

# **Electrocatalysts in Energy Technology**

Riaz Ahmed

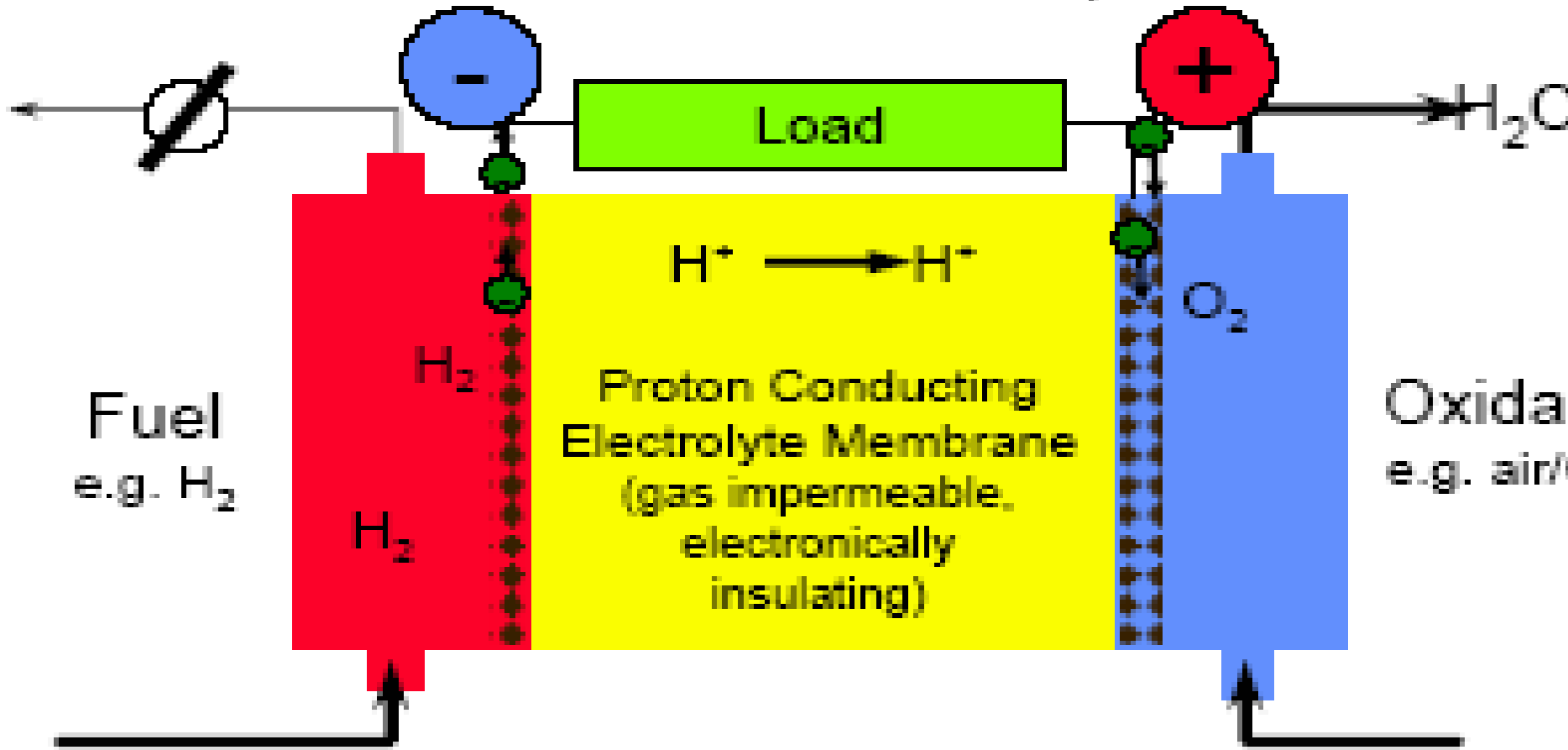
**Fuel Cell Group  
Pakistan Institute of Nuclear  
Science and Technology  
P.O Nilore Islamabad, Pakistan**

# Main Points

- Introduction
- Preparation of Catalysts
- Properties of Catalyst
- Characterization of Catalysts
- Durability studies
- FC electrodes
- MEAs
- Fuel Cells
- Power/Hydrogen

# Fuel Cells

○ are electro-chemical Devices,



○ converting chemical energy directly into electricity

## Target: Fuel Cell Vehicles

2020 5M  
2030 15M



## Target: Stationary PEFC

2020 10.0GW  
2030 12.5GW



2002

2005

2010

2020

R&D stage

Introduction stage

Diffusion stage

Full-Scale  
Diffusion stage

Infra-  
structure

Demonstration  
Projects

Step-by-step  
Introduction

Market Growth  
without Support

Organic Growth

Codes

Review and Modification of Regulations  
Standardization for IEC/JIS

R&D

R&D on  
FC and H<sub>2</sub>

Further R&D for Higher Performance  
and Lower Cost

# As per current state of the art FC Technology

100 kW FC stack needs 100 gms of Pt

1 Vehicle = 100 kW

5M vehicles = 500 tons of Pt

10GW = 10 tons of Pt

2020 Japan will need about 600 tons of Pt  
world will need 6000 tons of Pt.

2030 18000 tons of Pt

# Nanoparticles

- For a metal with a face centered cubic unit cell, the fraction of surface atoms on a cube with an edge length of 1,2,5,10 and 20 lattice constants corresponds to 100,79,45,31 and 14% of the total number of atoms present, respectively. If we assume a lattice constant of 0.2 nm, the edge lengths of those cubes will be 0.2,0.4,1,2 and 4 nm respectively. **Thus 15% dispersion is realized only for particles smaller than 4 nm** . The use of metal particles larger than 4 nm would be a waste of resources and particularly for Pt. This shows the importance of Nanoparticles in energy technology.
- Morphology of the catalyst surface is also important . The surface should activate the reactants without being poisoned by irreversible adsorption of reactants or products.
- Electronic effects
- Geometric effects

# Conc. of Pt in Catalysts

- In 1990's Pt. 4-10 mg cm<sup>-2</sup> of MEA
- 1997-2000 Pt <1mg cm<sup>-2</sup> " "
- 2003 Pt. 0.2-0.4 mg cm<sup>-2</sup>
- Presently Pt Approx. 1.0 gm is required for 1 kW FC
  
- Pt. <0.1 mg cm<sup>-2</sup> of MEA  
0.04 mg cm<sup>-2</sup> " "
  
- Target Pt. 0.03 mg cm<sup>-2</sup>

# Preparation of Pt/C catalysts

- Impregnation method
- Colloidal method
- Thin film method
- Electro-deposition method
- Sputter deposition method



# Different types of carbon supports

The form of carbon can affect the dispersion of the particles . Two main types of carbon black have successfully been used as supports for Pt catalysts: oil furnace black and acetylene black

Carbon area	Type	BET surface $\text{m}^2 \text{g}^{-1}$
Vulcan XC72	Furnace black	250
Ketjen EC300J	" "	800
Shawinigan	Acetylene black	80
Denka black	" "	65

Nanotubes

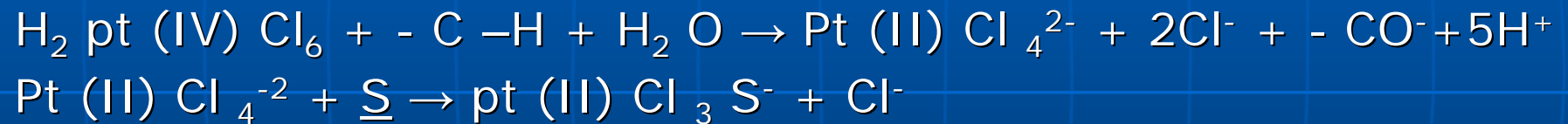
# Surface treatment of carbon supports

Surface oxygen functional groups on carbon materials are important. The oxidative treatment of the carbon surface

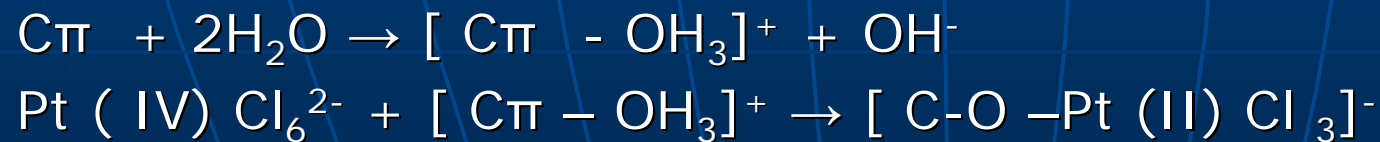
- **Oxidative**,  $\text{HNO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}_2, \text{O}_2, \text{K}_2\text{ClO}_3, \text{KMnO}_4$
- **Thermal**, Heat treatment at 600°C for 30min in inert atmosphere increases pregraphitization, which act as anchoring centres for platinum
- **Chemical**, Treatment with  $\text{CuCl}_2$  and  $\text{PdCl}_2$ , improved the electronic interaction between the Pt catalyst layer and carbon support, and subsequently enhanced the electrocatalytic activity of Pt/C catalyst
- **Use of Nanotubes** after oxidative treatment

# Interaction of Pt with carbon supports

Carbon support alters the system's Galvanic potential, raise the electronic density in the catalysts and lower the Fermi level, accelerate catalytic reaction. Metal –support interaction is through electron transfer from platinum clusters to atoms of the surface of support.



The ligand site S is assumed to be either a  $\pi$  - complex structure or an oxygen surface group.



# Heat treatment effects on electro-catalysts

- At 400-550°C improved the Pt particle –size distribution on the support surface and showed the increase in Pt Crystallinity
- For Pt-M/C catalysts heat treatment at 600-650°C produced highest catalytic activity and catalyst stability.
- Non- noble metal catalysts also improve stability and catalytic activity by heat treatment at about 600°C for ORR.

# Pt –M/C Catalysts

Pt/ Cr, Pt/Co, Pt/Ni      20-30mV

Pt/ Fe, Pt/ Mn      20-40 mV

Pt/Cr/Cu      Two times activity

Pt/Au      Highly durable and stable catalysts

Pt/ Ni (111)      Ten times higher activity.

F. Robert, Science, 315, 172, 2007

# CHARACTERIZATION OF CATALYSTS

## 1. Platinum surface area measurement

$$S_{pt} = QH / 210 \mu\text{c cm}^{-2}$$

$$R_f = S_{pt} / A$$

## 2. Electrochemical reactions

Methanol and other compounds

## 3. Polarization curves (Tafel Plots)

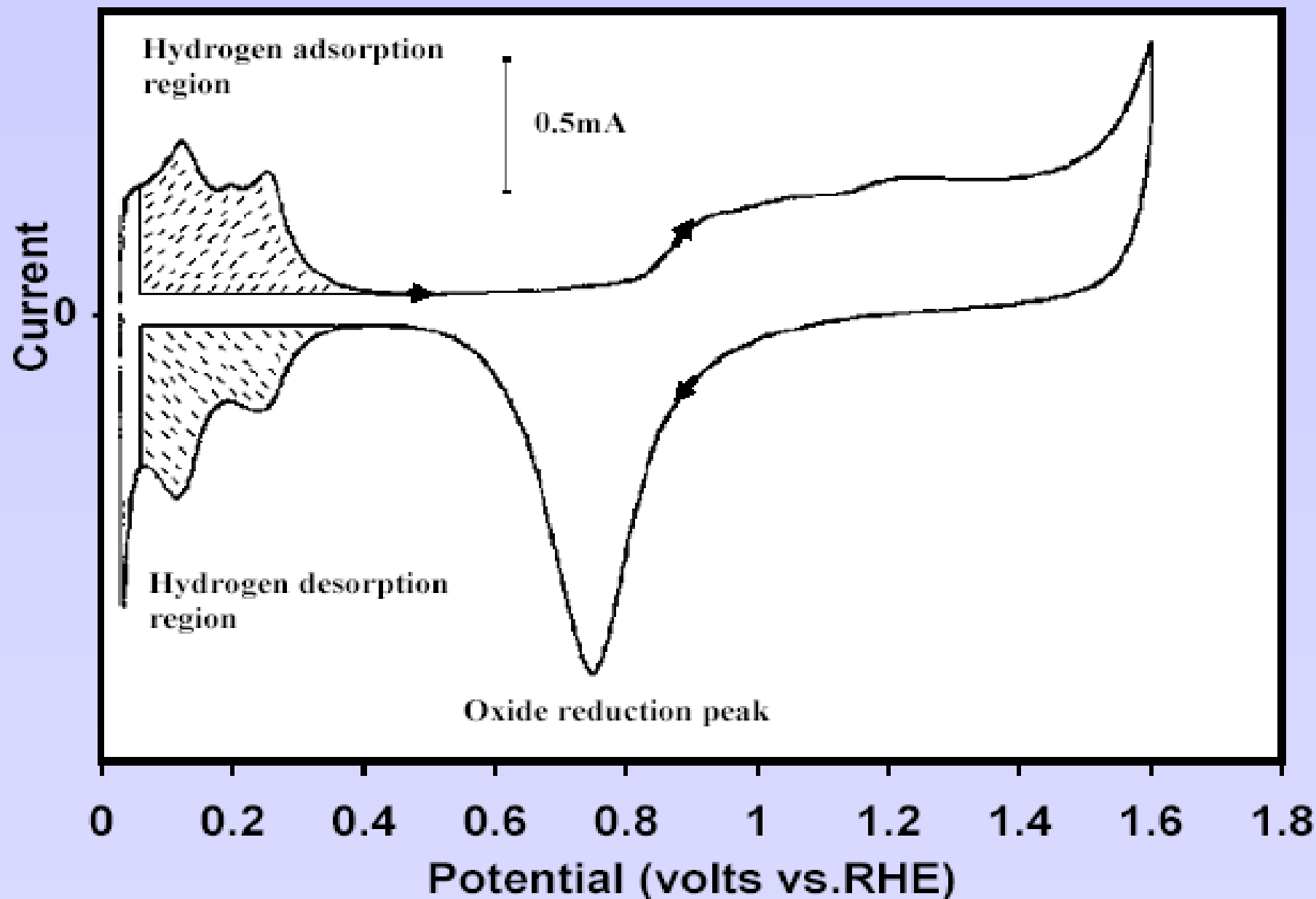
## 4. Current –voltage curves of fuel cells

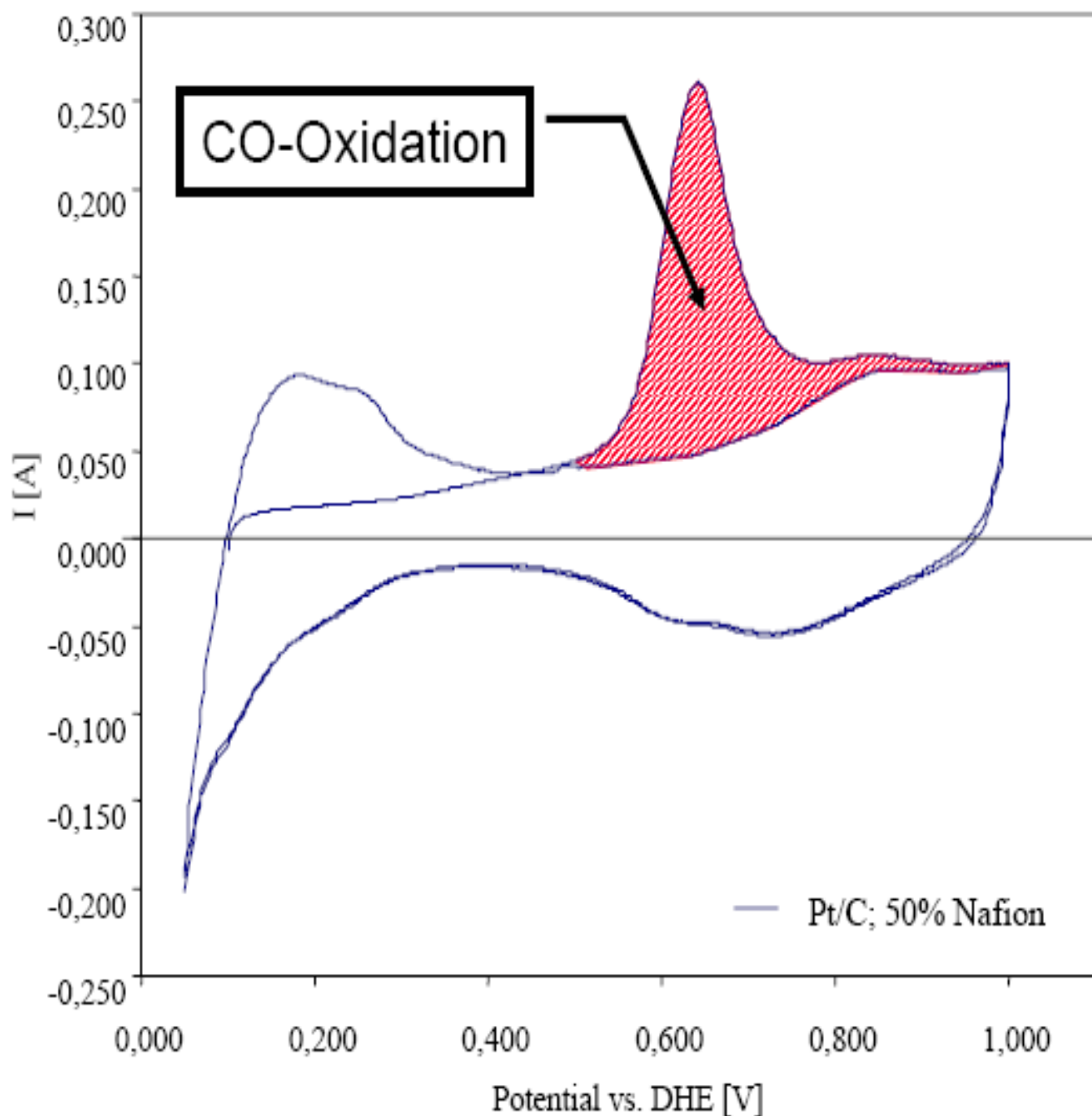
## 5. Total surface area measurements , physical and chemical

## 6. Impedance measurement

XRD, SEM, TEM, X-ray photoelectron spectroscopy, Raman spectroscopy

# Hydrogen adsorption desorption (HAD) testing can reveal structural changes in the catalyst layer.

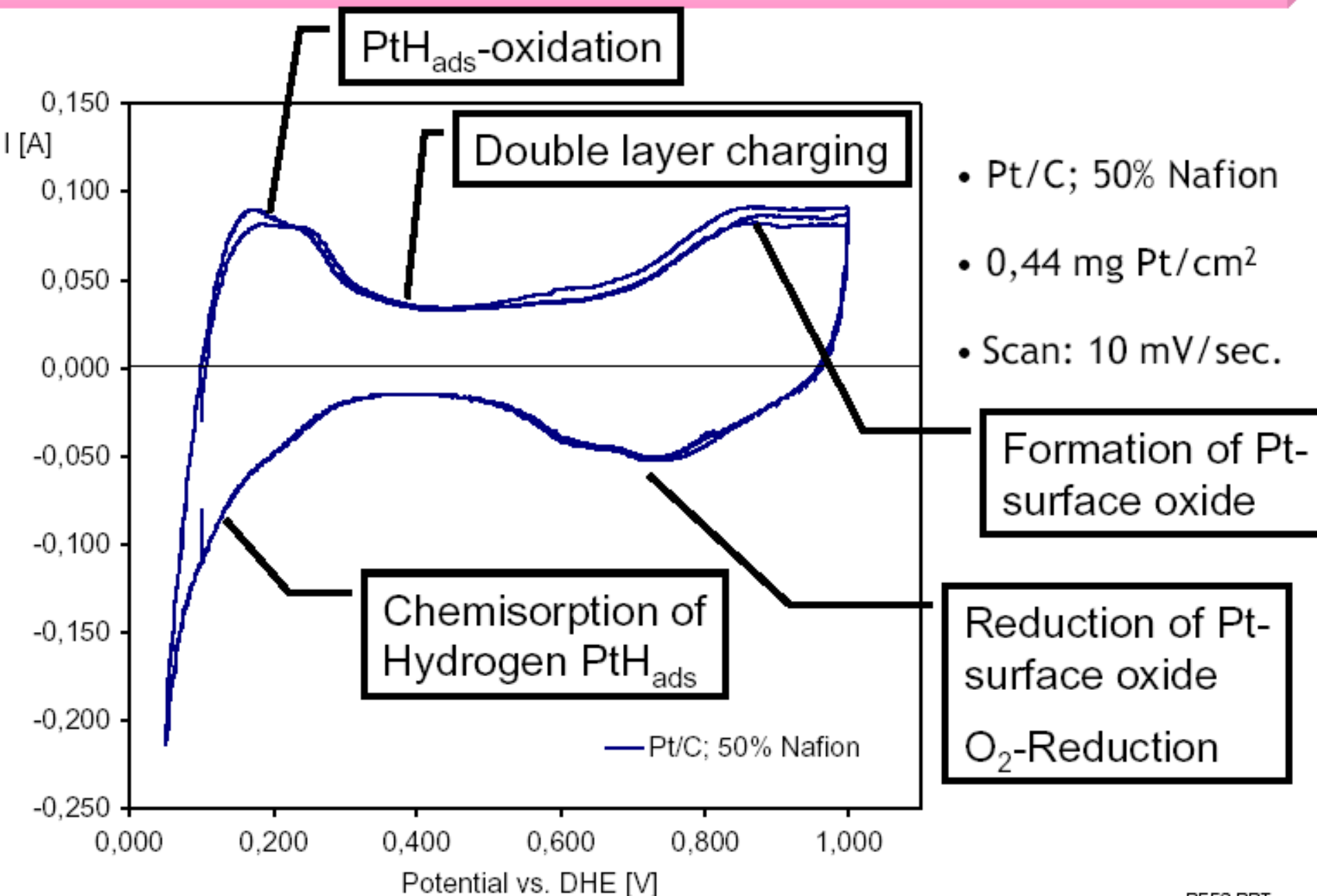




- Determination from Charge required to oxidize a CO monolayer
- 0,44 mg Pt/cm<sup>2</sup>
- Charge difference:  
 $I_{CO} = 2,38 \text{ C}$   
 $\Rightarrow 1,23 \cdot 10^{-5} \text{ mol CO}$   
 $\Rightarrow \sim 70\% \text{ of theoret. Platinum surface}$



# Cyclic Voltammetry: MEA in H<sub>2</sub>



# Cyclic Voltammetry

- **Electro-oxidation of methanol, ethanol, Formaldehyde etc**
- **Different kinetic parameters e.g. real surface area, roughness factor, apparent peak current density, exchange current density and heterogeneous electron transfer rate constant etc.** were evaluated for better comparison of the catalytic activity of different electrocatalysts. The importance of evaluation of apparent peak current densities has been emphasized because many other kinetic parameters can be evaluated from the analysis of peak current densities for better comparison of catalytic activity of different electrocatalysts.

# Basic Equations

$$S_{\text{Pt-H}} = \left( \frac{Q_{\text{Pt-H}} \mu C}{210 \mu C} \right) \text{ real surface area}$$

$$k_s = Z_{\text{het}} \exp\left[-\frac{\Delta G^*}{RT}\right]$$

$$\text{R.F} = \left( \frac{\text{Real surface area}}{\text{Apparent surface area}} \right)$$

$$E = E_{\text{rev}} + b \log \frac{i}{i^0}$$

$$\ln \left( \frac{k_s}{Z_{\text{het}}} \right) = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R}$$

$$k^0 = \frac{I_p}{0.227nFAC} \exp\left[\frac{-\alpha F}{RT} (E_p - E^0)\right]$$

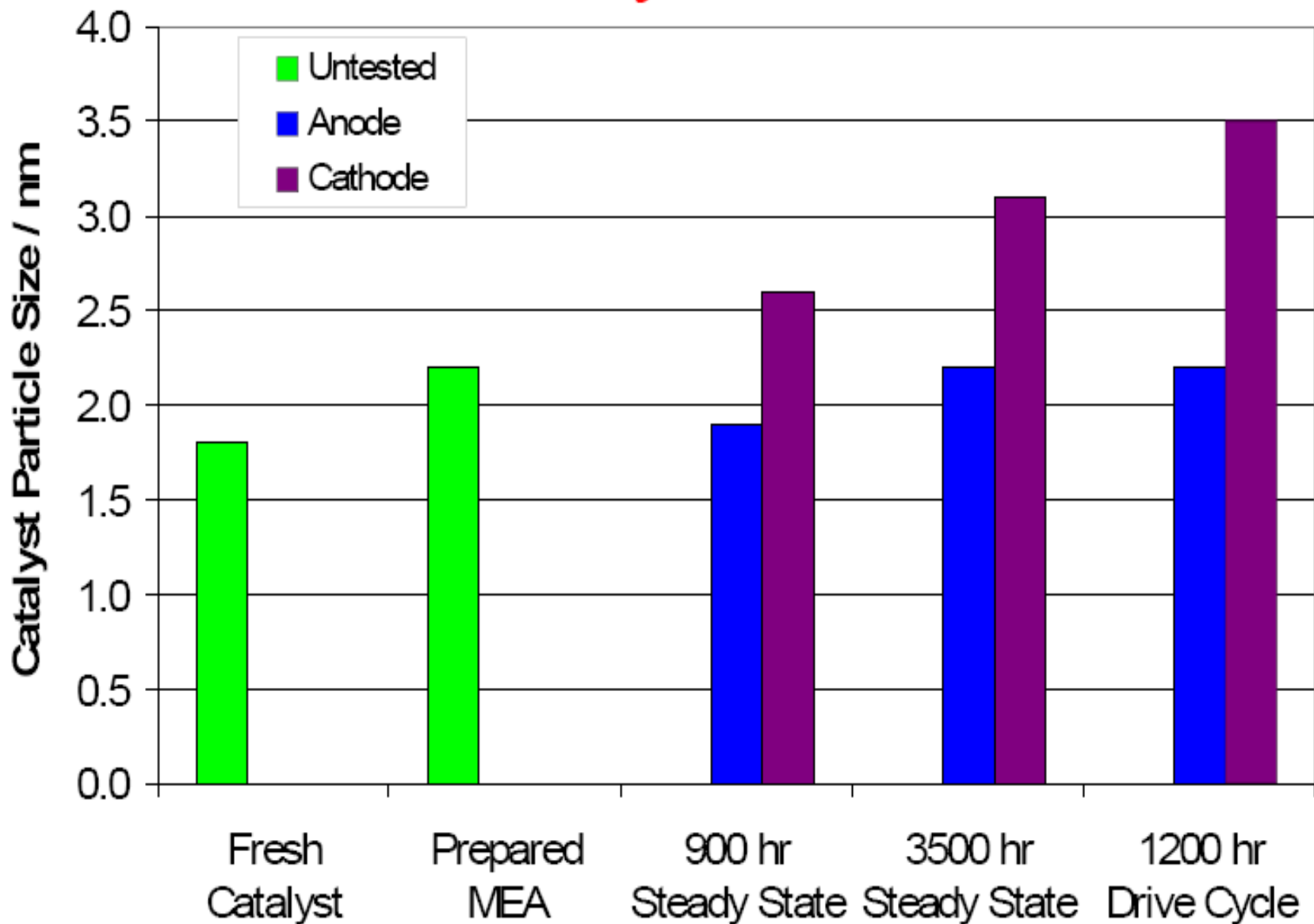
<b>Type of catalysts</b>	<b>Bulk mass of catalyst material (mg)</b>	<b>Mass of only Pt in the catalyst material (mg)</b>	<b>Apparent surface area (cm<sup>2</sup>)</b>	<b>Real surface area (cm<sup>2</sup>)</b>	<b>Roughness factor (R.F)</b>
<b>Smooth Pt-strip</b>	<b>525.2</b>	<b>525.2</b>	<b>3.04</b>	<b>7.05 ± 0.68</b>	<b>2.32 ± 0.22</b>
<b>10 % Pt on Vulcan carbon</b>	<b>0.240</b>	<b>0.024</b>	<b>0.785</b>	<b>58.7 ± 6.7</b>	<b>74.8 ± 8.2</b>
<b>20 % Pt + 10% Ru on Vulcan carbon</b>	<b>0.240</b>	<b>0.048</b>	<b>0.785</b>	<b>76.0 ± 11.5</b>	<b>96.8 ± 14.7</b>
<b>30 % Pt on Vulcan carbon</b>	<b>0.240</b>	<b>0.072</b>	<b>0.785</b>	<b>130 ± 19.5</b>	<b>166 ± 24.8</b>

Type of catalysts	Interce pt “a”	Tafel slope “b” (V decade <sup>-1</sup> )	$\alpha$	Exchange current density at 0.70V “ $i_0^{(0.70V)}$ ” (mA cm <sup>-2</sup> )	Apparent current density at 0.70V (mA cm <sup>-2</sup> )
Smooth Pt-strip	0.848	0.162	0.366	0.120	0.115
10 % Pt	0.646	0.254	0.233	1.64	1.73
20 % Pt + 10% Ru	0.572	0.225	0.263	3.71	3.91
30 % Pt	0.465	0.239	0.248	9.62	10.22

<b>Type of catalysts</b>	<b>Peak current (mA)</b>	<b>Apparent peak current density (mA cm<sup>-2</sup>)</b>	<b>Apparent specific peak current density (mA cm<sup>-2</sup> mg<sup>-1</sup> Pt)</b>
<b>Smooth Pt-strip</b>	<b>2.90</b>	<b>0.954</b>	<b>0.00182</b>
<b>10 % Pt</b>	<b>5.51</b>	<b>7.02</b>	<b>292</b>
<b>20 % Pt + 10% Ru</b>	<b>12.4</b>	<b>15.80</b>	<b>329</b>
<b>30 % Pt</b>	<b>18.1</b>	<b>23.10</b>	<b>320</b>

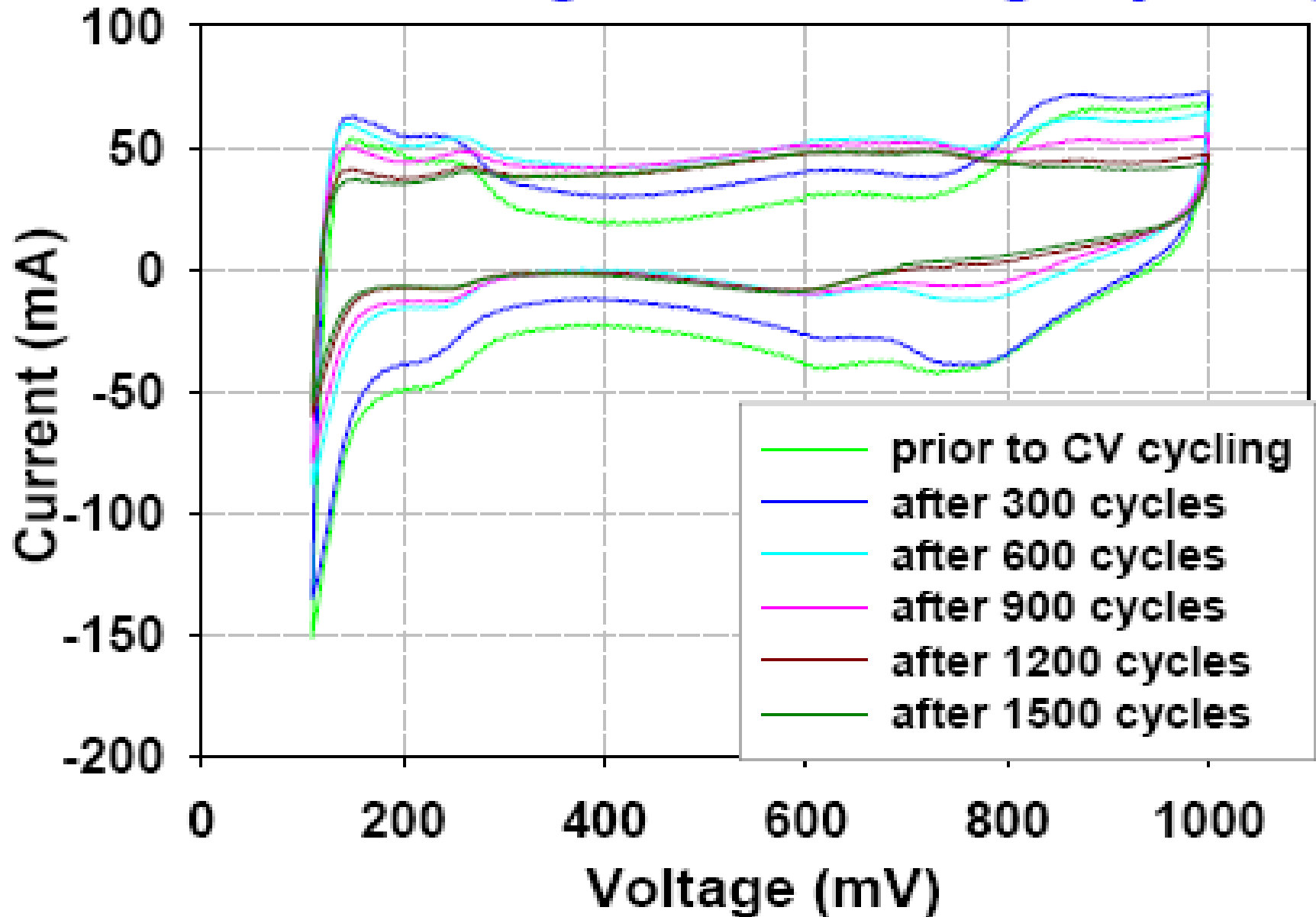
Type of catalysts	$E_p$ at 50 $mV s^{-1}$ (V)	$\log I_p /$ $\log v$	$E_p / \log v$ V decade <sup>-1</sup>	$k^0 \times 10^{-5}$ (cm $s^{-1}$ )
Smooth Pt-strip	0.850	0.373	0.071	$0.421 \pm 0.045$
10 % Pt	0.928	0.555	0.156	$3.22 \pm 0.21$
20 % Pt + 10% Ru	0.940	0.428	0.191	$5.44 \pm 0.38$
30 % Pt	0.940	0.419	0.247	$8.80 \pm 0.59$

# Electrocatalyst Particle Growth Stationary vs. Automotive





# Voltammograms during Cycling



# Stability study of catalysts by potential cycles from 0.6 to 1.1 V under the oxidizing condition of the O<sub>2</sub> reduction reaction.

Catalyst and kinetic data	Pt dispersion (m <sup>2</sup> / gPt)	Half wave potential at 1600 rpm (V)	Kinetic current density at 0.85 V (mA/ cm <sub>2</sub> )	Specific Current density at 0.85 V (A/m <sup>2</sup> Pt)
Pt/ C initial	65.5	0.841	4.56	5.80
Pt/C after 30,000 cycles	35.5	0.802	1.60	3.72
Au/ Pt/C initial	63.1	0.838	4.23	5.64
Au/ Pt/C after 30,000 cycles	60.6	0.833	4.10	5.69

J. Zhang et.al; Science,315, 220-222,2007.

# SUBSTRATE

Electrode substrate is usually carbon paper or carbon cloth. For better removal of water these substrates are wet proofed using a PTFE emulsion (60 wt% PTFE). After wetting the paper with PTFE emulsion, it is dried in air and sintered in an oven at 345°C for 30 min. The PTFE content of the substrate is usually 30wt %. With a diffusion layer carbon cloth gives better performance (11).

# Preparation of catalyst ink

- **SUSPENSION OF CATALYST POWDER IN WATER**
  - agitation by ultrasonic
  - Continuous stirring
- **ADDITION OF ELECTROLYTE SOLUTION**
  - Nafion (alcoholic or aqueous solution, optionally other solvent ) 15 to 50wt % depending on the catalyst surface area
  - Optionally addition of pore former
  - Optionally adjustment of pH
  - Addition of wet proofing agent
    - PTFE suspension 3 to 15 wt%
- **CONTINUOUS AGITATION**
  - e.g. by slow stirring for 3 days
  - Too severe agitation results in breakdown of catalyst agglomerates

# Catalyst Layer Preparation

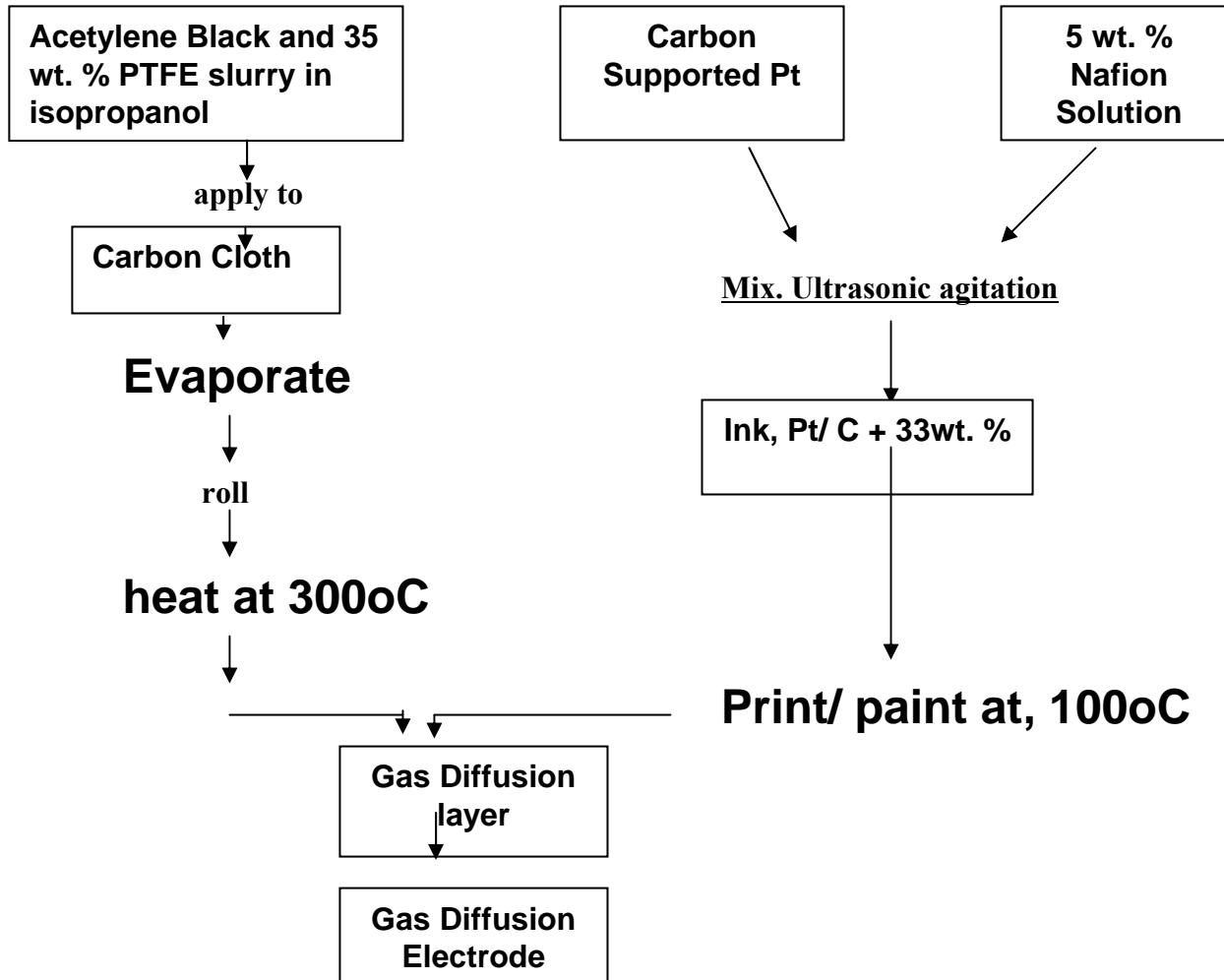
- Catalyst preparation techniques are highly proprietary.
- Generally-Catalyst/Support is prepared as an 'ink' and applied to the GDL and hot pressed onto the electrolyte leading to an intimate mixture of polymer and catalyst.
- A hydrophobic component is often added to the catalyst (PTFE) to avoid flooding
- Catalyst can be applied directly to the electrolyte via rolling, spraying, screen printing, sputtering etc.
- Roughness factor in the order of 100+

# PTFE-bound methods

- 20 wt.% percent of Pt/C catalyst particles were mechanically mixed for 30 min in a solvent.
- PTFE emulsion was added until it occupied 30% of mixture.
- A bridge-builder and a peptization agent were added, followed by 30 min of stirring.
- The slurry was coated onto the water-proofed carbon paper using a coating apparatus.
- The electrodes were subsequently dried for 24 h in ambient air, and then baked at 225°C for 30 min
- The electrodes were rolled and then sintered at 350°C for 30 min
- A 5 wt.% Nafion solution was brushed onto the electrocatalyst layer (2mg cm<sup>2</sup>).
- The Nafion –impregnated electrodes were placed in an oven at 80°C and allowed to dry for an hour in ambient air.
- Once dry, the electrodes were bonded to the H<sup>+</sup> form of the polymer electrolyte membrane through hot pressing at 145°C for 3 min at a pressure of 193 atm to complete the membrane electrode assembly.

# Thin film methods

- Thin film catalyst layers have been found to operate at almost twice the power density of PTFE-bound catalyst layers (25). These methods are mostly used for stack application (26.3) The Procedure for forming this type of electrode is:
- Combine a 5% solution of solubilized perfluorosulfonate ionomer (such as Nafion) and 20% wt Pt/ C support catalyst in a ratio of 1:3 Nafion/ Catalyst.
- Add water and glycerol to weight ratios of 1:5:20 carbon-water-glycerol.
- Mix the solution with ultrasound until the catalyst is uniformly distributed and the mixture is adequately viscous for coating.
- Ion-exchange the Nafion membrane to the Na<sup>+</sup> form by soaking it in NaOH, then rinse and let dry.
- Apply the carbon-water-glycerol ink to one side of the membrane. Two coats are typically required for adequate catalyst loading.
- Dry the membrane in a vacuum with the temperature of approximately 160°C
- repeat Steps 5 and 6 for the other side of the membrane.
- Ionexchange the assembly to the protonated form by lightly boiling the MEA in 0.1M H<sub>2</sub> SO<sub>4</sub> and rinsing in de-ionized water.
- Place carbon paper/ cloth against the film to produce a gas diffusion layer.





# Gas Diffusion Layer (GDL)

- GDL is situated between the fluid-flow plate and the electrocatalysts.
- Conducts electrons between the plate and the electrocatalysts.
- Supply reactant to area under the lands.
- Aid water management (stop water from blocking pores)
- Provide mechanical support to MEA.
- Improves contact resistance between plate and electrocatalysts.
- Over-compression leads to loss of porosity under lands and “tenting” in channels.
- Electrical and thermal conductivity highly anisotropic due to in-plane ordering of fibres. Higher electrical and thermal conductivity in the in-plane direction.

- Carbon-carbon composite 'paper' most common type of GDL SGL (Germany) Toray Ind. (Japan) Ballard Materials products (Canada) Spectracorp material (USA) Lydall (USA)
- Thickness 100-400 $\mu\text{m}$
- >75% porosity
- Large majority of void volume from pores > 10 $\mu\text{m}$  average pore size typically 20-40  $\mu\text{m}$

# Membrane electrode assembly

At the heart of the PEMFC is the membrane electrode assembly (MEA). It consists of a proton exchange membrane, catalyst layers and gas diffusion layers (GDL) performance of MEA depends on the catalysts and fabrication methods of MEA. Characterization of fuel cell catalysts and MEA are important.

# MEA

## **Catalyst Deposition**

**Preparation of Screen printing of catalysts on carbon paper /cloth catalysts inks/ binders**

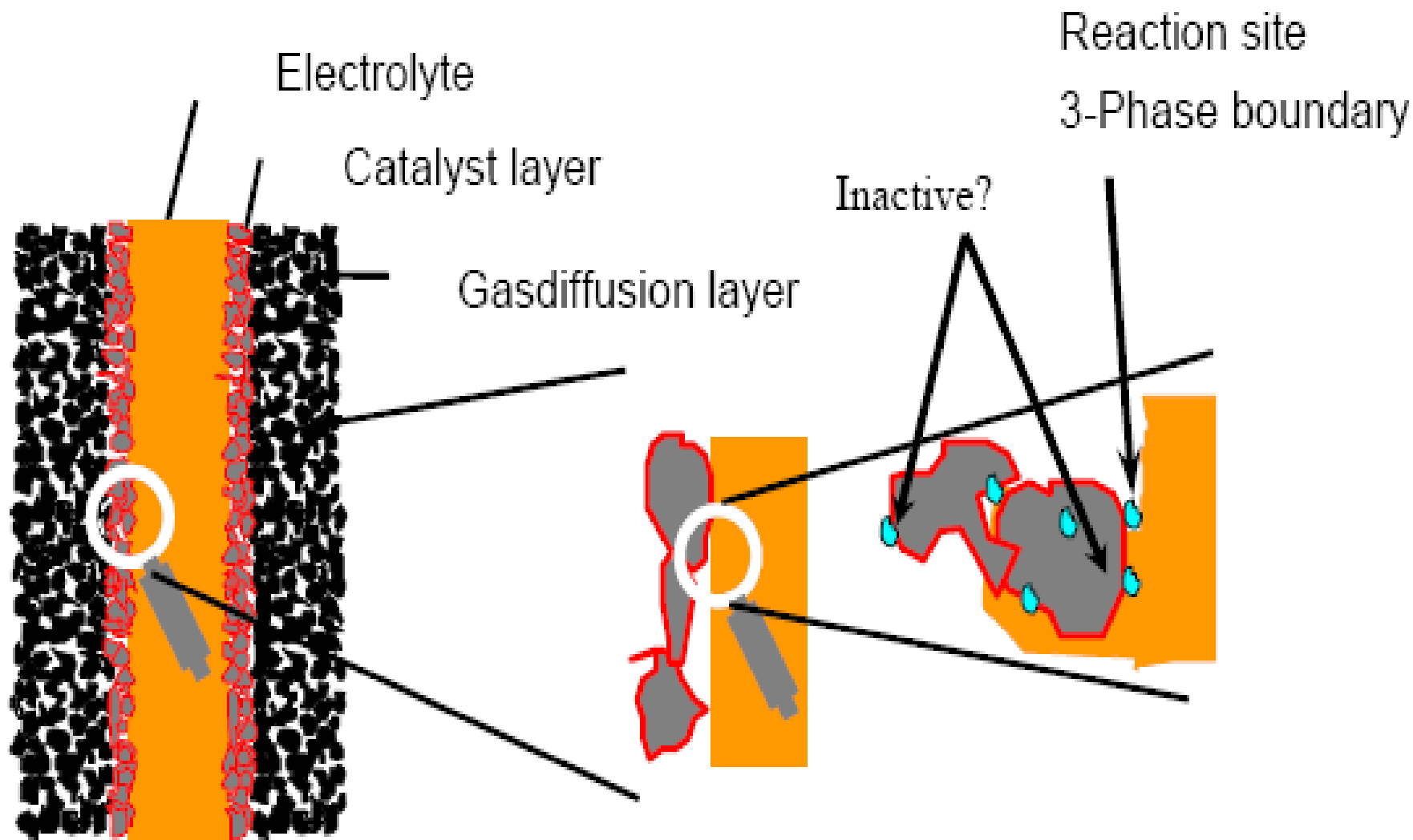
**Treatment of proton exchange membranes**

**Sizing and preparing of membranes and electrodes**

**Hot pressing at specified temperature and pressures**

**Preparation of MEAs of 10cm<sup>2</sup>, 25cm<sup>2</sup>, 50cm<sup>2</sup> and 100cm<sup>2</sup> active areas.**

**Effect of catalysts and membranes on the performance of MEAs**



 Carbon black/Graphite (hydrophobic)



Catalyst particle

 (supported) Catalyst



Polymer electrolyte

**Comparison of the performance of various MEAs (Nafion 115 membrane, H<sub>2</sub>/O<sub>2</sub> pressure =1/1 atm, H<sub>2</sub>/O<sub>2</sub> feed rate= 8.5/3.81/min ) [6]**

<b>Type of electrode</b>	<b>power density at 200mA/cm<sup>2</sup> (mW/cm<sup>2</sup>)</b>	<b>Power density at 0.6v (mW/cm<sup>2</sup>)</b>
<b>Commercial PTFE-bound</b>	<b>140</b>	<b>233</b>
<b>Thin-film, direct membrane coating</b>	<b>114</b>	<b>93</b>
<b>Thin-film, transfer printing (20%)Pt/C</b>	<b>145</b>	<b>200</b>
<b>Thin-film, transfer printing (40% Pt/ C)</b>	<b>129</b>	<b>147</b>
	<b>123</b>	<b>132</b>

**Power densities of thin-film electrodes, with a Pt loading of 0.4mg/cm<sup>2</sup>, containing various Nafion ionomer concentrations in the catalyst layer [19]**

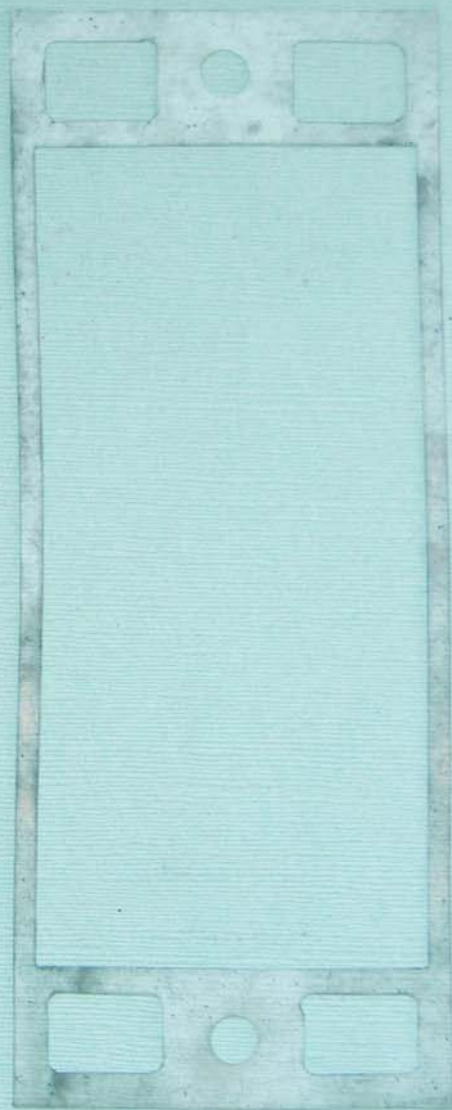
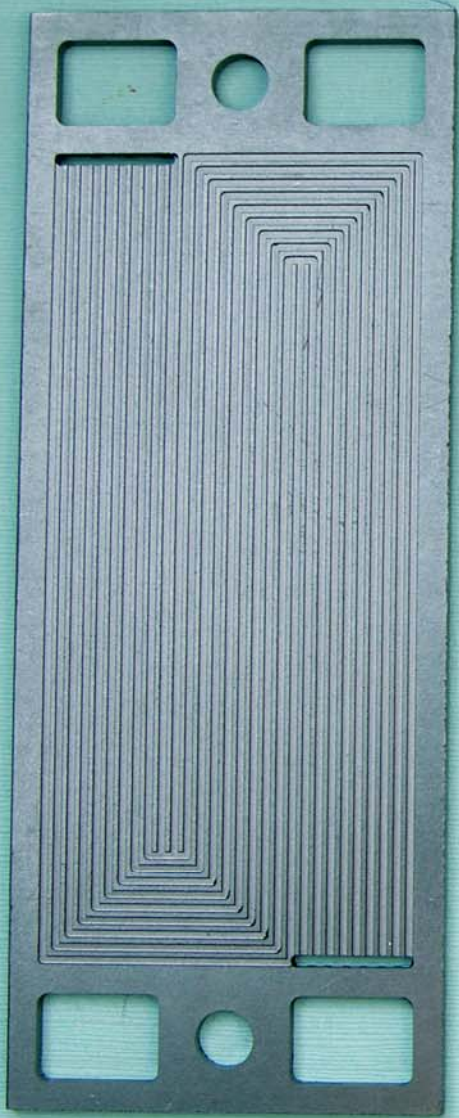
<b>Nafion ionomer Concentration (mg/ cm<sup>2</sup>)</b>	<b>Power density at 200mA/ cm<sup>2</sup> (mW/ cm<sup>2</sup>)</b>	<b>power density at 0.6V (mW/ cm<sup>2</sup>)</b>
<b>0.2</b>	<b>110</b>	<b>72</b>
<b>0.8</b>	<b>144</b>	<b>240</b>
<b>2.0</b>	<b>140</b>	<b>204</b>







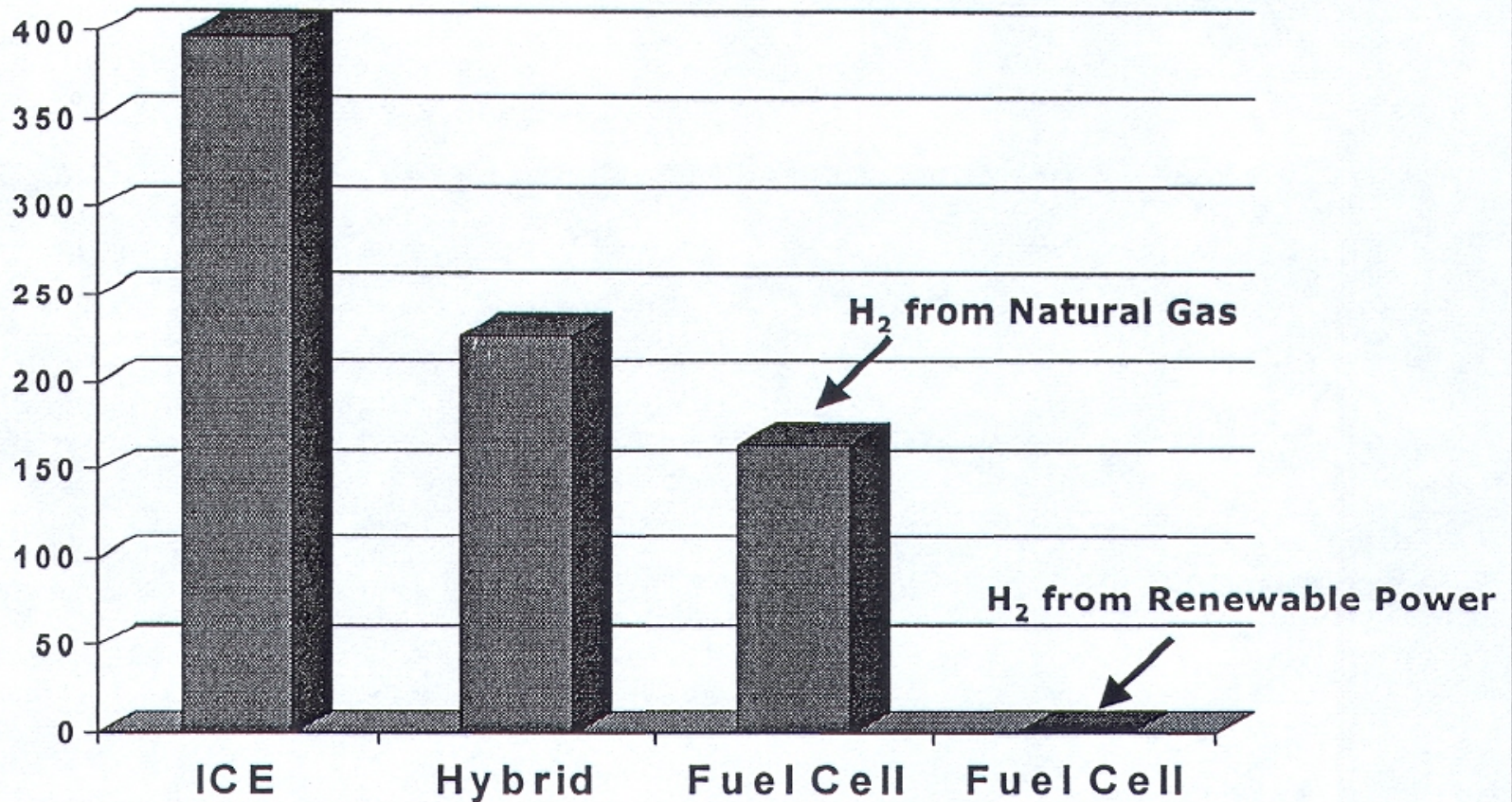




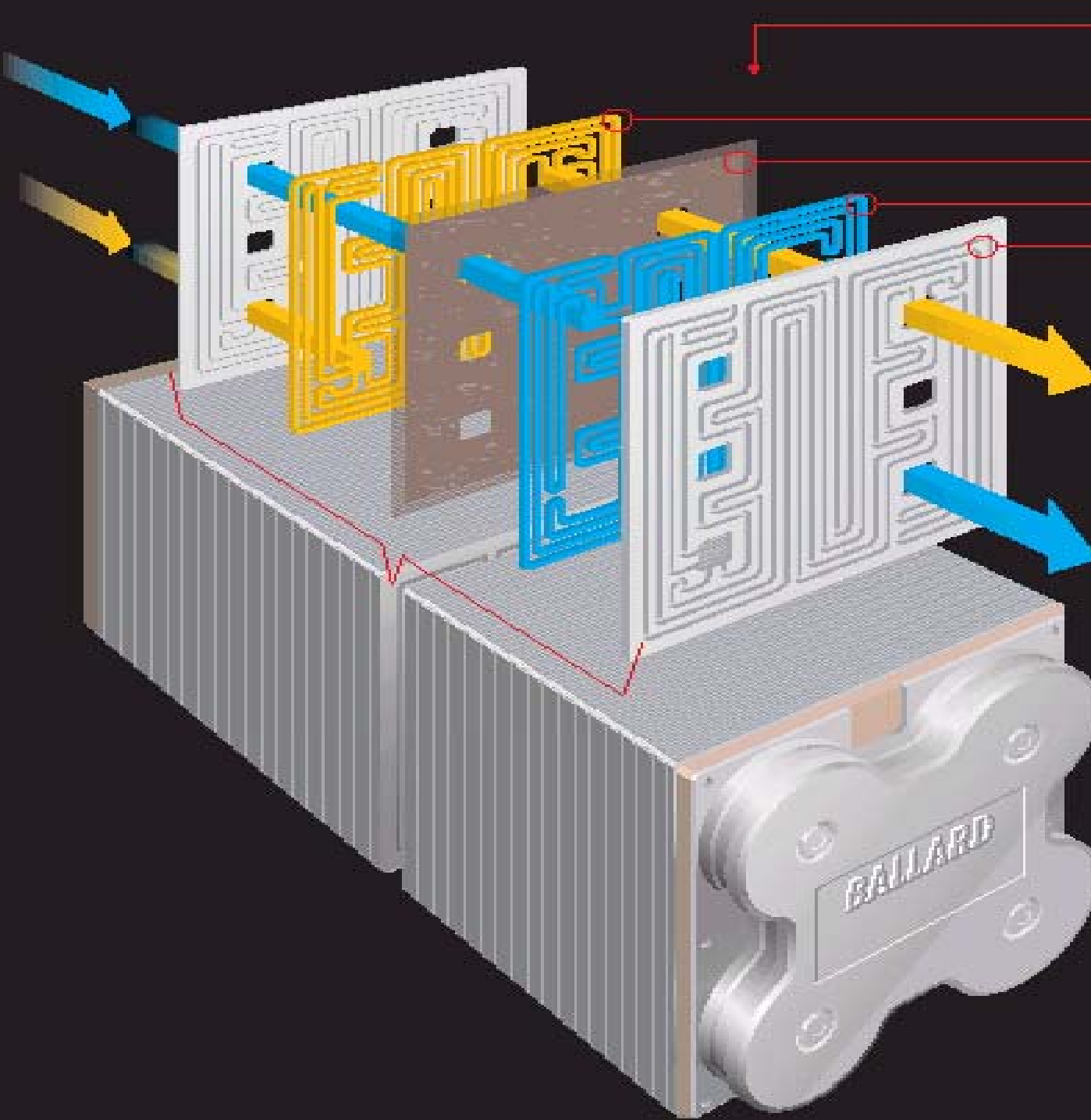
# Fuel Cells Contribute to GHG Reduction

BALLARD\*

## Well-to-Wheels GHGs (g/mi)



Data Source: US DOE



## Single cell

Manufactured electrochemical assembly that converts hydrogen and oxygen into electricity.

## Hydrogen flow

Hydrogen is split into protons and electrons. Hydrogen may be supplied to a fuel cell directly or through a reformer.

## MEA

Membrane Electrolyte Assembly (anode and cathode) with a thin layer of catalyst, bonded to either side of a proton exchange membrane (PEM).

## Air flow

Air is drawn into the fuel cell through the PEM. The air stream also removes the water created as a by-product of the electrochemical reaction.

## Separator

## Stack

Single cells are combined into a fuel cell stack to produce the desired level of electrical power.

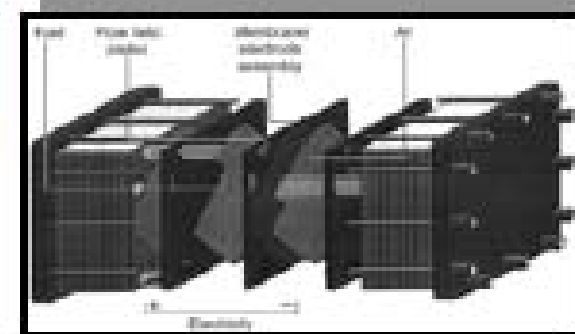
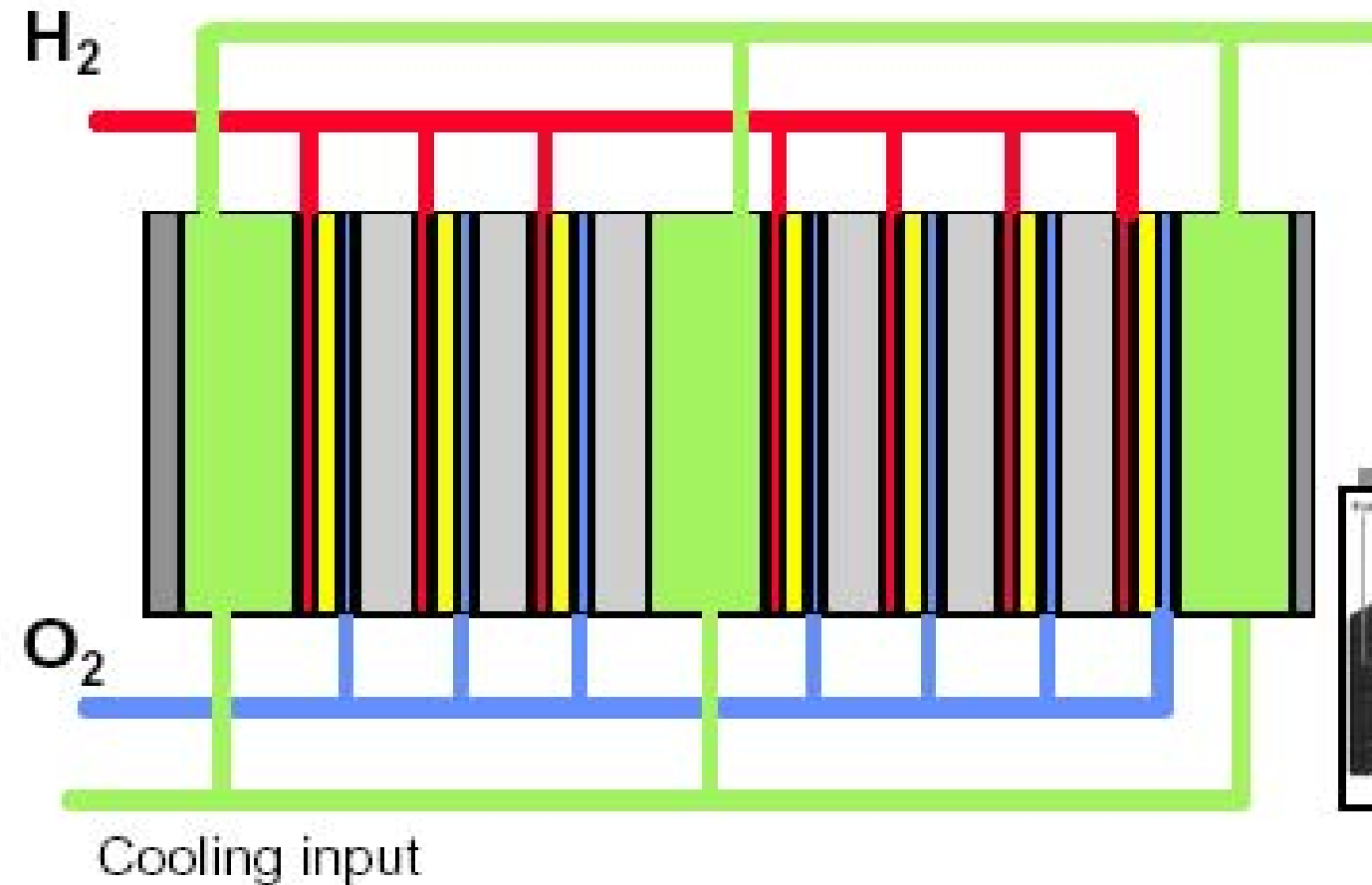
# Fuel Cell Stack

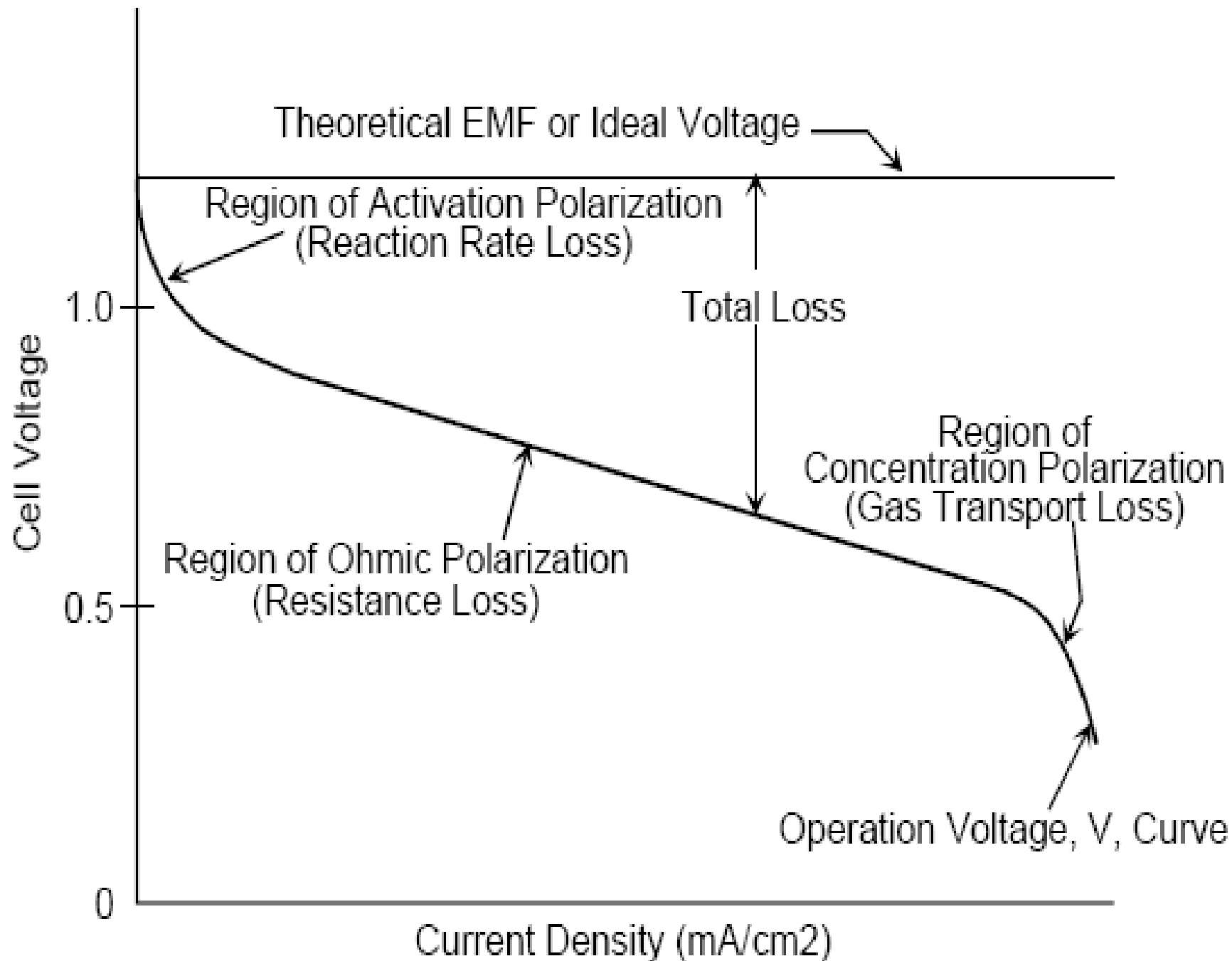
Single Cell Voltage: 1,23 V

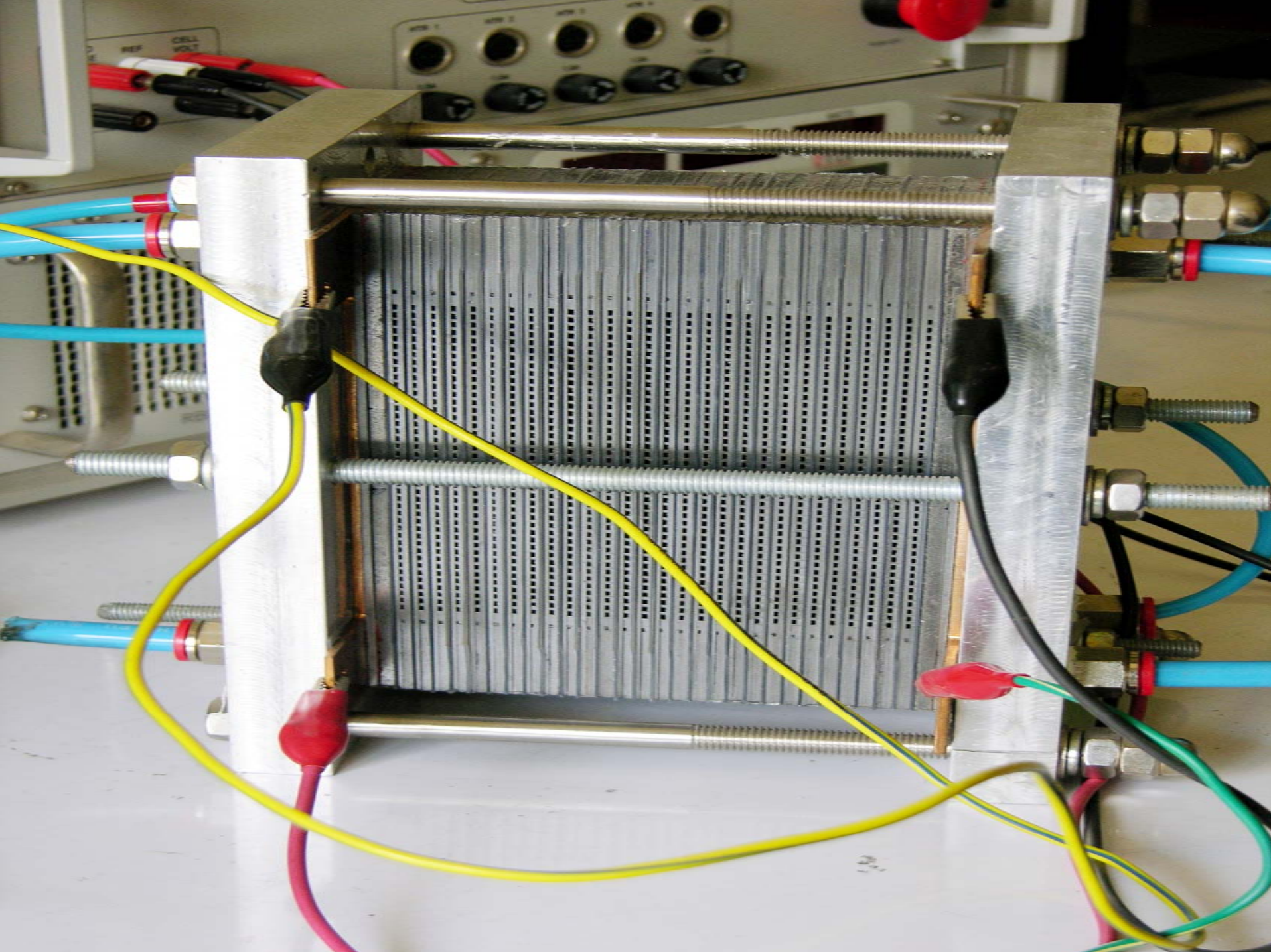
Therefore serial connection in „bipolar“ Arrangement

Cooling Outlet

- End plate
- Cooling plate
- Hydrogen
- MEA
- Oxygen/Air
- Bipolar plate

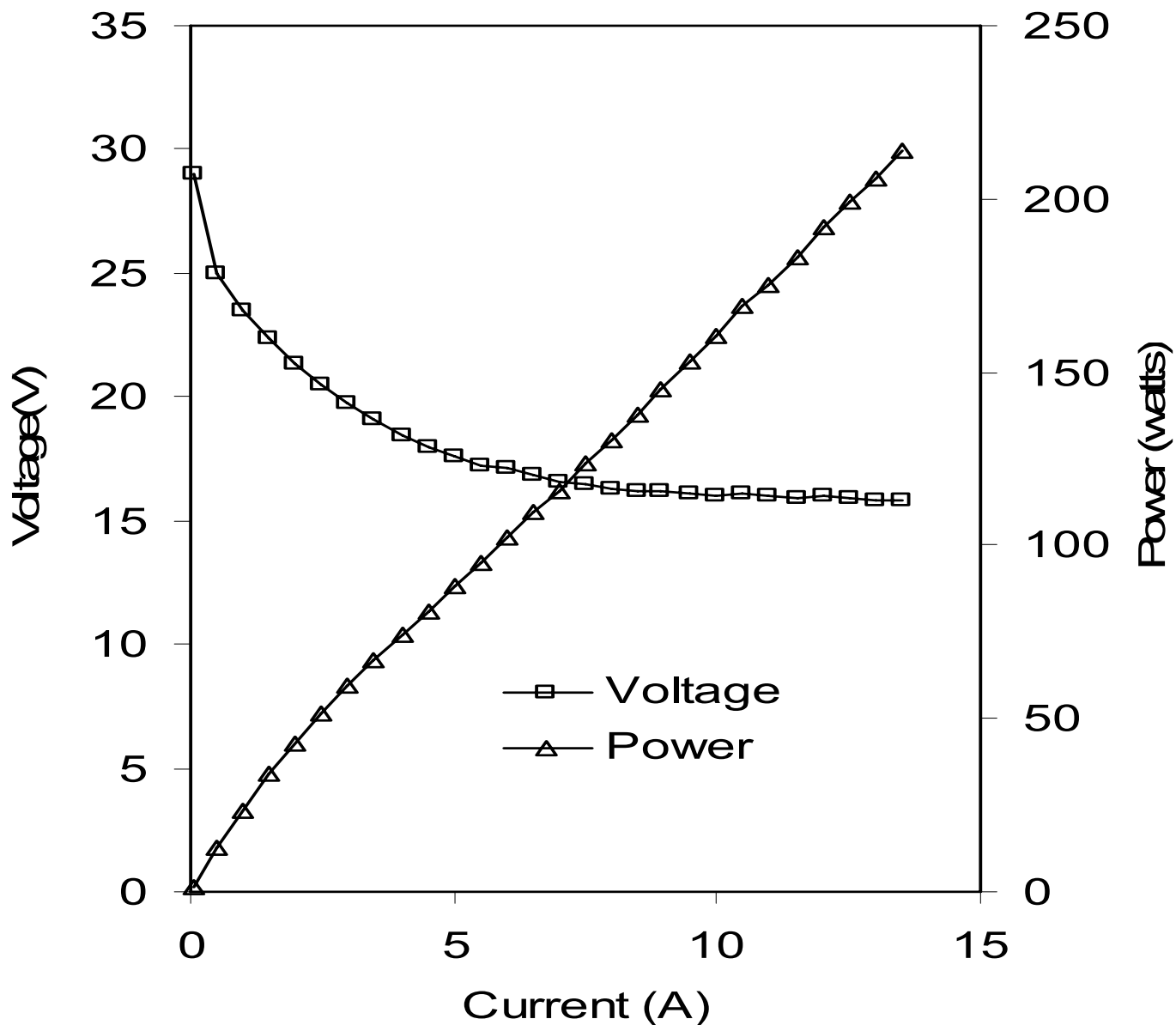








# Performance curves of 29 Cells Stack



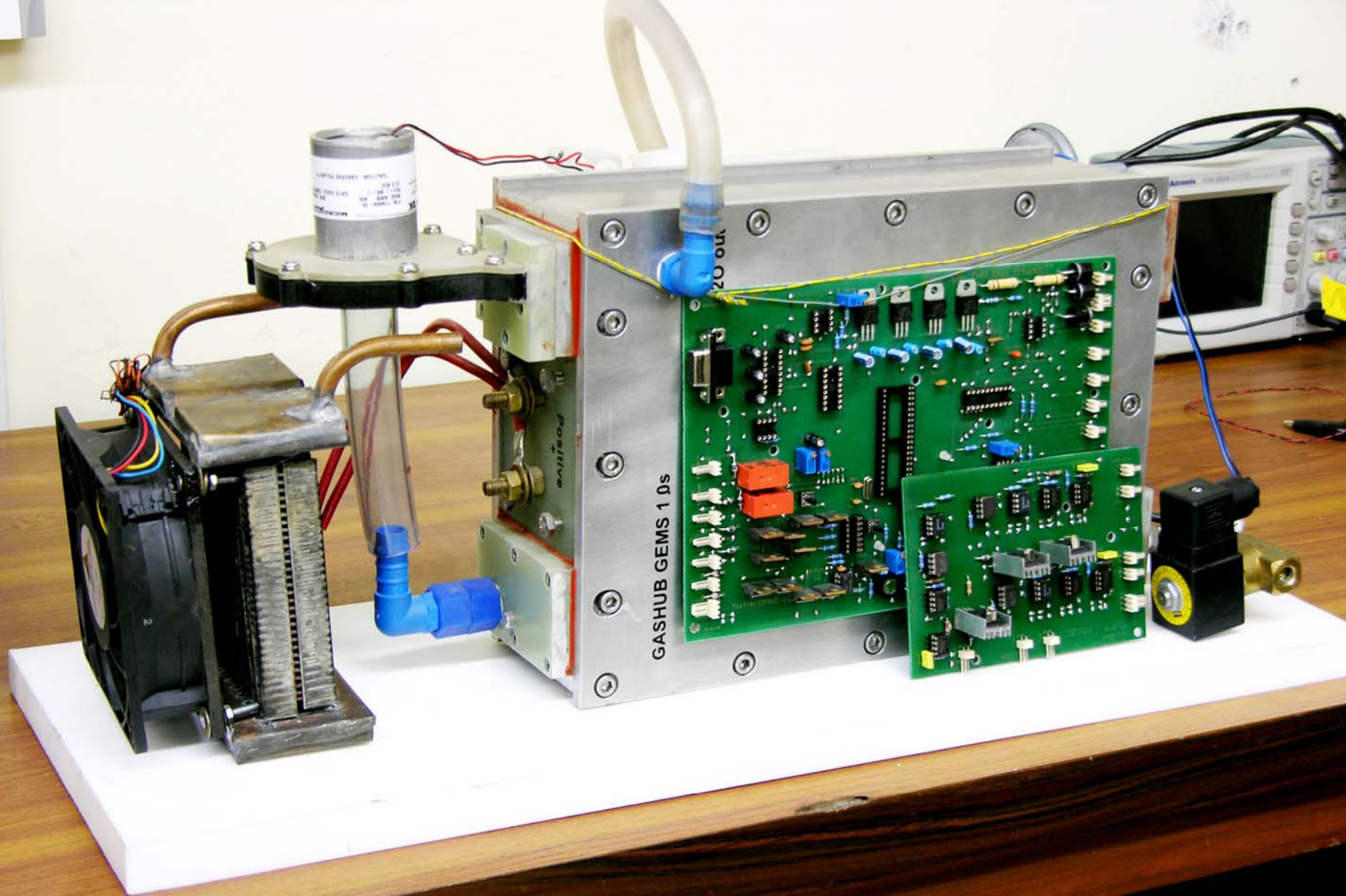


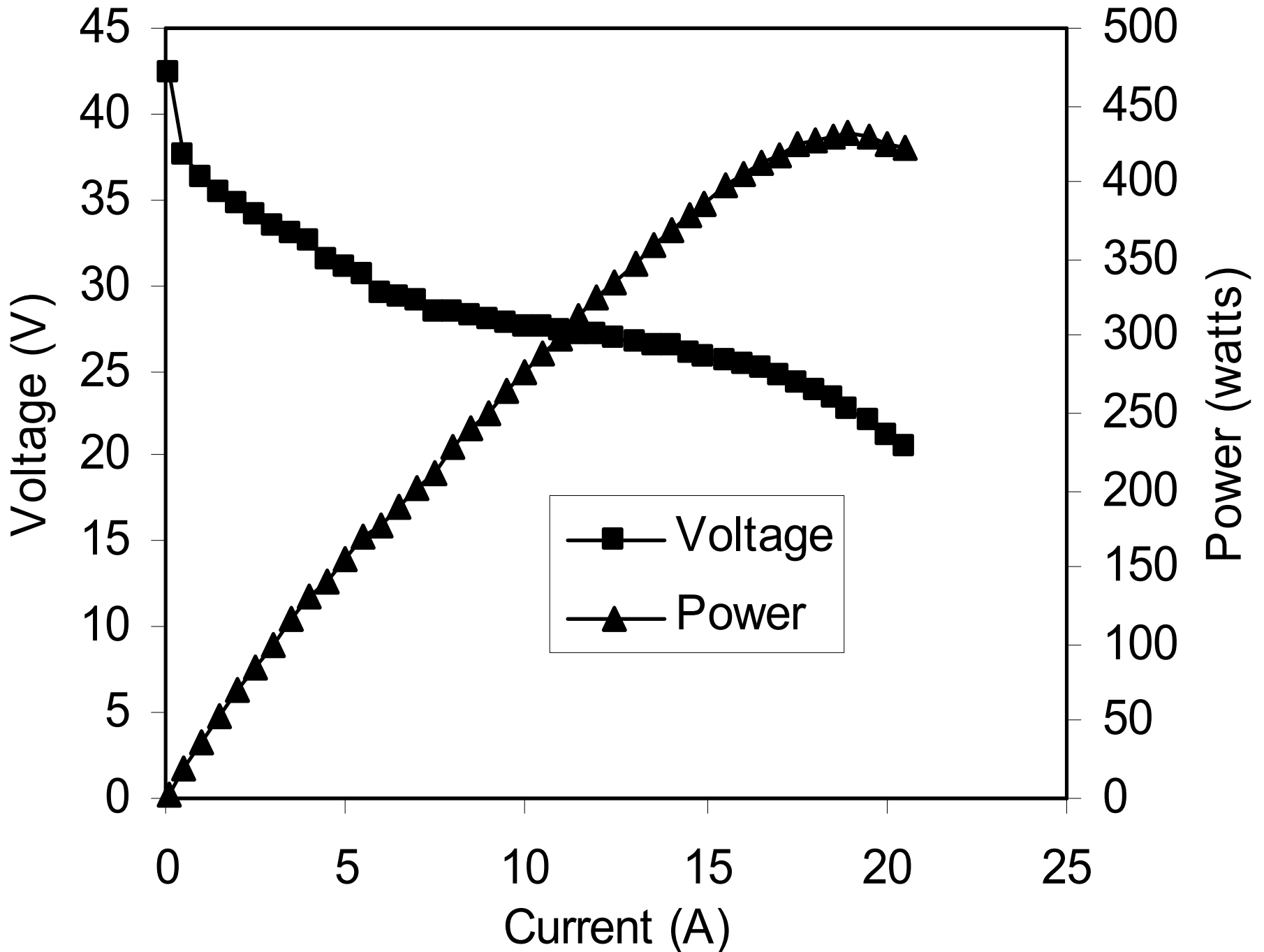
H<sub>2</sub>

H<sub>2</sub>O

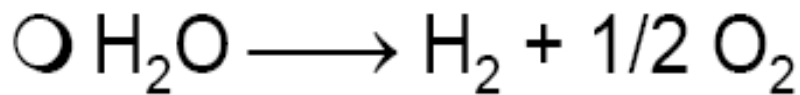
H<sub>2</sub>

O<sub>2</sub>





# Electrolytic Hydrogen Generation



–  $\Delta G_{(l)25^\circ\text{C}} = -237,141 \text{ kJ/mole} \equiv 1,23 \text{ V}$

–  $\Delta H_{(l)25^\circ\text{C}} = -285,830 \text{ kJ/mole} \equiv 1,48 \text{ V}$

○ Alkaline Electrolysis

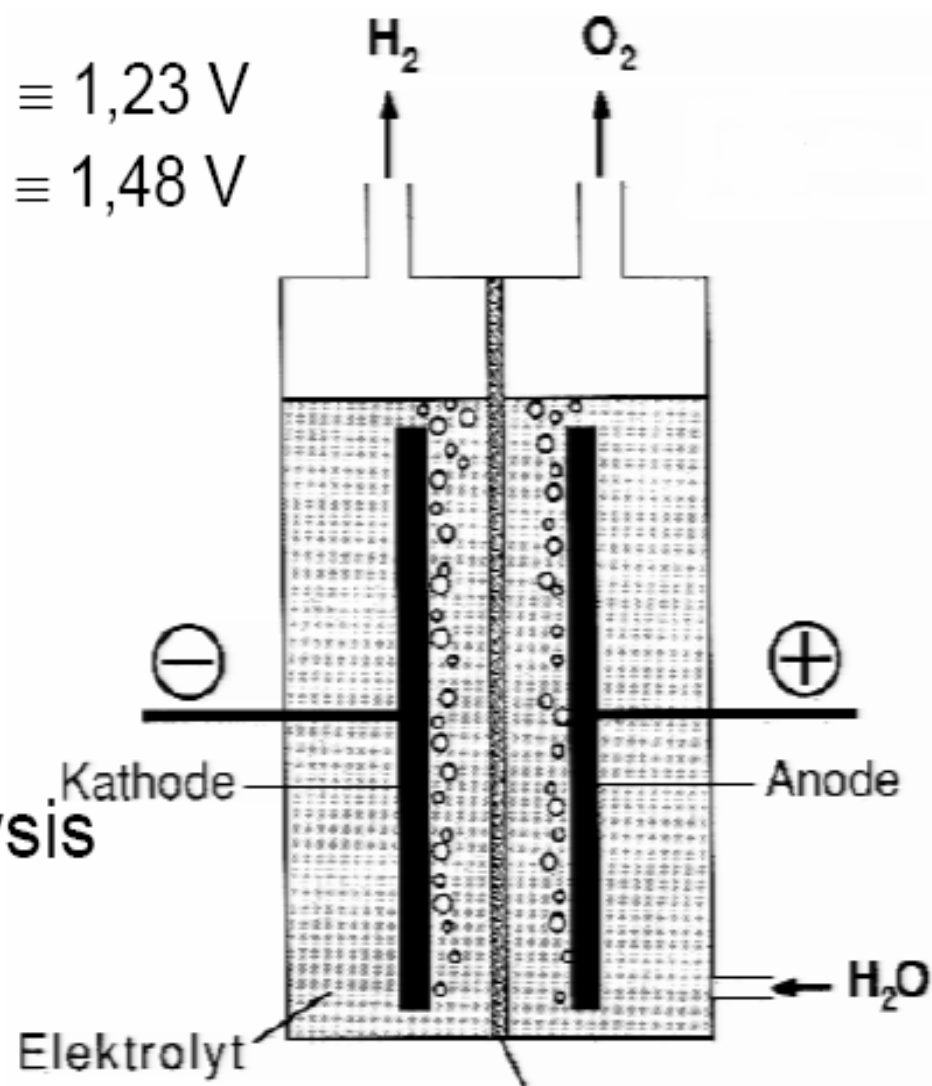
- conventional Electrolysis
- advanced Electrolysis

○ Membrane electrolysis

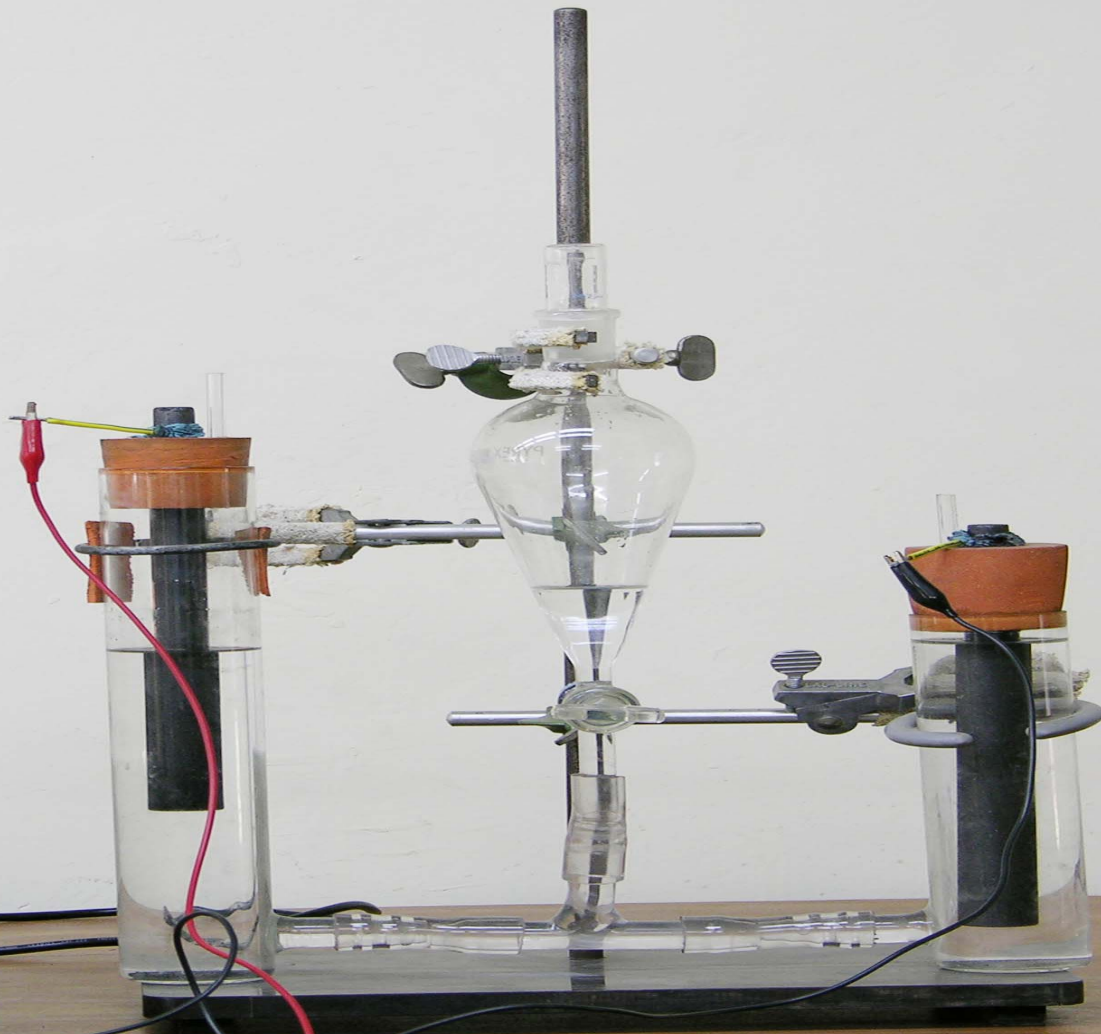
- Polymer electrolyte

○ Hight temperature electrolysis

- Solid state electrolyte

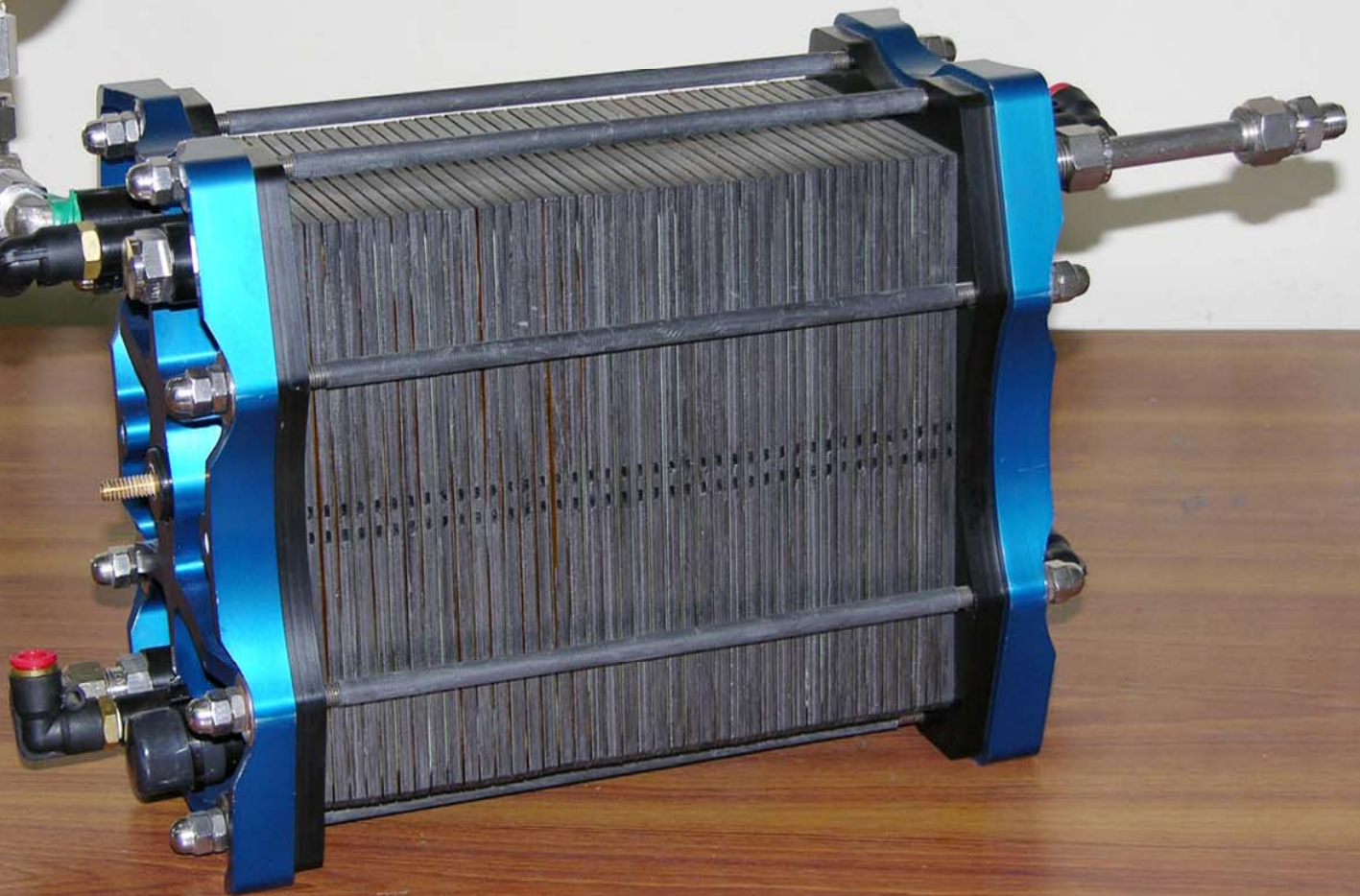






Thank You





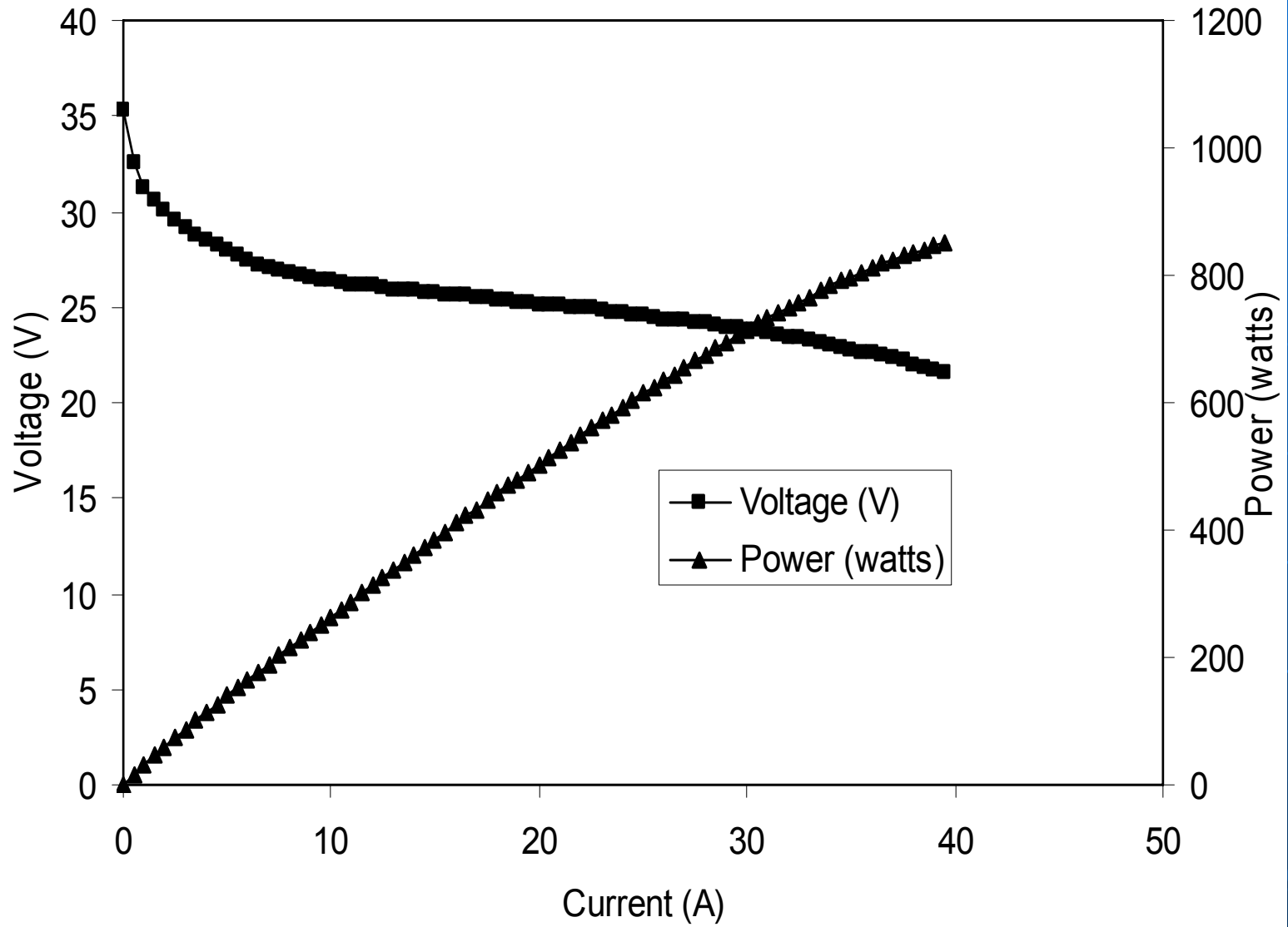


Fig.2 Performance curve of 40 Cells Palcan Fuel cell stack 19<sup>th</sup> March, 2007