
900	NM	1.04	1.2

(NM = not measured)

* heat-treated FeTPP/CDX975 at 600 °C showing higher activity

CVs of untreated FePc/CDX975



123



CVs of heat-treated FePc/CDX975 at 500 °C

124

Heat treatment temp (°C)	Wt % of 'Fe' by redox titration method	Wt % of 'N' by Kjeldahl method	Oxygen reduction activity at 0.503 V vs. Ag/AgCl, sat KCl (mA/cm ²)
untreated	1.86	1.94	0.0
100	NM	1.62	0.0
200	NM	1.58	0.0
300	NM	1.5	0.13
400	NM	1.48	0.4
500	NM	1.4	2.4
600	1.85	1.2	2.2
700	NM	1.1	0.44
800	NM	0.4	0.31
900	NM	0.18	0.18

(NM = not measured)

* heat-treated FePc/CDX975 at 500 °C showing higher activity

Synthesis of Iron and Cobalt Tetramethoxyphenylporphyrins (FeTMPP-Cl and CoTMPP) 56 ml of N,N'-dimethylformamide

refluxed under Ar

 $\bullet 0.67 \text{ g H}_2 \text{TMPP}$

- 0.22 g metal acetate (10% extra)
- refluxed under Ar for 2 hr
 - cooled in an ice bath and a portion of ice-water mixture was added
- filtered and dried at 110 °C

M-TMPP (M = Fe and Co)

Finally it was purified by column chromatography using benzene-chloroform (1:1) as the eluant.

Treatment of carbon support (CDX975) with HNO₃

1 g of carbon black, CDX975 + 20 mL of 70 wt % HNO₃

- refluxed for 7 hr
- filtered, washed with deionized water and methanol
- dried at 373 K

CDX975 (T)

Literature reports

According to the studies of Ehrburger et al. on iron phthalocyanine (FePc), oxygen surface complexes on the edge carbon atoms anchor the FePc particles and aid in improved dispersion of these particles. P. Ehrburger, A. Mongilardi, and J. J. Lahaye, *J. Colloid Interface Sci.* 91(1983) 151–159.

Gou'erec et al. studied the activity and stability of cobalt tetraazaannulene (CoTAA) on two different carbon supports varying in the amount of surface oxygen complexes, and concluded that strong interactions between the metal complex and the carbon support are established via the surface oxygen complexes thus increasing the sintering resistance of these particles.

P. Gou'erec, M. Savy, and J. Riga, *Electrochim. Acta* 43 (1998) 743–753.

Jaouen et al. showed that pre-treatment of carbon resulted in an improvement in the performance of Fe-based non-precious metal catalysts to oxygen reduction reaction (ORR).

F. Jaouen, S. Marcotte, J. P. Dodelet, and G. Lindbergh, J. Phys. Chem.B 107 (2003) 1376–1386.

Preparation M-TMPP (M = Fe & Co)/CDX975 (UT &T)

- M-TMPP + Acetone (M = Fe and Co)
 - required amount of CDX 975 (UT & T)
 - ultrasonicated for 30 min
 - solvent was removed under
 - vacuum with a water aspirator

M-TMPP/CDX975 (UT &T)

(Metal loading: 2 wt%)

- The prepared catalyst was grounded into fine powder and heat treated at 800 $^{\rm o}{\rm C}$ in Ar atm for 2 hr

Electrode fabrication



Electrochemical Conditions

Electrolyte: 0.5 M H₂SO₄ Working electrode: Catalyst deposited GC Disk Reference electrode: Ag/AgCl, 3.5 M KCl (+0.205 V vs. NHE) Counter electrode: Pt Scan rate: 10 mV/sec



CVs of untreated and treated CDX975 in 0.5 M H₂SO₄: Scan rate 10 mV/sec

The redox peaks are characteristic of quinone/hydroquinone groups present on the carbon surface.



LSV of heat-treated FeTMPP-Cl/CDX975(UT) at 800 °C

LSV of heat-treated FeTMPP-Cl/CDX975(T) at 800 °C





LSV of commercial 2 wt% Pt/Vulcan carbon XC72R (E-TEK)

Comparison of ORR activities of Fe and Co-based catalysts and commercial Pt catalyst

Catalyst	Metal loading (wt%)	ORR activity at 0.7 V vs NHE (mA/cm ²)
FeTMPP-Cl/CDX975(UT)	2.01	0.2
FeTMPP-Cl/CDX975(T)	2.03	0.35
Heat treated FeTMPP-Cl/CDX975(UT) at 800 °C	1.96	4.2
Heat treated FeTMPP-Cl/CDX975(T) at 800 °C	1.97	4.9
CoTMPP/CDX975(UT)	1.98	0.16
CoTMPP/CDX975(T)	1.97	0.24
Heat treated CoTMPP/CDX975(UT) at 800 °C	1.89	3.2
Heat treated CoTMPP/CDX975(T) at 800 °C	1.93	4.5
Pt/Vulcan XC72R (E-TEK)	2.07	4.9

Heat-treated CoTMPP/CDX975(T) at 800 °C and FeTMPP-Cl/CDX975(T) at 800 °C are displaying comparable activity with that of commercial 2 wt% Pt/Vulcan XC72R.



100 nm

100 nm

D

TEM of (A) Heat treated FeTMPP-Cl/CDX975(UT) at 800 °C (B) Heat treated FeTMPP-Cl/CDX975(T) at 800 °C (C) Heat treated CoTMPP/CDX975(UT) at 800 °C and (D) Heat treated CoTMPP/CDX975(T) at 800 °C 136



Chronoamperometric responses of non-noble and noble metal metal based electrocatalysts in oxygen saturated 0.5 M H₂SO₄ polarized at +0.7 V for 3 h



 H_2/O_2 PEM fuel cell polarization curves with as-synthesized Fe and Co based catalysts and 2 wt% Pt/Vulcan XC72R (E-TEK) for oxygen reduction at 80 °C;





THANK YOU