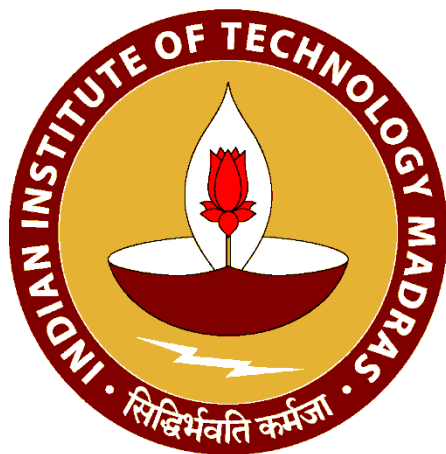


Carbon Support for Fuel Cell Applications



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National Centre for Catalysis Research, IIT Madras

Renewable Energy Day
20th August 2010

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- 2. Carbon materials as catalyst support**
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- 5. Conclusion**

1. What are Fuel Cells?

- ❖ Fuel cells are future energy sources
- ❖ Direct conversion of chemical energy into electrical energy is possible

❖ Typical applications

Space missions
 Military operations
 Mobile electronic devices
 Domestic needs

❖ Key Components

Electrodes (anode and cathode)
 Membrane
 Bipolar plates

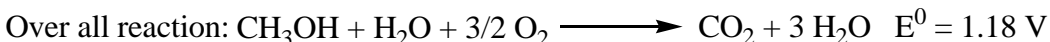
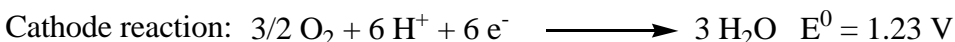
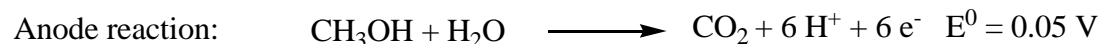
❖ The Direct Methanol Fuel Cells (DMFCs)

Expected to approach commercialization sooner owing to the possibility of adopting the existing and well developed infrastructure for the distribution of petroleum products for the distribution of the fuel (methanol) for DMFCs

❖ Problems in DMFCs

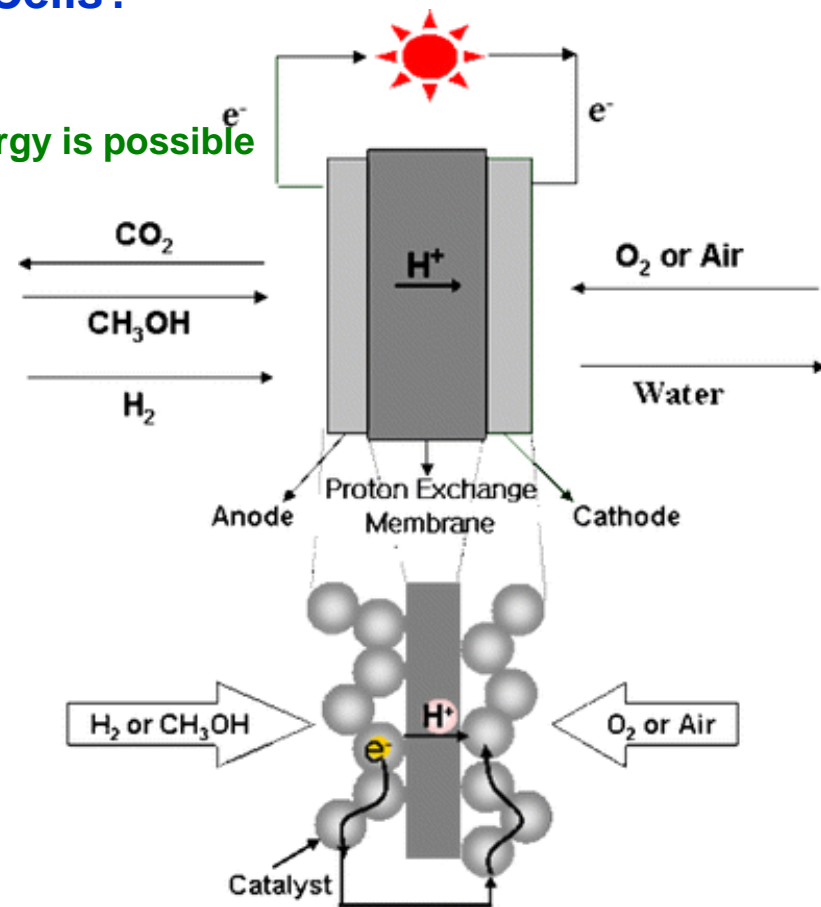
Low power density
 Poisoning of electro catalyst
 Expensive nature of electro catalyst

❖ Redox reactions taking place in DMFC



Objective:

To develop an anode electro catalyst, from a renewable carbon source, with improved performance compared to the state-of-the-art PtRu/C catalyst for the electro oxidation of CH_3OH



Schematic representation of a fuel cell

(Lim *et al.*, 2008, *Catal. Surv. Asia*, 12, 310-325)

2. Carbon Materials as Catalyst Support

- ✓ Decrease Pt loading
- ✓ Increase specific surface area of the catalyst
(Maximize the utilization of active component)

Major electrochemical applications of Carbon:

Fabrication of electrodes

As electro catalyst

As **conductive support** for the electrochemically active material

Why carbon is attractive?

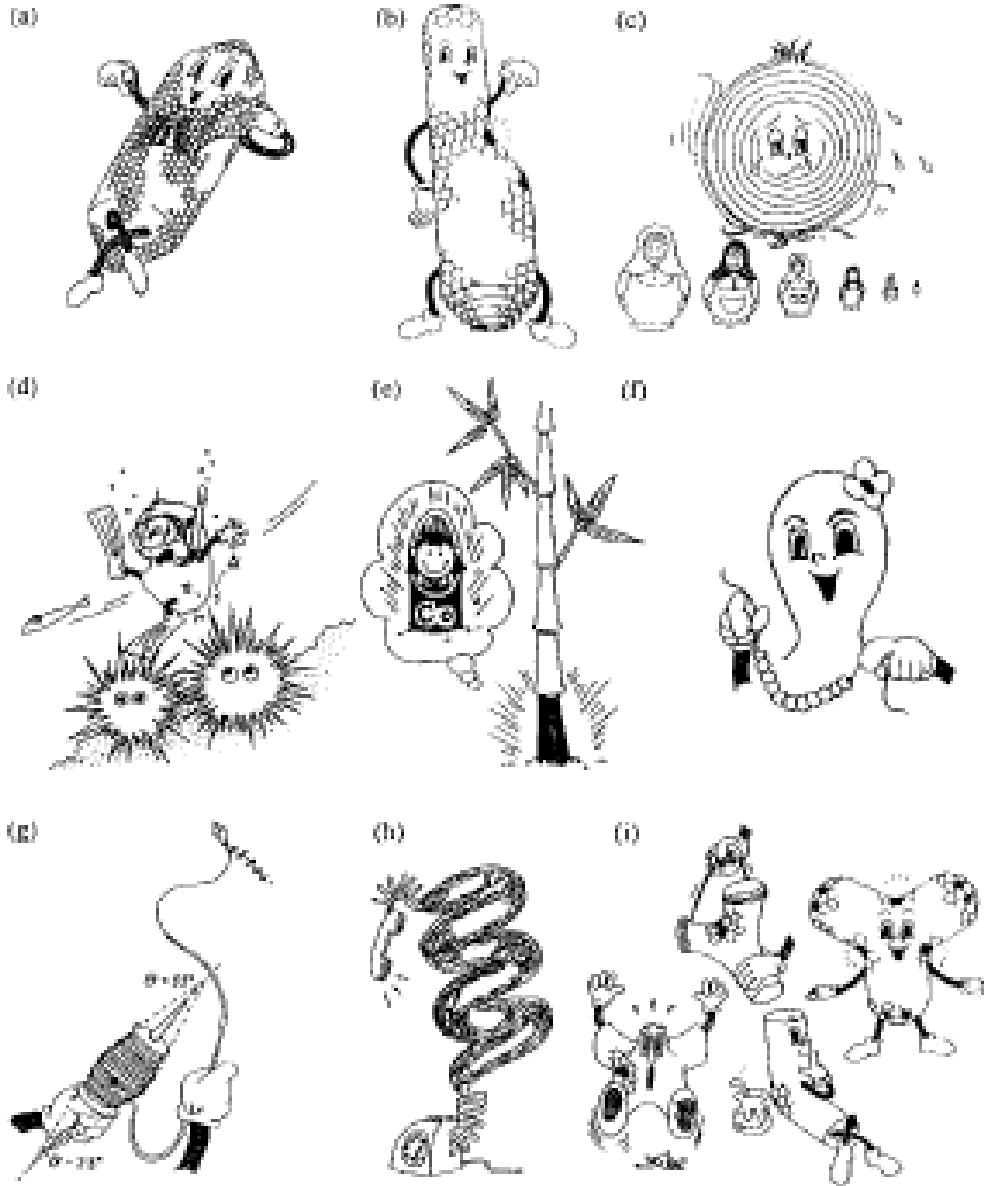
Availability in a wide variety of physical structures

Relatively low chemical and electrochemical reactivity

Carbon - Ideal material as support

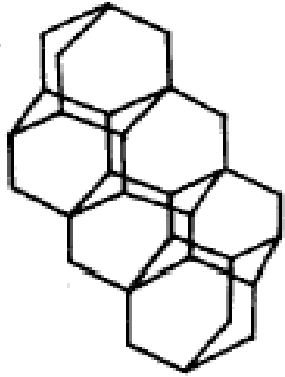
- ❖ **Electronic conductivity**
- ❖ **Corrosion resistance**
- ❖ **Surface properties**
- ❖ **Low cost**

Carbon materials exhibit many different *morphologies*

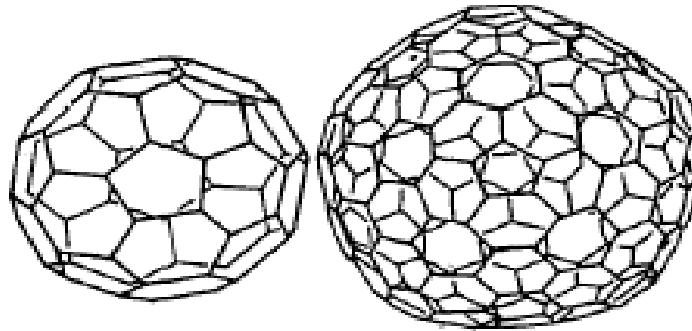


A simple representation of carbon materials with PECULIAR morphologies

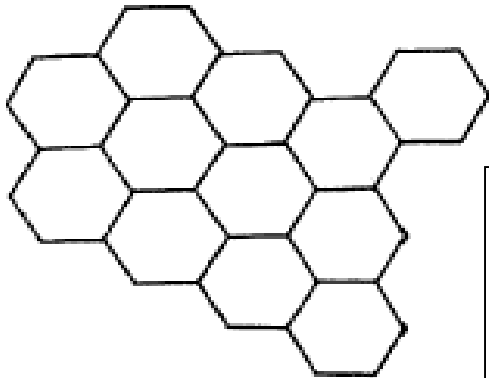
Different allotropic forms of Carbon materials



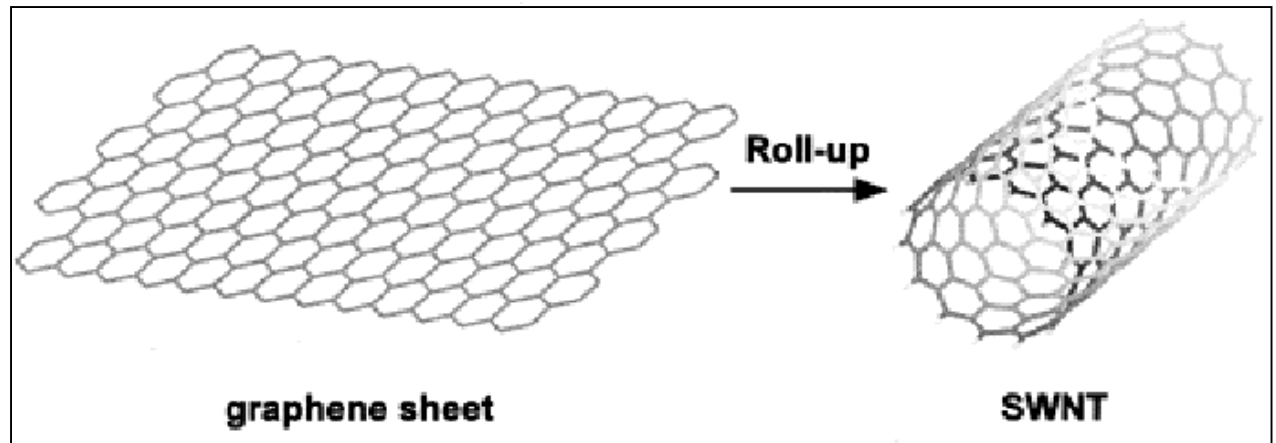
Diamond



Fullerenes



Graphite



graphene sheet

SWNT

3. Carbon Materials from Renewable Sources

❖ Production of activated carbon – Designing economic way

➤ Major Sources

- i. Coal
- ii. Petroleum pitch
- iii. Lignocellulosic materials

❑ Lignocellulosic materials for Activated Carbon

- i. Renewable
- ii. Inexhaustible supply
- iii. Evenly distribution around the globe
- iv. Viable option compared to fossil fuels
- v. Retention of the structural features of the original plant tissue (biotemplating feature)
- vi. High carbon content (because of easy removal of H and O)

❑ Exploration of new sources of carbon materials - Necessary

Desired physico-chemical properties

- i. High specific surface area
- ii. Porosity
- iii. Surface functionality
- iv. Thermal stability
- v. Carbon content
- vi. Carbon purity
- vii. Adsorptive capacity

Michal Kruk, Bruno Dufour, Ewa B. Celer, Tomasz Kowalewski, Mietek Jaroniec and Krzysztof Matyjaszewski, *J. Phys. Chem. B*, 109 (2005) 9216

An-Hui Ru and Jing-Tang Zheng, *Journal of Colloid and Interface Science*, 236 (2001) 369

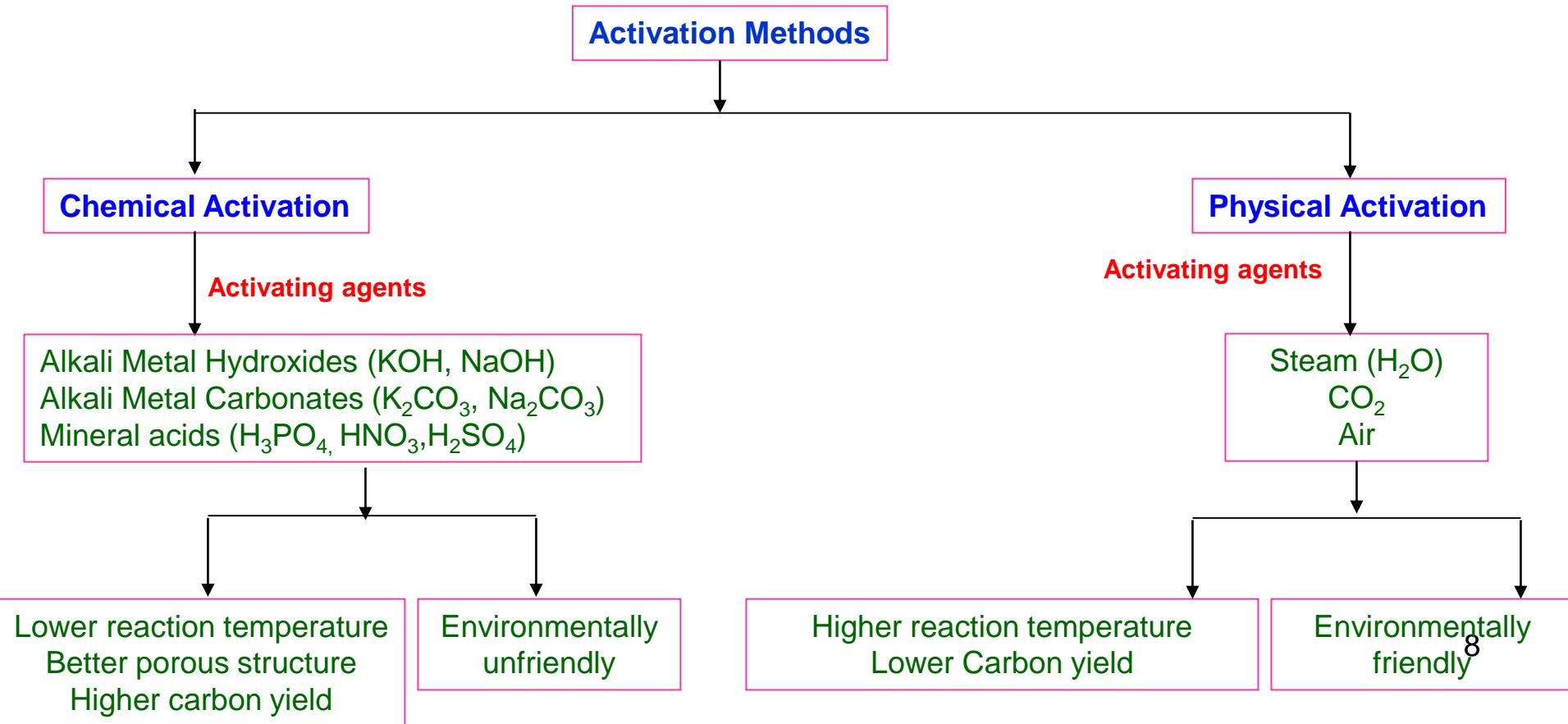
Junichi Hayashi, Atsuo Kazehaya, Katsuhiko Muroyama, A. Paul Watkinson, *Carbon* 28 (2000) 1873

Activated Carbon Materials – Methods of Activation

- ❑ Surface area values can be modulated from few m^2/g to few 1000 m^2/g due to the micro architecture of the pores.
- ❑ Variety of activating agents can be used.
- ❑ Functional groups can be easily introduced and altered

Process of Activation

- Creates porosity
- Generates desired surface functional groups



Activated Carbon Materials - Applications

- ❑ Highly porous structure
- ❑ High specific surface area and tunable porosity
- ❑ Hydrophobic and Hydrophilic surface co-exist

Applications

- i. Catalysts
- ii. Catalyst supports
- iii. Energy storing media
(Methane, Hydrogen, Batteries, Electrodes for super capacitors)
- iv. Energy conversion (Fuel cells, Solar cells)
- v. Effective in removing pollutants
(regulate SO_x and NO_x emissions from fuel combustion in automobiles)
- vi. Production of fine and bulk chemicals and catalysis



Structure of Activated Carbon

Carbon Material from *Limonea acidissima* (Wood Apple Shell), C_{WA}



Carbon precursor : Shells of wood apple
Tree : Wood apple tree, Bilva patra, Bel, Elephant wood
Binomial nomenclature: *Limonia acidissima*, *Feronia limonea*, *Limonea elephantum*
Habitat : Found all over the deciduous forests in India

Synthesis

Dried Shells of Wood Apple Fruit (50 g)

100 mL, 50 wt.% KOH solution

soaking for 2 h

excess KOH decanted

drying of shells in air oven

Thermo chemical activation
 N₂ atm., 1073 K, 2 h

Char

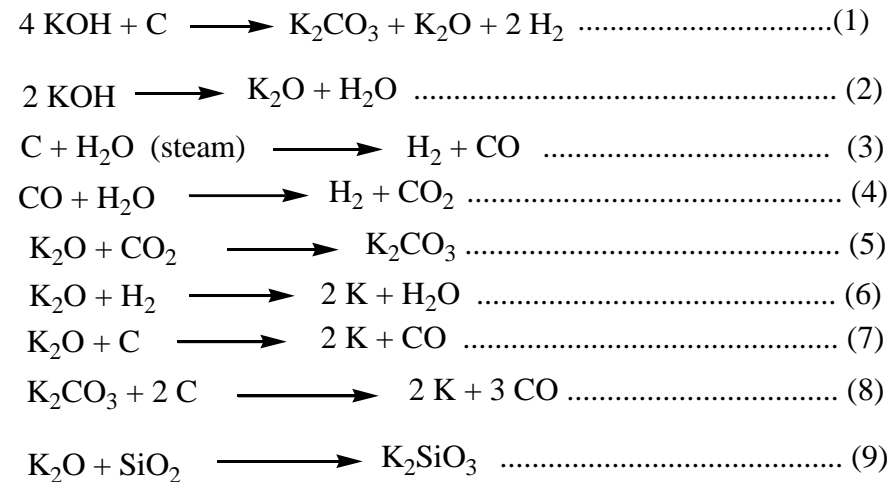
HNO₃ treatment

Char : HNO₃ (wt.%/wt.%), 1:5

filtration, washing with water

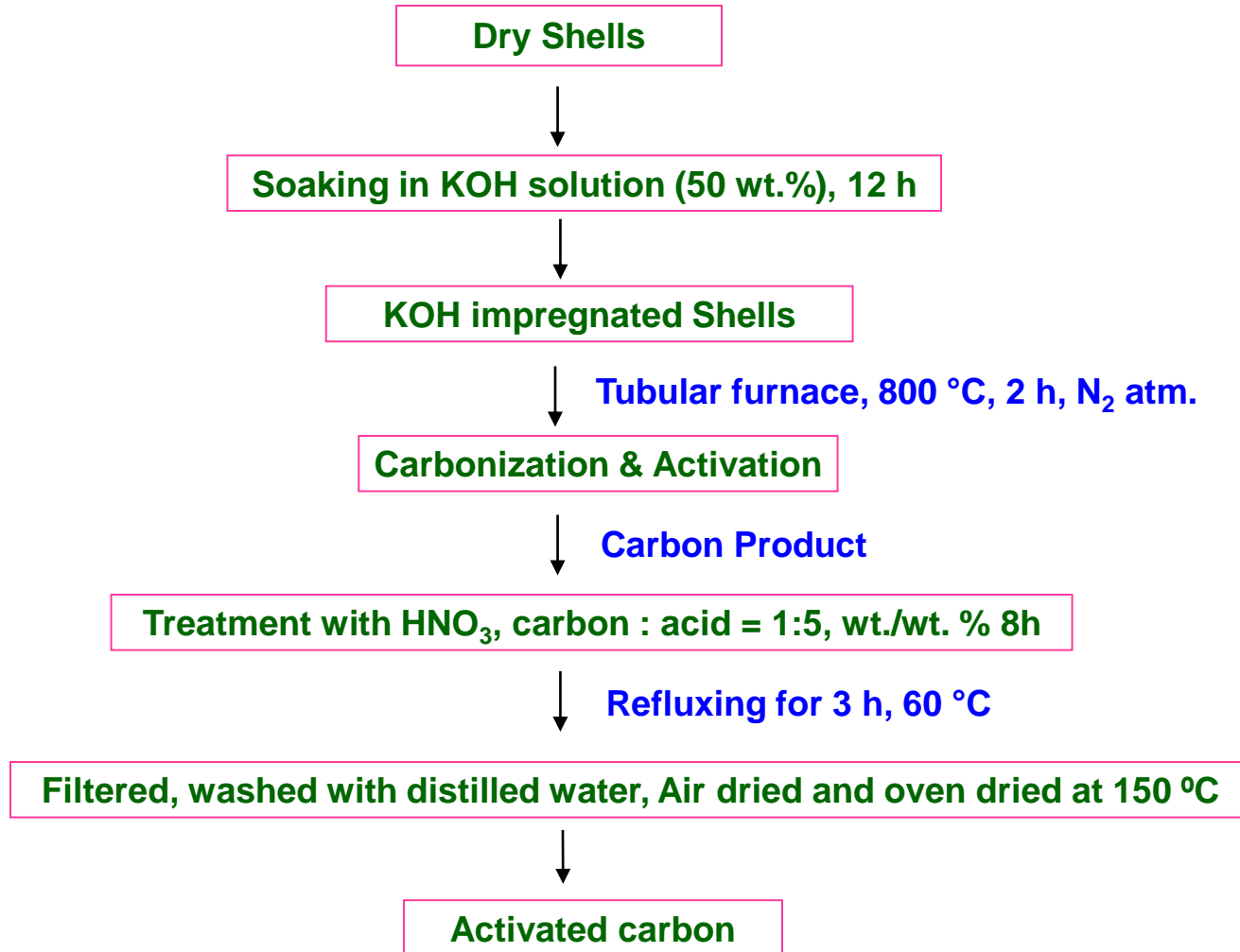
Activated Carbon Material (C_{WA})

Chemistry in Activation Step

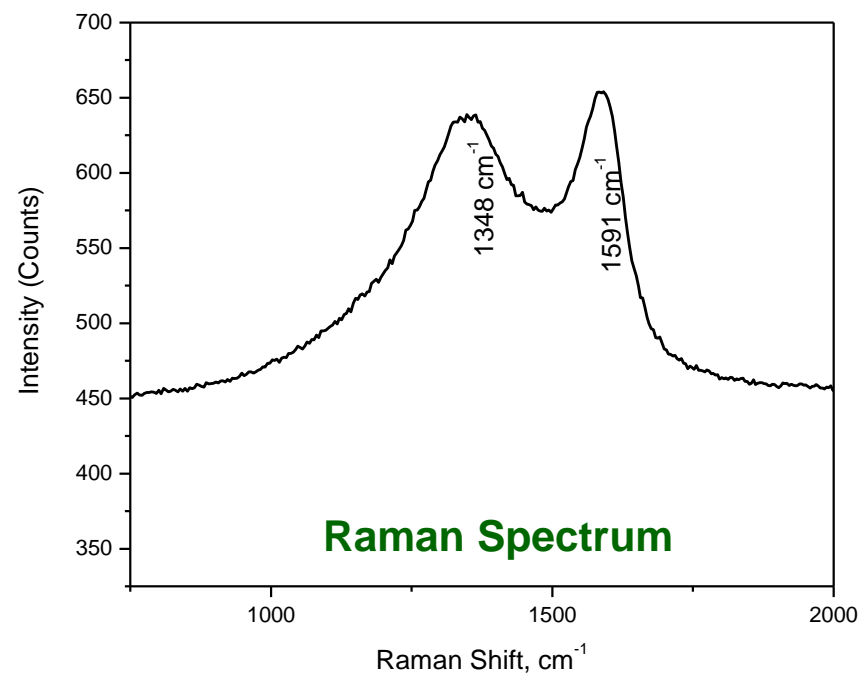
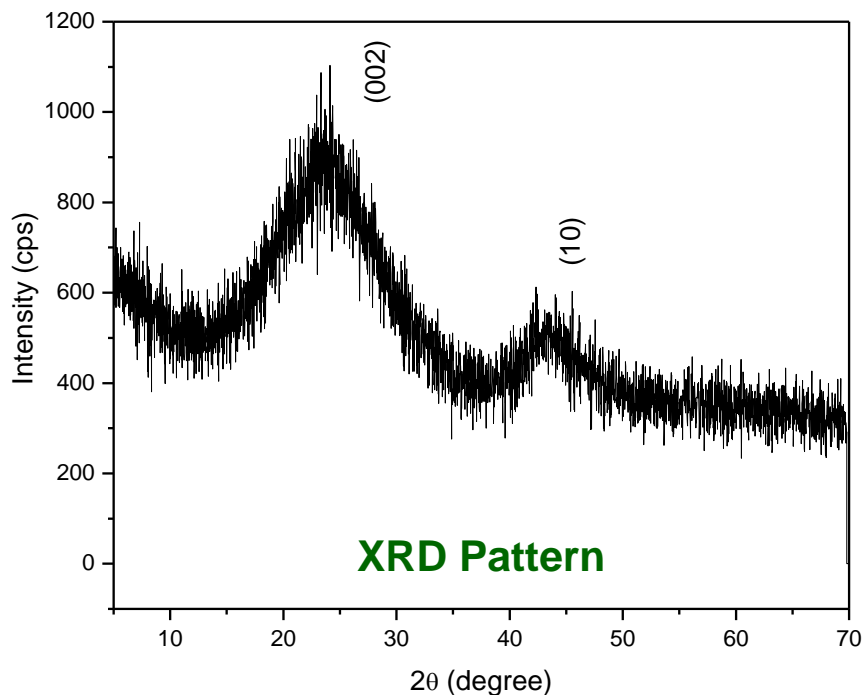


- Reactions (1) to (9) contribute to the evolution of porosity
- Carbon surface gets oxidised with HNO₃ treatment
- C-O type groups (carbonyl and carboxyl) are generated on the carbon upon treatment with HNO₃

Activated Carbon from *Limonea Acidissima* – Method of Preparation



Activated Carbon from Limonea Acidissima - Structural Properties



Crystallographic structural details deduced from XRD studies

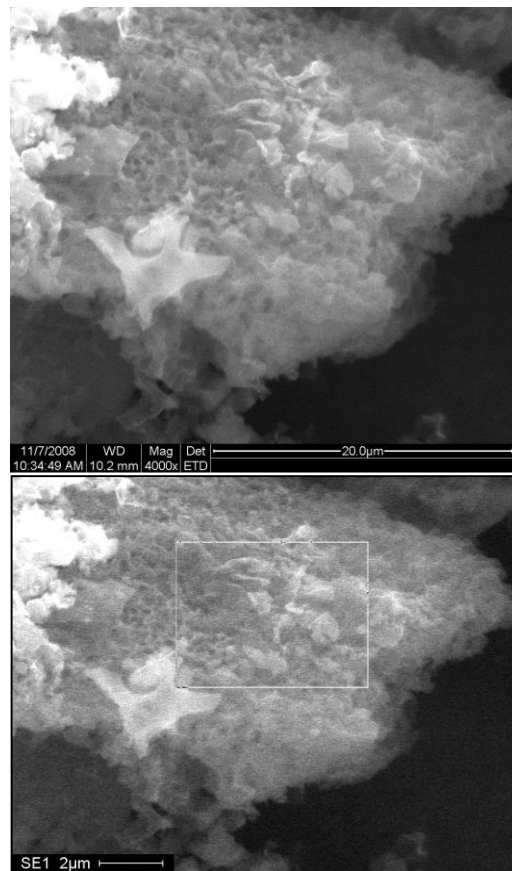
S. No.	Sample	d_{002} (nm)	* L_c (nm)	* L_a (nm)
1	Activated Carbon, C_{WA}	0.377	1.1	3.656

Structural parameters deduced from the confocal Raman spectroscopic studies

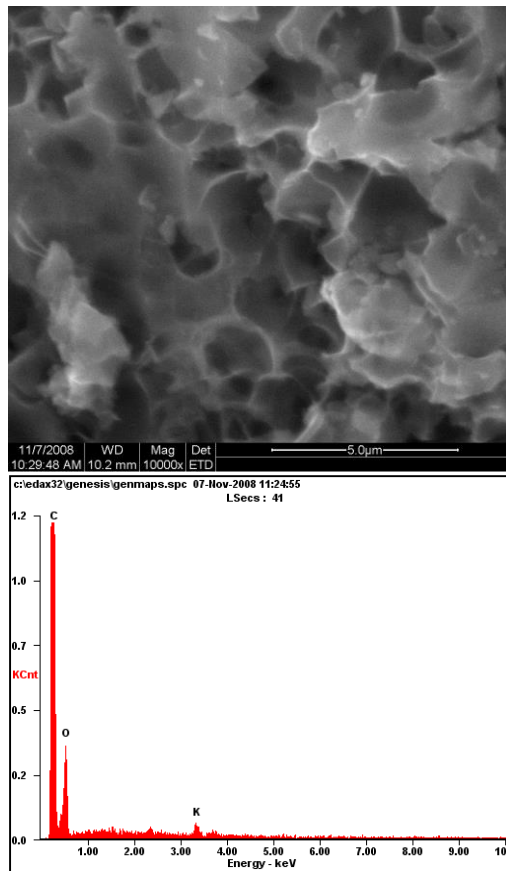
S. No.	Sample	Peak Intensity Frequency, ν_x , cm^{-1}		$R = I_D/I_G$	L_a (nm) = $4.4/R$ (From Raman)	L_a (nm) (from XRD)
		G band	D band			
1	C_{WA}	1591	1348	1.408	3.125	3.656

Activated Carbon from *Limonea Acidissima* – Morphology and Composition

4000 x



10,000 x



SEM images and EDAX spectrum

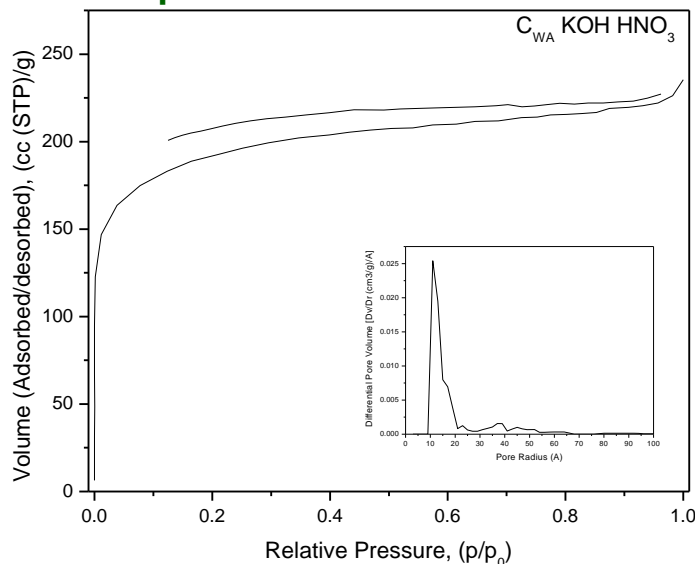
S. No.	Element	Wt. %	At. %
1	Carbon	74.84	80.02
2	Oxygen	24.70	19.83
3	Potassium	0.45	0.15

The elemental composition from EDAX

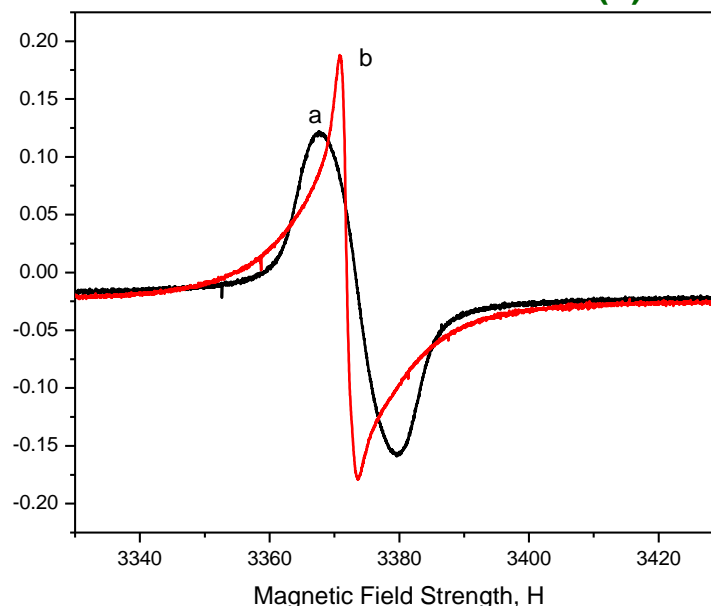
❖ Ash content – 1.04%

Activated Carbon from *Limonea Acidissima* Textural Properties and Electron Spin Density

N₂ adsorption-desorption isotherm and pore size distribution curve



EPR spectrum of (a) Activated Carbon from *Limonea Acidissima* and (b) DPPH



Textural Properties deduced from Isotherm

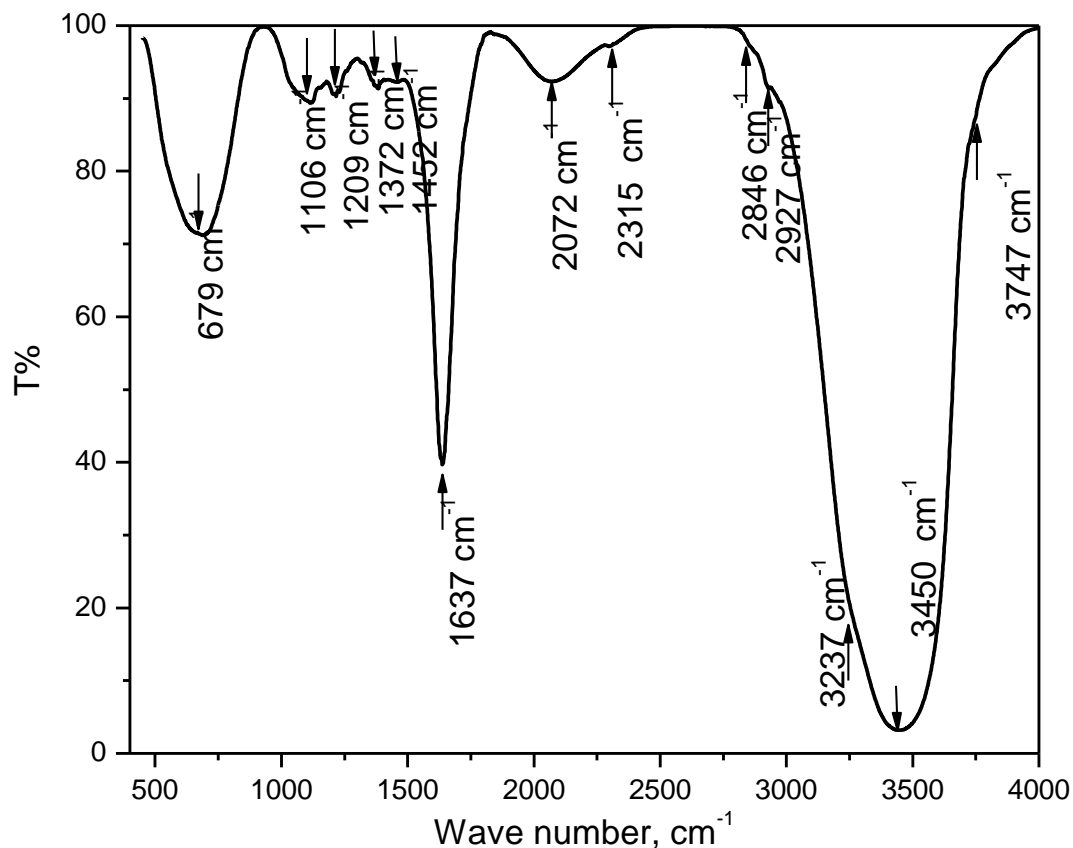
S. No.	Sample	S_{BET} (m ² /g)	V_p (cm ³ /g)	Mean Pore Diameter ⁱ (nm)
1	Activated carbon, C _{WA}	698	0.35	2.0

Electron Spin Concentration deduced from Isotherm

S. No.	Carbon Material	g-factor value	ΔH (in Gauss) Peak to peak separation	Spin Concentration per gram of carbon material
1	C _{WA}	2.03095	12	0.13×10^{19}

The spin concentration value is comparable to those of commercial acetylene black (3.8×10^{19}) and graphon (1.1×10^{19})

Activated Carbon from *Limonea Acidissima* – Surface Functionality

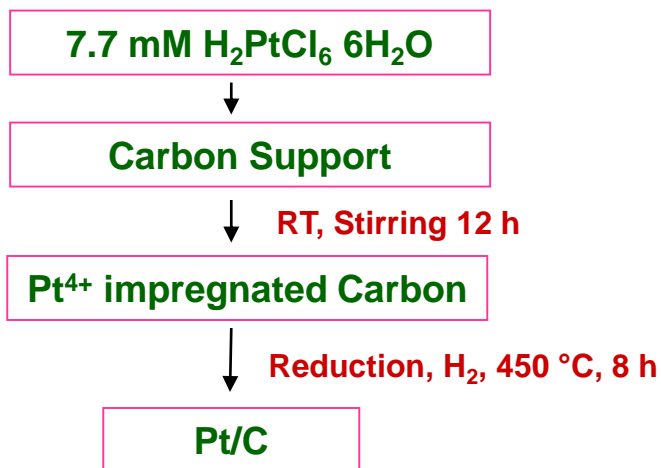


FT – IR spectrum of Activated Carbon (KOH activation)

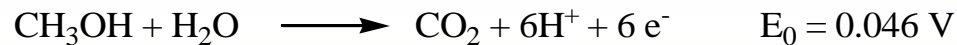
Band position ν, cm⁻¹	Assignment
3747	Isolated –OH groups
3450	O-H stretching vibration of surface hydroxyl groups and adsorbed water. Asymmetry (shoulder like feature at 3237 cm ⁻¹) indicated presence of hydrogen bonding interaction
2927	Aliphatic, asymmetric C-H stretching vibration of methylene group
2846	Aliphatic, symmetric C-H stretching vibration of methylene group
2315	Ketone group
1637	C=O (carbonyl) stretching vibration in quinone
1452	In plane bending vibration of C-H of methylene group
1372	In plane bending vibration of C-H in methyl group
1000 - 1300	C-O stretching in phenols, alcohols, acids, ethers and esters
679	Out of plane deformation vibration of C-H groups located at the edges of aromatic planes

4. Evaluation of electro catalytic activity

Catalyst Preparation: Dry impregnation



Evaluation of Electrocatalytic Activity of Pt/C catalysts:

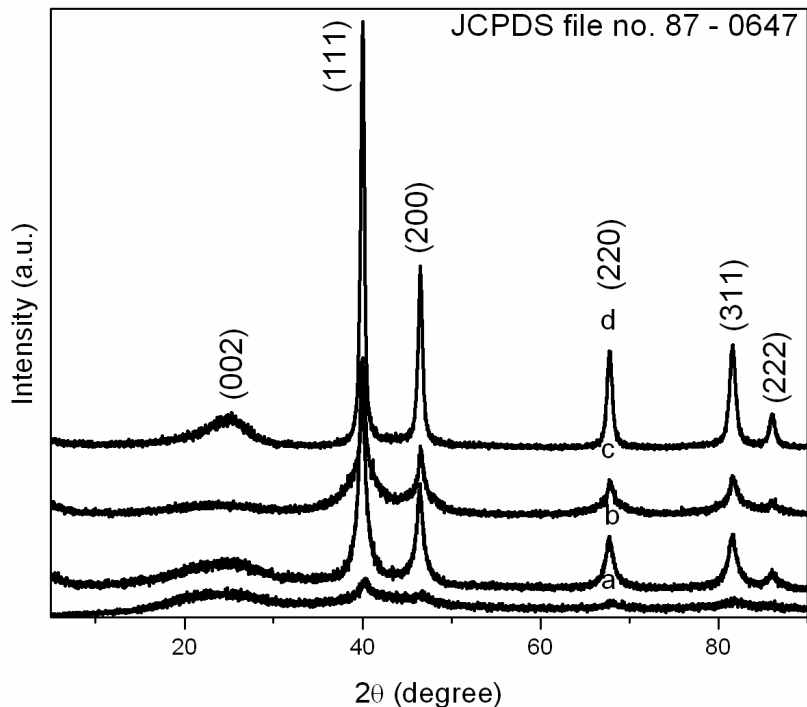


Reaction studied: MeOH electrooxidation

Objective

- i. Increase Pt utilization
- ii. Produce active, stable and CO tolerant electrocatalyst

Dispersion of Pt crystallites on Carbon Support

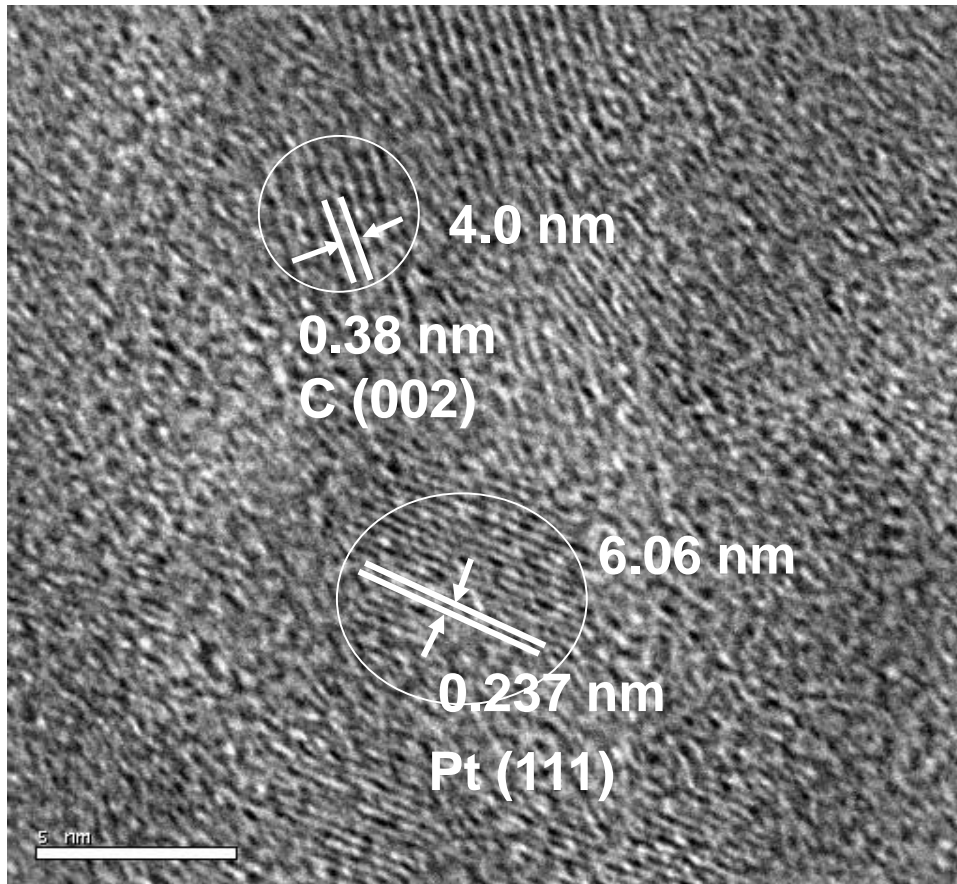


❖ The crystallite size of Pt is found to be dependent on the Pt loading and also on the nature of the carbon support

X-ray diffraction patterns of (a) 5 wt. % Pt/C_{WA} (crystallite size ~5.0 nm) (b) 10 wt. % Pt/C_{WA} (crystallite size ~10.2 nm) (c) 20 wt. % Pt/C_{WA} (crystallite size ~10.4 nm) and (d) 20 wt. % Pt/Vulcan XC 72 R (crystallite size ~13.1 nm)

S. No.	Electro catalyst	S _{BET} (m ² /g)	iS _{Micropore} (m ² /g)	iiV _P (cm ³ /g)	Mean Pore Diameter ⁱⁱⁱ (nm)
1	5 wt. % Pt/C _{WA}	505	267	0.289	2.28
2	10 wt. % Pt/C _{WA}	526	318	0.288	2.19
3	20 wt. % Pt/C _{WA}	195	102	0.119	2.447
4	20 wt. % Pt/Vulcan XC 72 R	123	-	0.29	9.43

Dispersion of Pt particles on Carbon Support



The Pt particle size of ~ 6 nm with a d spacing value of 0.237 nm corresponding to the Pt (111) is indicated in the TEM image

The carbon particles of 4.0 nm size with a d spacing value of 0.38 nm corresponding to the (002) plane of carbon is also marked in the TEM image

TEM image of electro catalyst based on the activated carbon from *Limonea acidissima*, 5 wt.% Pt/C_{WA}

4 (a) Methanol electro oxidation in acidic medium

Electrode Fabrication

Catalyst (Pt/C) dispersed in distilled water 20 mg/ml

Ultrasonicated for 10 min

10 μ L ink pipetted onto the GC disk

Dried in air oven at 60 °C

5 μ L nafion pipetted onto the catalyst deposited on the GC disk

Dried at room temperature

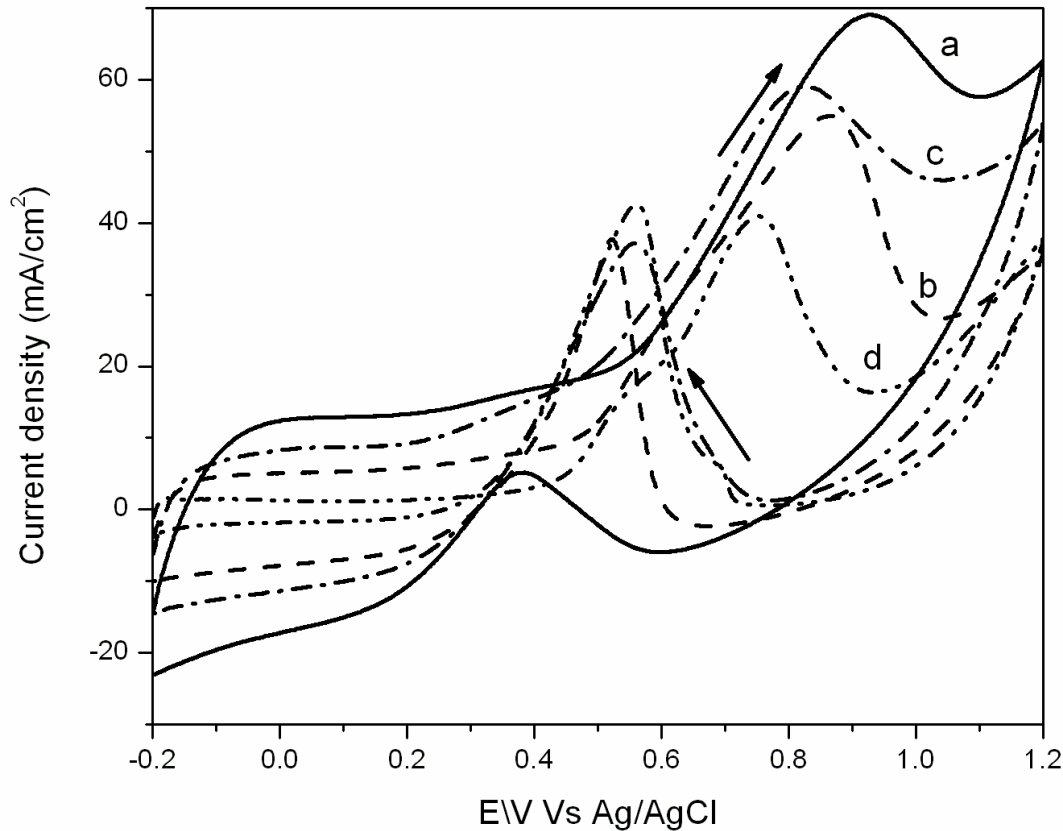
GC/Carbon- Pt - Nafion electrode

Experimental Conditions

- Electrolyte** : 0.5 M H₂SO₄
Working Electrode : Pt/C catalyst deposited on GC disk
Reference Electrode : Ag/AgCl, 3.5 M KCl (+ 0.205 V Vs NHE)
Counter Electrode : Pt foil (1.5 cm²)
Scan rate : 5, 10, 15, 20 and 25 mV/sec



Methanol (CH_3OH) Electro-oxidation Activity of Pt/C catalysts



One anodic peak is observed in the forward scan and another in the reverse scan.

The anodic peak in the forward scan is attributed to oxidation of methanol

The anodic peak in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species (mostly in the form of linearly bonded $\text{Pt}=\text{C}=\text{O}$) formed in the forward scan

Cyclic Voltammetric response of (a) GC/ C_{WA} - 5 wt.% Pt - Nafion electrode

(b) GC/ C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/ C_{WA} - 20 wt.% Pt - Nafion electrode and

(d) GC/Vulcan XC 72 R - 20 wt.% Pt - Nafion electrode in 0.5 M H_2SO_4 and 1 M CH_3OH , at a scan rate of 25 mV/sec between -0.2 to 1.2 V Vs Ag/AgCl

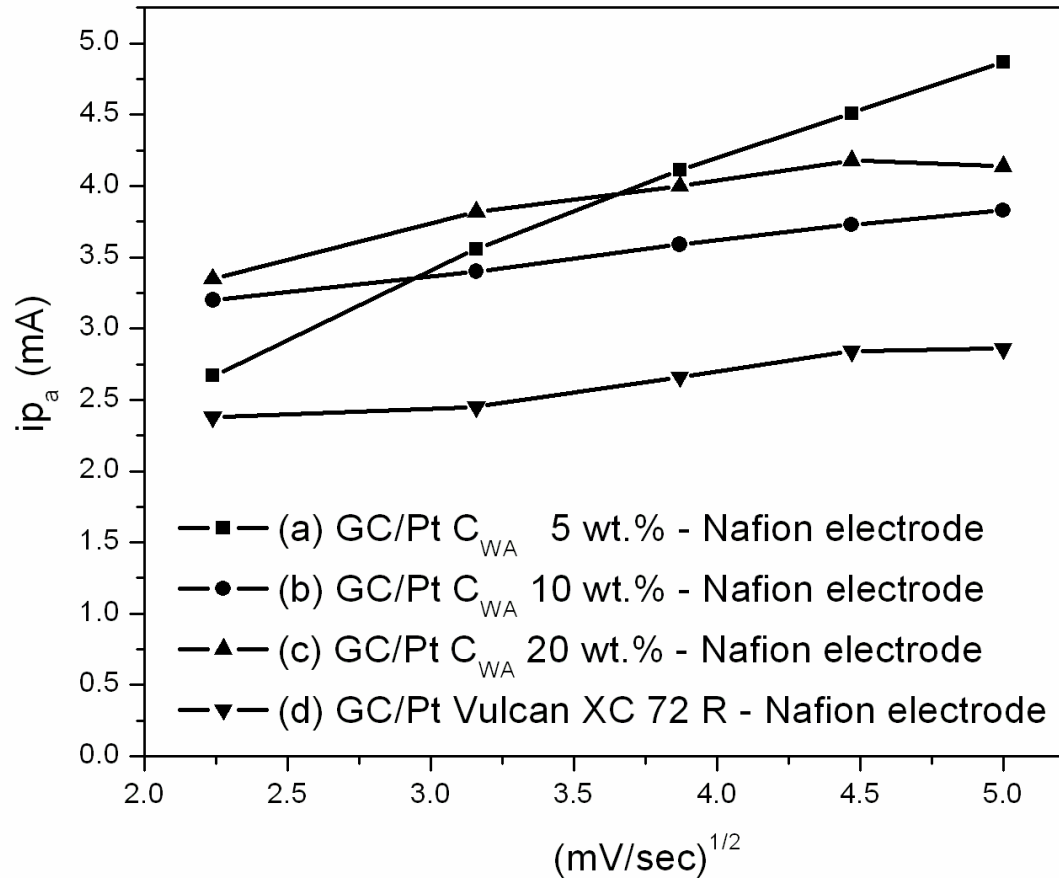
MeOH Electro-oxidation Activity of Pt/C catalysts

S. No.	Electrode	Onset Potential, V	i_r/i_b	Activity*			
				Forward sweep		Reverse sweep	
				I (mA/cm ²)	E (V)	I (mA/cm ²)	E (V)
1	GC/C _{WA} -5 % Pt-Nafion	0.21	14.4	69.0	0.92	4.97	0.37
2	GC/C _{WA} -10 % Pt-Nafion	0.18	1.45	55.0	0.86	37.6	0.52
3	GC/C _{WA} -20 % Pt-Nafion	0.18	1.60	58.9	0.82	37.28	0.51
4	GC/Vulcan XC 72 R-20 % Pt-Nafion	0.25	0.96	40.9	0.75	42.6	0.56

*Activity evaluated in 0.5 M H₂SO₄ and 1 M CH₃OH, at a scan rate of 25 mV/sec between -0.2 to 1.2 V Vs Ag/AgCl

- ❖ Onset potential is the critical parameter that determines the usefulness of an electrode
- ❖ A less positive value of the onset potential is preferred
- ❖ Lower onset (less positive potential) potential value implies the requirement of lower energy for the methanol oxidation reaction to take place
- ❖ Onset potential value is related to the breaking of the C-H bond of methanol which is the primary step involved in the mechanism of electro oxidation of methanol
- ❖ 5 wt.% Pt/C_{WA} showed a higher current density at a lower onset potential value (0.21 V) which is an indication of higher electrochemical catalytic activity

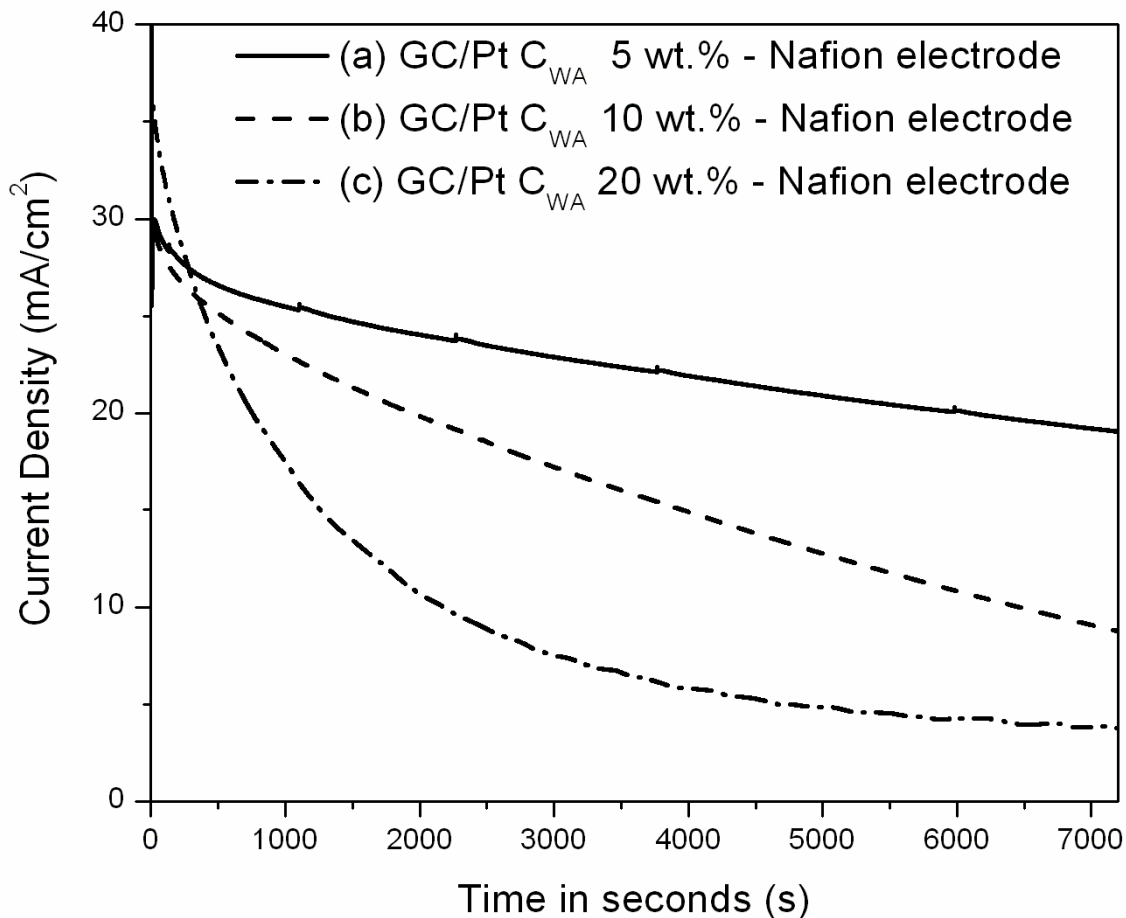
Effect of Scan Rate on Current response of GC/Carbon- Pt – Nafion electrode



Dependence of peak currents on the square roots of scan rates for Pt/C electrocatalysts in 0.5 M H_2SO_4 and 1 M CH_3OH , at different scan rates (5, 10, 15, 20 and 25 mV/sec) between -0.2 to 1.2 V Vs Ag/AgCl

- Current varied linearly as a function of sq. root of scan rate
- MeOH electro oxidation on Pt/C catalysts is diffusion controlled

Electrochemical Stability of Pt/C catalysts - Chronoamperometry



❖ 20 wt. % Pt/C_{WA} catalyst based electrode showed least stability with a 89 percentage decrease of initial activity at the end of 3 h

❖ Electrode fabricated using 5 wt.% Pt/C_{WA} possessing the smallest Pt crystallites (5.0 nm) as well as high i_f/i_b ratio showed highest stability

❖ Thus the stability of the electrode is based on the smaller crystallite size of Pt as well as the high CO tolerance (high i_f/i_b ratio value)

Chrono amperometric response of (a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode (b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode and (c) GC/CWA - 20 wt.% Pt – Nafion electrode polarized at + 0.6 V Vs Ag/AgCl in 0.5 M H₂SO₄/ 1 M CH₃OH for 3 hours

Evaluation of the stability of C_{WA} based electrodes for the electro oxidation of Methanol in half cell mode

S. No.	Electrode	Activity*		% Decrease in activity after 3 h at + 0.6 V
		Initial (I), mAcm^{-2}	Final (I), mAcm^{-2}	
1	GC/ C_{WA} -5 % Pt-Nafion	25.2	19.1	24
2	GC/ C_{WA} -10 % Pt-Nafion	29.7	19.0	36
3	GC/ C_{WA} -20 % Pt-Nafion	36.1	3.7	89

*Activity evaluated in 0.5 M H_2SO_4 and 1 M CH_3OH for 3 h with the electrode being polarized at + 0.6 V Vs Ag/AgCl

4 (b) Methanol electro oxidation in alkaline medium

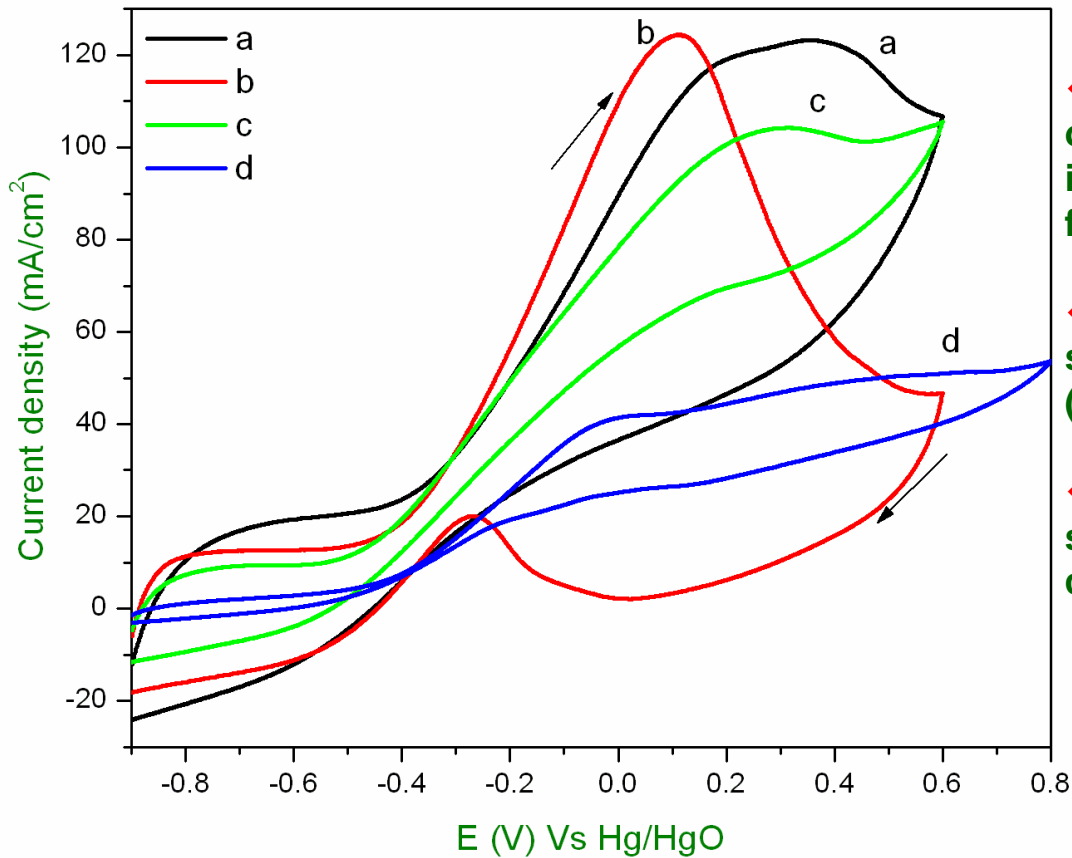
Electrochemical Measurements

Experimental Conditions:

Electrolyte : 1.0 M KOH
Working Electrode : Pt/C catalyst deposited on GC disk
and Commercial PtRu/Vulcan (JM)
Reference Electrode : Hg/HgO
Counter Electrode : Pt foil (1.5 cm²)
Scan rate : 5, 10, 15, 20 and 25 mV/sec



CH₃OH Electro Oxidation - Cyclic voltammetry



- ❖ Features typical of methanol electro oxidation in acidic medium are also observed in the alkaline medium also but at more favourable (lower) potential values
- ❖ The anodic peak in the forward (anodic) scan is attributed to the oxidation of methanol (step wise dehydrogenation of methanol)
- ❖ Another anodic peak in the reverse (cathodic) scan is to the removal of incompletely oxidized carbonaceous species

Cyclic Voltammetric response of

(a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode

(b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and

(d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) - Nafion electrode

in 1.0 M KOH and 1 M CH₃OH, at a scan rate of 25 mV/sec between -0.9 to 0.8 V Vs Hg/HgO

Electro Catalytic Activity of Pt/C_{WA} Vs PtRu/Vulcan carbon (JM) – A Comparison

Effect of Pt loading and the nature of the carbon support on the electro catalytic activity of CH₃OH Electro oxidation of Pt/C_{WA} and PtRu/Vulcan carbon

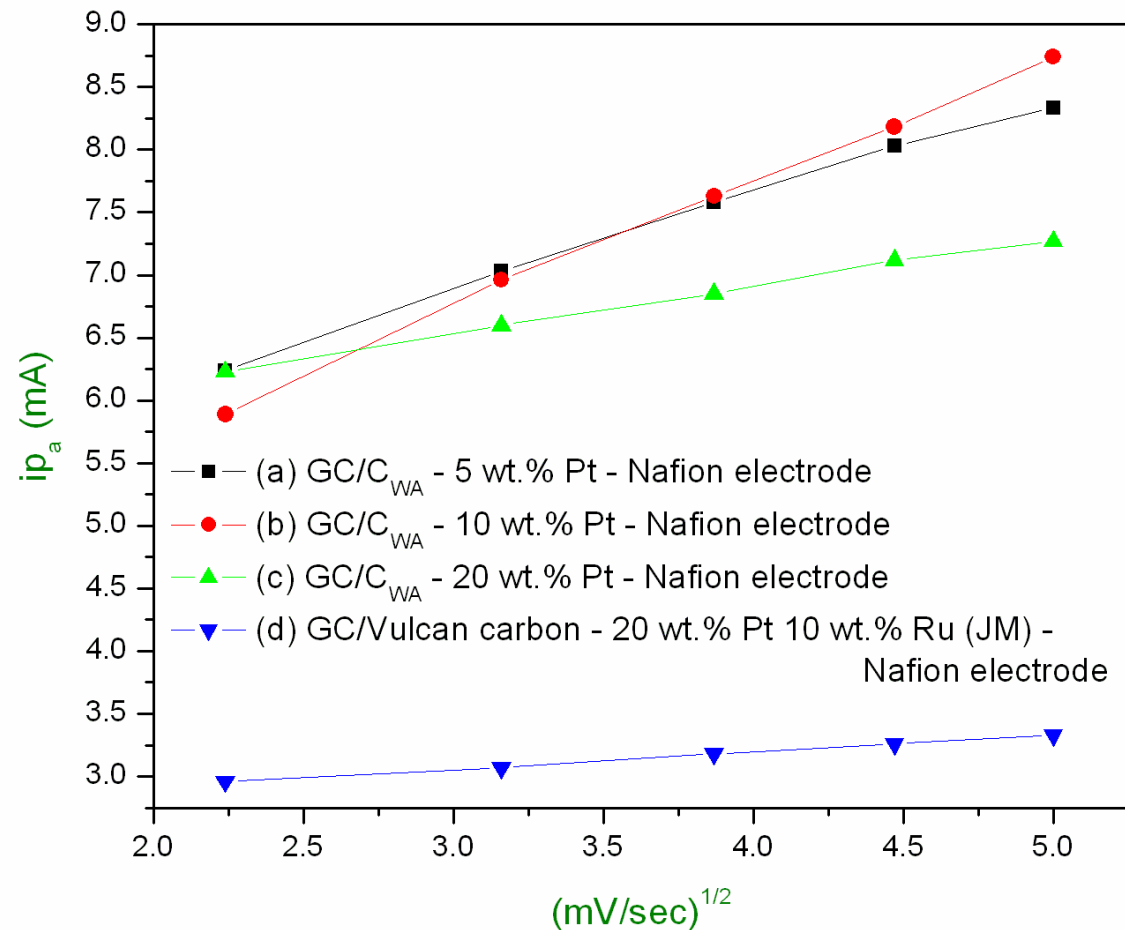
S. No.	Electrode	Onset Potential V	Activity*	
			Forward sweep	
			I (mA/cm ²)	E (V)
1	GC/C _{WA} -5 % Pt-Nafion	- 0.42	123	0.35
2	GC/C_{WA}-10 % Pt-Nafion	- 0.52	124	0.15
3	GC/C _{WA} -20 % Pt-Nafion	- 0.54	104	0.27
4	GC/Vulcan carbon – 20 % Pt 10 % Ru - Nafion	- 0.52	50.9	0.57

*Activity evaluated in 1.0 M KOH and 1 M CH₃OH, at a scan rate of 25 mV/sec between -0.9 to 0.8 V Vs Hg/HgO

❖ Pt/C_{WA} catalysts (at all Pt loadings) showed higher activity (current) at relatively lower potential values compared to the commercial (PtRu/C) catalyst

❖ 10 wt.% Pt/C_{WA} showed better performance compared to either 5 or 20 wt.% Pt/C_{WA} or the commercial PtRu/Vulcan carbon catalyst with the higher current output

CH₃OH Electro Oxidation – Effect of Scan Rate



- ❖ Peak currents were found to be linearly proportional to the square root of scan rates
- ❖ Such a linear variation of current with the square root of scan rate indicates that the process of the methanol electro oxidation is controlled by diffusion
- ❖ Such a linear variation is predominant in the Pt/CWA catalyst with 10 wt.% Pt loading
- ❖ At all scan rate values, the current derivable for Pt/C_{WA} based system is nearly double that of the commercial PtRu/Vulcan carbon (JM) catalyst

Dependence of peak currents on the square root of scan rates for

(a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode

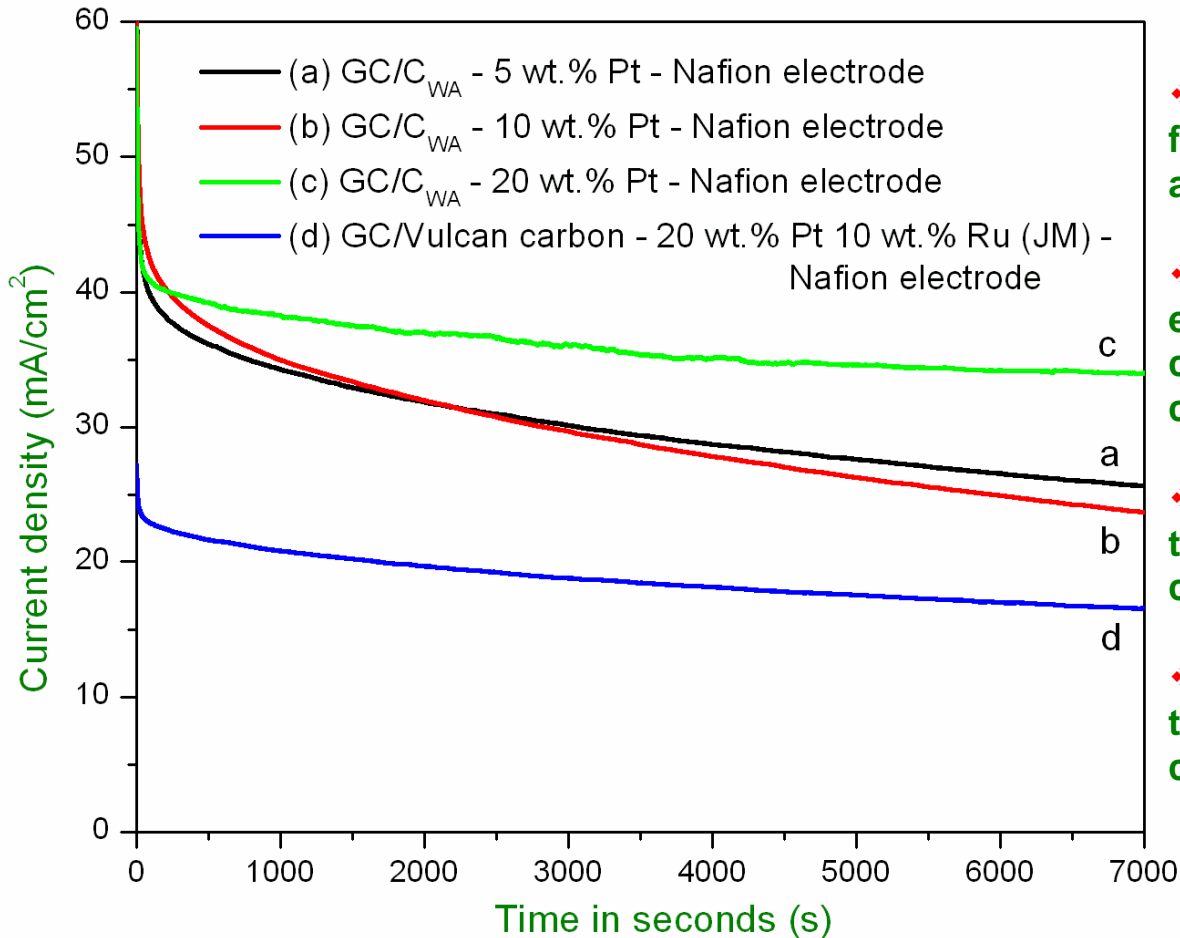
(b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and

(d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) - Nafion electrode

in 1.0 M KOH and 1.0 M CH₃OH, at different scan rates (5, 10, 15, 20 and 25 mV/sec), between - 0.9 to 0.8 V Vs Hg/HgO

CH₃OH Electro Oxidation - Cyclic voltammetry



❖ Current density Vs time plots derived for Pt/C_{WA} and PtRu/C electrocatalysts are shown in the plot

❖ Long term stability of the fabricated electrodes and that of the commercial catalyst (JM) was evaluated by chronoamperometry

❖ Pt/C_{WA} catalysts offered better long term stability compared to the commercial PtRu/C catalyst

❖ Increasing the Pt loading improved the Stability of the Pt/C_{WA} electro catalysts

Chronoamperometric response of

(a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode

(b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and

(d) GC/Vulcan carbon - 20 wt.% Pt 10 wt.% Ru (JM) - Nafion electrode
polarized at 0.3 V Vs Hg/HgO in 1.0 M KOH/ 1.0 M CH₃OH for 3 hours

Summary

1. The activated carbon material produced from the renewable source, the shells of *Limonea acidissima* by KOH activation is a promising support for Pt for the electro oxidation of methanol.
2. The excellent performance of 5 wt. % Pt/C_{WA} (in acidic medium) and 10 wt.% (in alkaline medium) is attributed to the increase in the extent of utilization of Pt metal.
3. Thus the use of carbon material from a renewable source *Limonea acidissima* as support for Pt offers the promise of effective utilization of Pt, high electro oxidation (methanol) activity, high CO tolerance and long term stability.
4. A strong correlation was found between the Pt crystallite size and the electro oxidation activity and stability of the carbon supported Pt catalysts.

5. Conclusion

The carbon materials produced from renewable sources can be a panacea to many of the ills of modern world, namely the energy crisis, water pollution (by toxic and carcinogenic chemicals), air pollution (by the emission of CO_2 , NO_x and SO_x) by the combustion of fuels.