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De la **découverte**
à l'**innovation…**

Electrochemical Clean Energy Storage and Conversion: Fuel Cell Catalysts and Supercapacitors at NRC

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Conseil national
de recherches Canada

National Research
Council Canada

Canada

Global Energy Status: Types of Energy

Renewable Energy

- Hydropower
- Bioenergy
- Solar Energy
- Geothermal Energy
- Wind Energy
- Tidal Energy
- Wave Energy
- Ocean Thermal Energy Conversion

Nonrenewable Energy

- Coal
- Crude Oil and Natural Gas Liquids
- Oil Shale
- Natural Bitumen and Extra-Heavy
- Natural Gas
- Peat
- Uranium nuclear

Global Energy Status: Estimated dates of nonrenewable fuel exhaustion

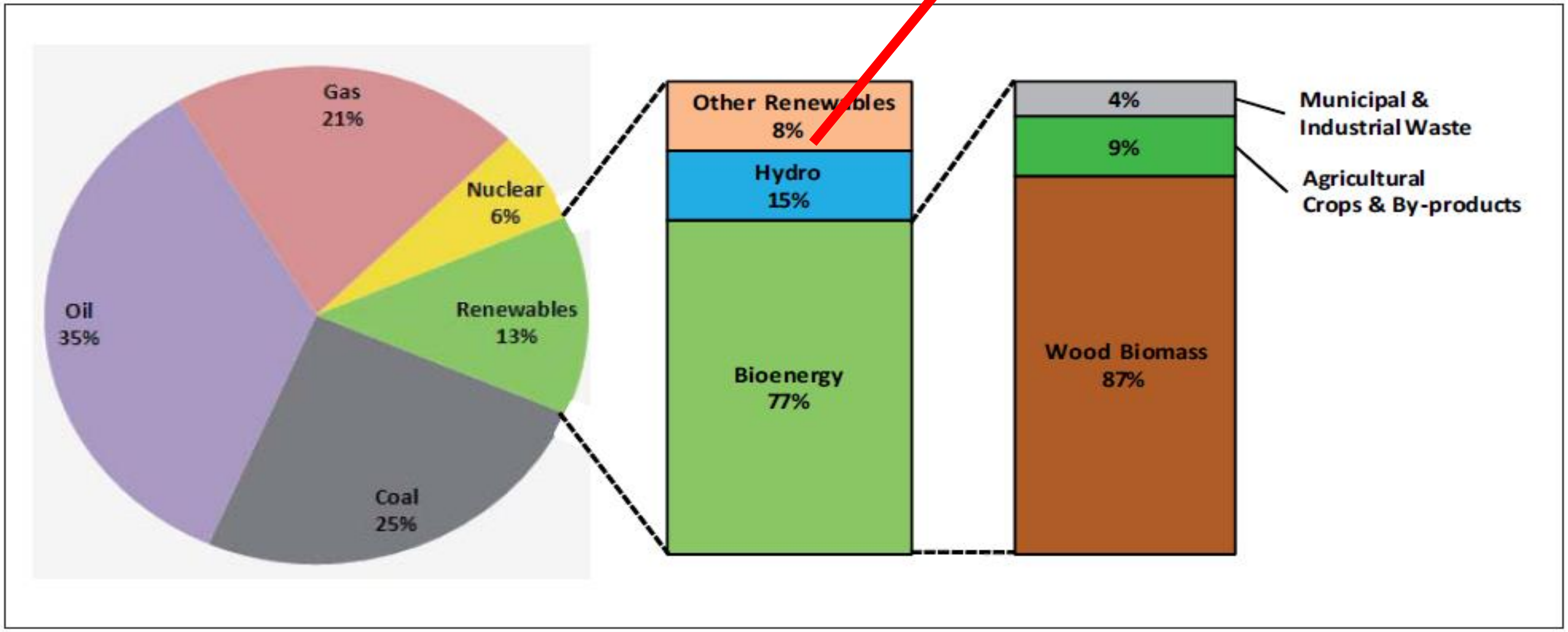
From Renewable Energy Sources (January 1st 2009)
http://www.renewable-energy-sources.com/2009/07/14/depletion-of-non-renewable-energy-sources-july-2009-status/

Energy type	Total world reserves	World Usage per year	Estimated date of exhaustion
Natural gas	175 trillion cubic meters	2920 billion cubic meters	September, 2068
Oil	1210 billion barrels	31 billion barrels	October, 2047
Coal	841 billion metric tonnes	6.4 billion metric tonnes	May, 2140
Uranium	18100 metric tonnes U-235	133 metric tonnes U-235	November, 2144

Global Energy Status: Portion of renewable energy

- Bioenergy is “sustainable energy” but not necessary the “clean energy”;
- Only Hydro and other renewables can be called “sustainable clean energy”.

•Solar Energy
•Geothermal Energy
•Wind Energy
•Tidal Energy
•Wave Energy
•Ocean Thermal Energy Conversion



From 2010 Survey of Energy Resources, World Energy Council (http://www.worldenergy.org/)

Global Energy Status: Sustainable clean energy driving forces

Major driving forces behind sustainable clean Energy:

- Sustainable living and developing of mankind need a sustainable energy supply (If all fossil energy is exhausted, globe will largely rely on sustainable energy);

- Sustainable living and developing of mankind need a sustainable clean environment free of pollution caused by fossil fuel burning (Fossil fuel consumption brings air pollution and global warming and their associated climate changes, such as rising ocean temperature, changing terrestrial geography, and causing acid rain fall and soil degradation).

Major Challenges for Sustainable Clean Energy

- Insufficient reliability (Disrupted Supply of electricity at around the clock whenever they are demanded)
- Difficult transmission and distribution (Limited remote locations from cities)
- Unbalanced integration of renewables on the power grid (Power grid balance between supply and demand)
- High capital cost (High energy infrastructure cost)

In overcoming these challenges, cost-effective, reliable and efficient clean-energy storage and conversion technologies are necessary and critical!

Technology Review for Sustainable Clean Energy Storage and Conversion

- **Electrochemical technologies (Thermal storage and conversion, Batteries, fuel cells, supercapacitors, Solar cells, Hydrogen, CO_2 electro-reduction, Flexible and diversified options, high efficiency, high power/energy densities, Environmentally-friendly)**

- **Fly Wheels (Mechanical storage and conversion, High energy density, Light, but Short cycle life)**

- **Compressed Air (Mechanical storage and conversion, Fast start-up, but Geological structure reliance)**

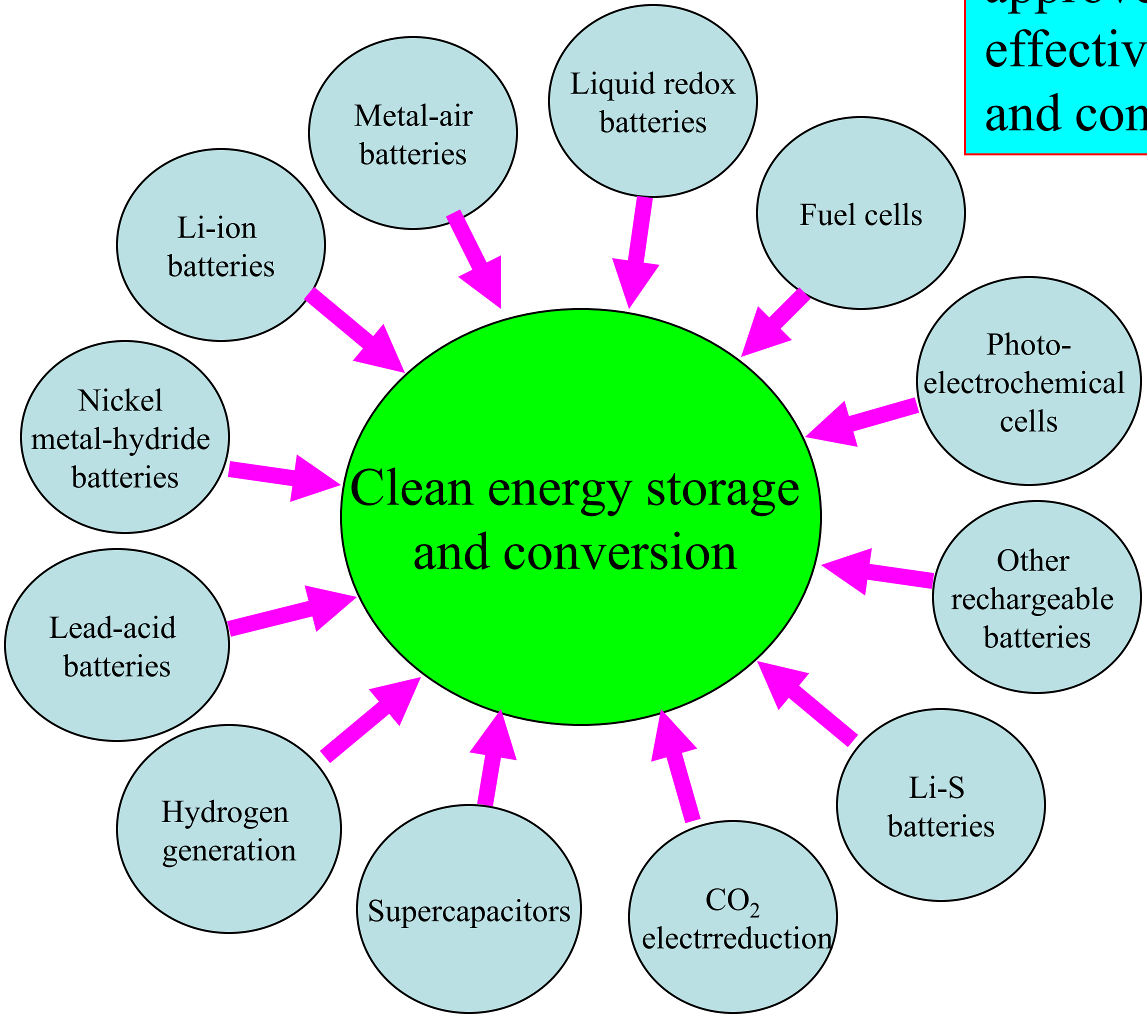
- **Pumped Hydroelectricity (Mechanical storage and conversion, Largest capacity of electricity (over 2000 MW), Low energy density, Geographical dependence, Massive capital cost, Soil erosion, Land inundation, and Silting of dams)**

- **Magnetic super-conductors (Thermal storage and conversion, Environmental friendly and Highly efficient but limited applications)**

- **Ice-melting, utility financing, etc.**

Electrochemical Clean Energy Storage and Conversion

Electrochemical technologies are approved as the most feasible and effective ways in clean energy storage and conversion.



Clean energy storage and conversion

Liquid redox batteries

Fuel cells

Photo-electrochemical cells

Other rechargeable batteries

Li-S batteries

CO_2 electrreduction

Supercapacitors

Hydrogen generation

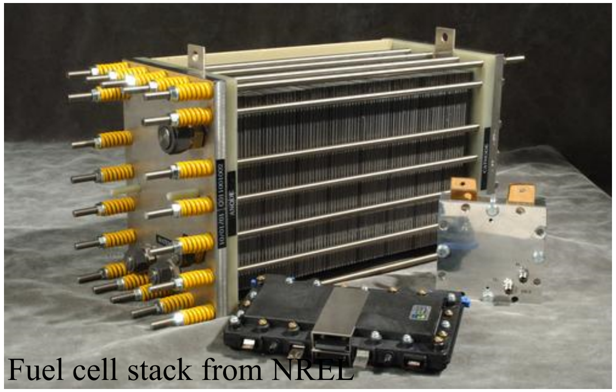
Lead-acid batteries

Nickel metal-hydride batteries

Li-ion batteries

Metal-air batteries

Batteries from rom Wikipedia, the free encyclopedia



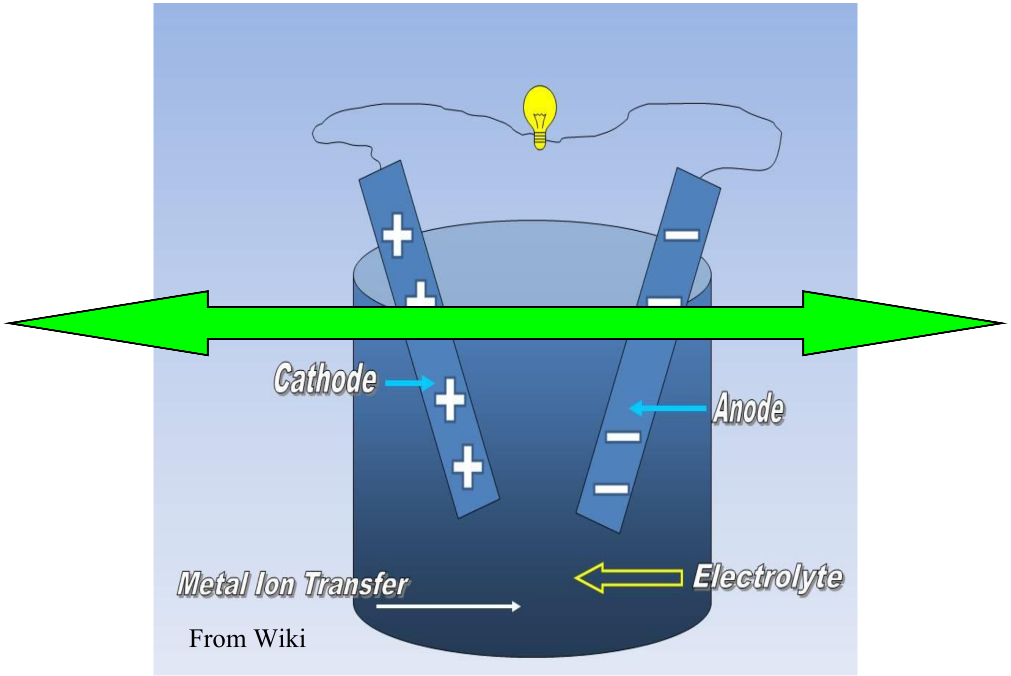
Fuel cell stack from NREL

Electrochemical Clean Energy Storage and Conversion

Working principle:

Electrochemical reactors convert electrical energy into chemical energy for storage, and/or chemical energy into electrical energy for conversion

Electrical energy

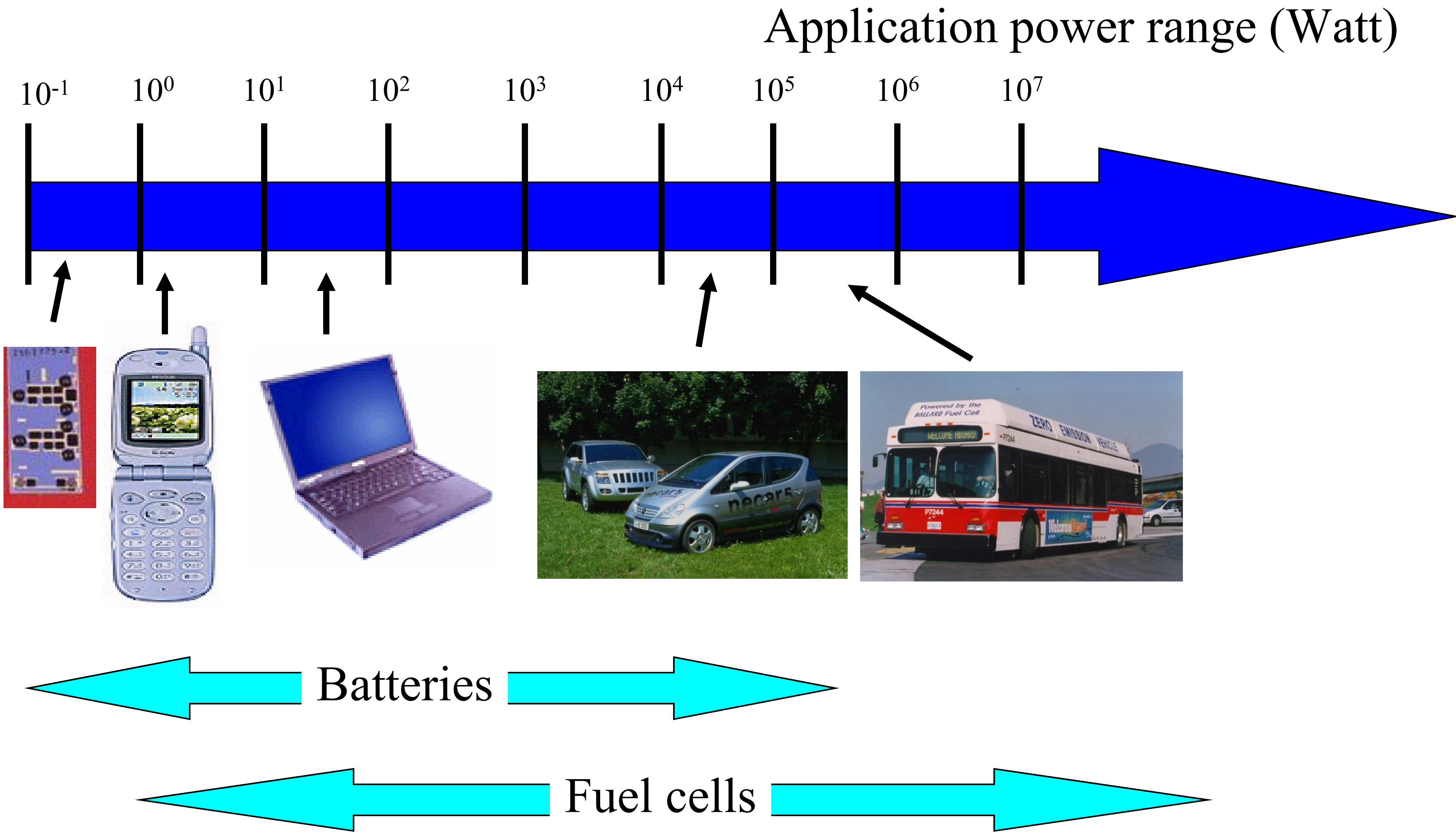


From Wiki

Chemical energy

Electrochemical reactor

Electrochemical Clean Energy Storage and Conversion



Application power range (Watt)

Batteries

Fuel cells

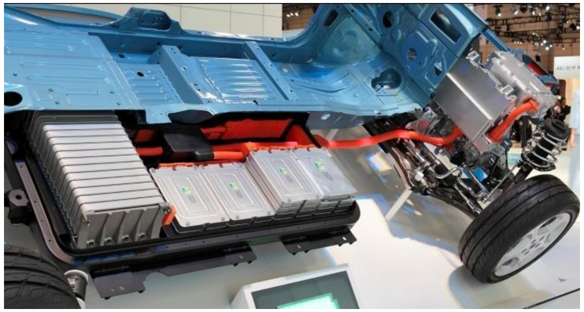
http://web.mit.edu/ese/energy_docs/energydiscussions-shaohorn.pdf

Electrochemical Clean Energy Storage and Conversion

Major advantages (different devices have their own advantages):

- Wide variety of applications in stationary, transportation, portable/micro electronics;

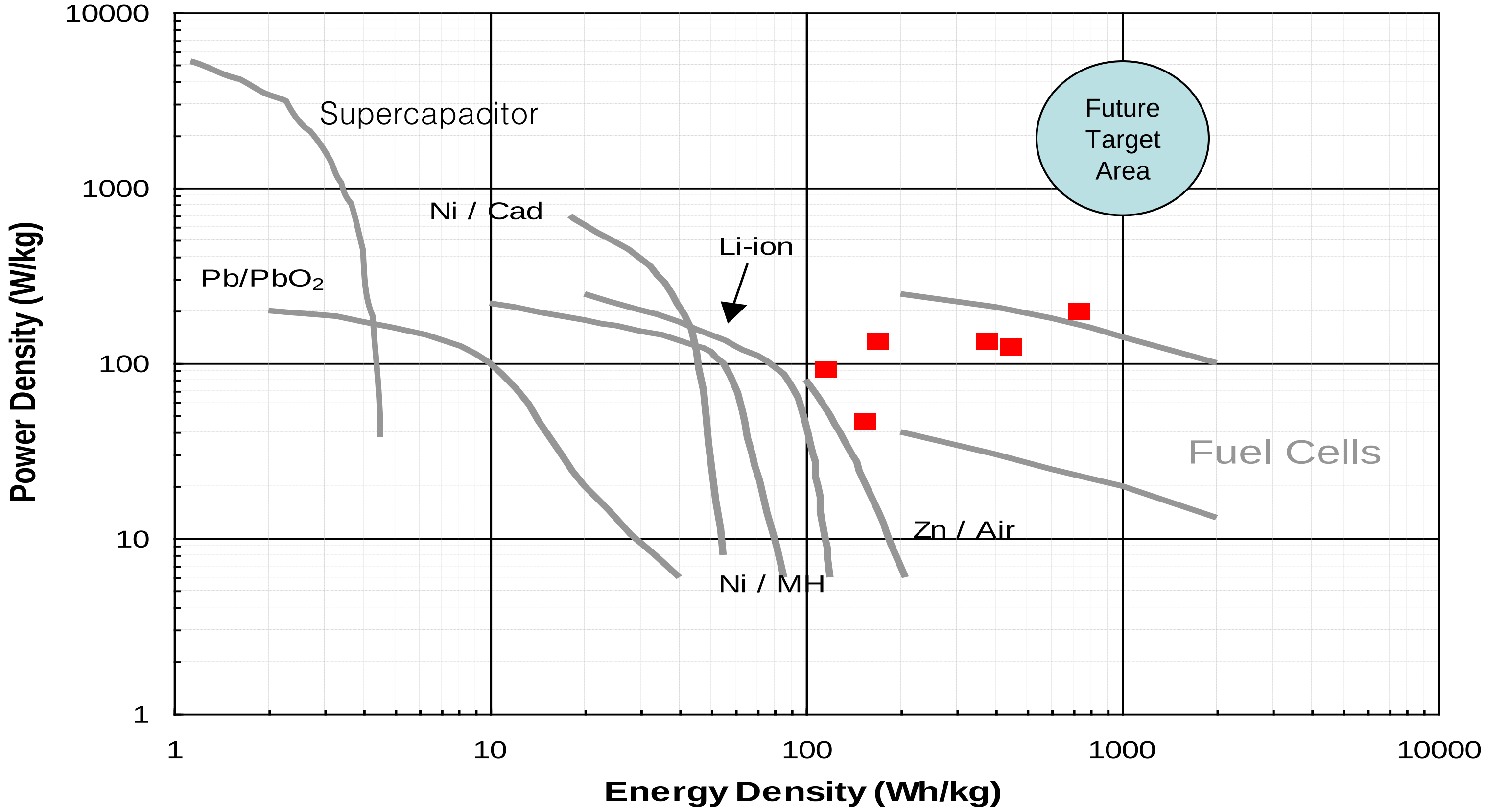
- Wide variety of power and energy density ranges;



- Mobile (wireless);
- High storage-conversion efficiency (40-95%);
- Rechargeable;
- Environmentally-friendly

Electrochemical Clean Energy Storage and Conversion

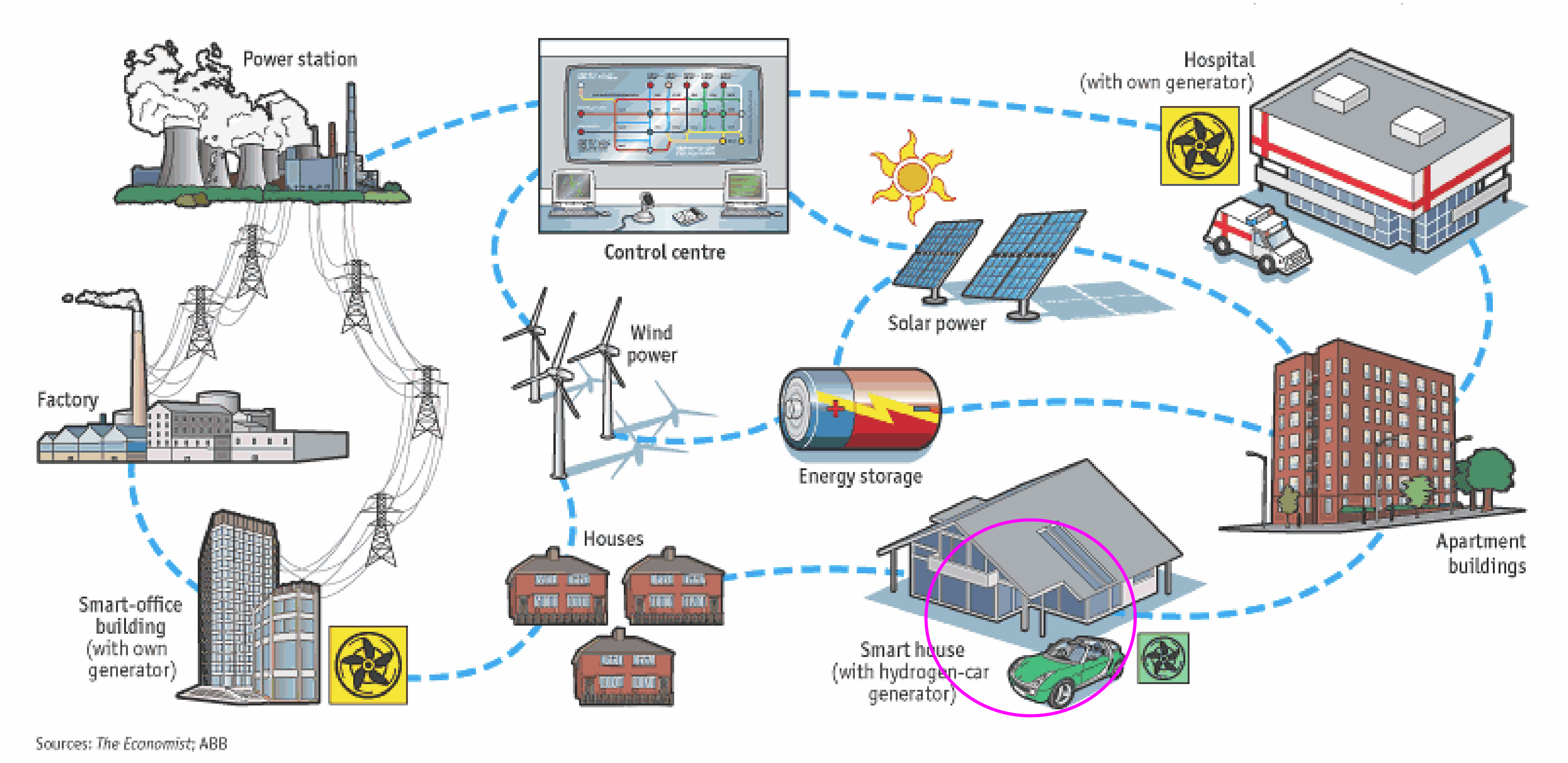
Power density vs. Energy density



Interface (The Electrochemical Society), Vol. 10, No. 1 (Spring 2001)

Electrochemical Clean Energy Storage and Conversion

Electrochemical energy storage-conversion will be a central component in the future Smart Grid!



Sources: *The Economist*; ABB

Future grid: *Two-way flow, multi-stakeholder interactions*

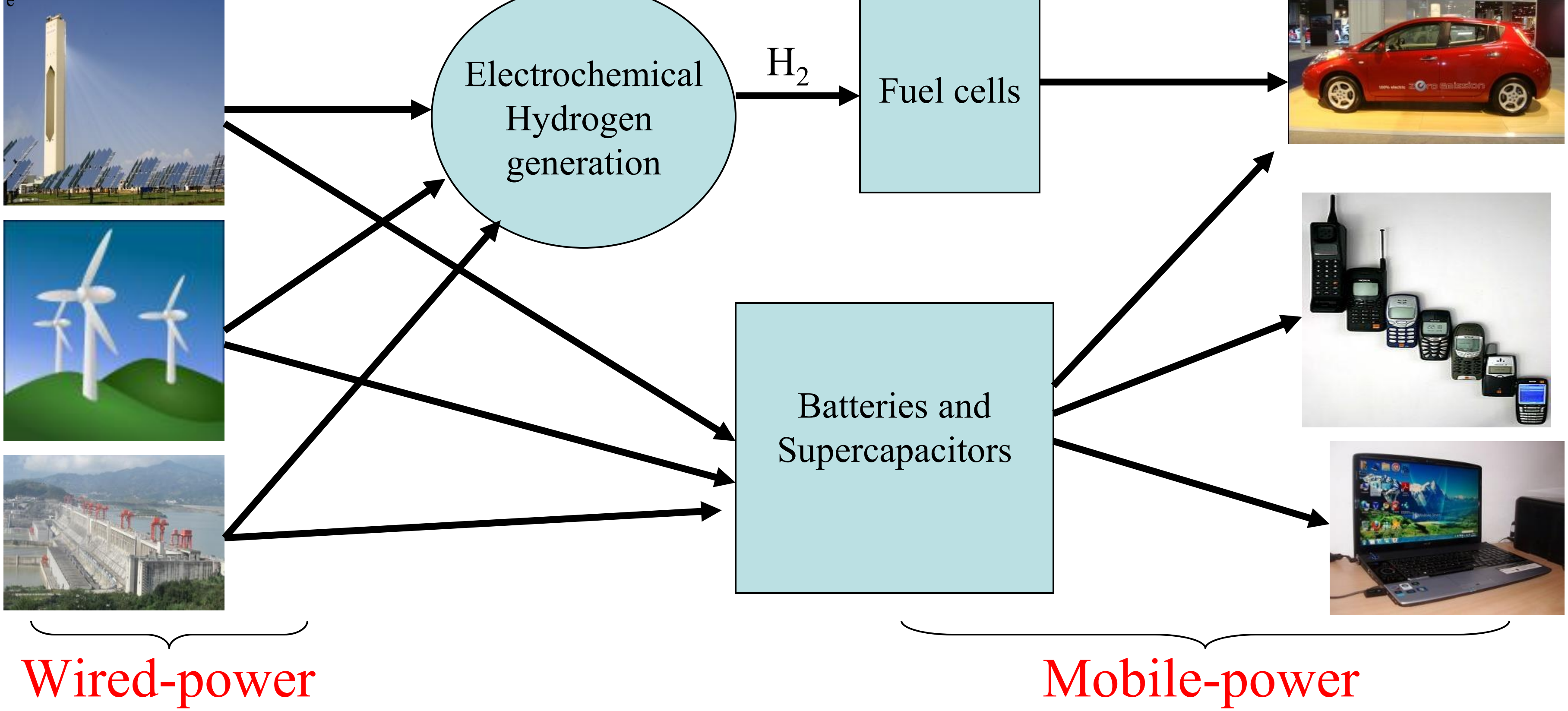
Courtesy AEP

Electrochemical Clean Energy Storage and Conversion

Present and future efforts will be largely put on how to convert wired-power into mobile-power used in cell-phones, portable electronics, and automotive vehicles.

Electrochemical energy storage-conversion is playing and will continuously play a central role in Mobile Powers!

http://en.wikipedia.org/wiki/Main_Page



Electrochemical Hydrogen generation

H_2

Fuel cells

Batteries and Supercapacitors

Wired-power

Mobile-power

Electrochemical Clean Energy Storage and Conversion

Cutting-edge research and development directions:

1. **Fuel cells in particular polymer electrolyte membrane fuel cells for automobile applications** (Exploring and developing nano-structured electrode catalysts and membranes to improve energy/power densities and durability as well as reduce the cost)

2. **Metal-air batteries in particular Li-air and Zinc-air batteries for automobile applications** (Exploring and developing nano-structured materials-based cathode (O_2 reactions) to significantly improve cycle life)

3. **Lithium-sulfur battery for automobile applications** (Exploring and developing nano-structured materials-based electrodes to significantly improve cycle life)

4. **Supercapacitors for automobile applications** (Exploring and developing nano-structured electrode & electrolyte materials (hybrid and composite materials and wide-potential-window electrolytes) to significantly improve energy densities)

5. **Photoelectrochemical cells for hydrogen generation** (Exploring and developing nano-structured photo-electrode materials to significantly improve photo-electricity conversion efficiency)

Current Technology Gaps for the PEM fuel cells

- Cost (factor of 2 – 10 times too high at volume)

- Reliability (early failure modes) and Durability (for many applications only 25-50% of target)

- Operational flexibility (issues with sub-zero operation, high temperature operation and duty cycles)
- Limited direct fuel capability and performance
- Technology simplification and integration
- Fundamental understanding and modeling of root causes of performance effects
- Materials and processes suitable for mass production
- Limited materials performance and availability
- New materials development

PEMFC key material breakthrough is the highest priority in order to achieve a real commercialization:

(1) Catalysts (Cost-effective (50% more in the total stack cost), high activity, availability and high stability, suitable for mass production)

(2) Membranes (Cost-effective, high conductivity, high operating temperature, low humidity and high durability)

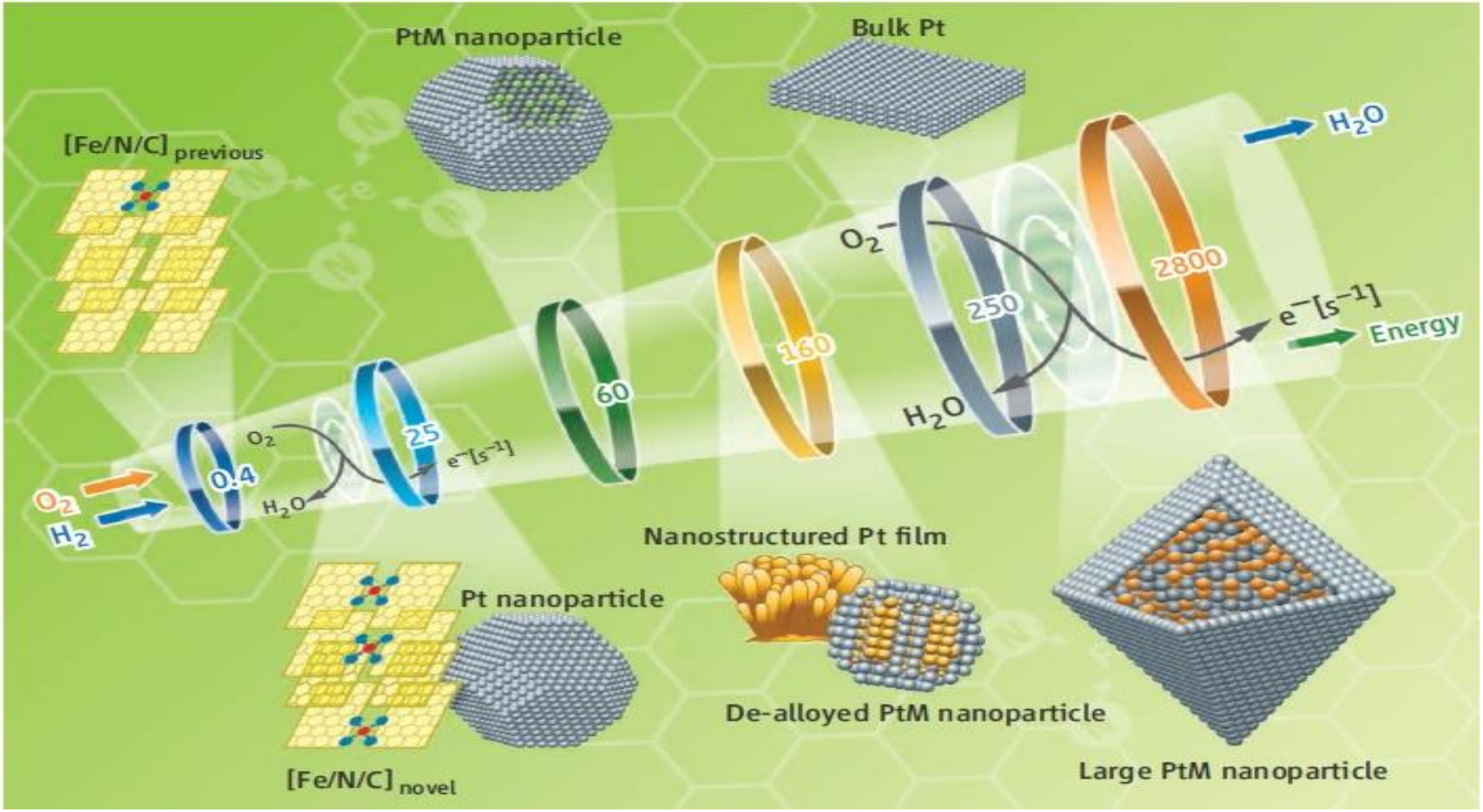
(3) GDLs (Cost-effective and high durability)

(4) Bipolar plates (Cost-effective and high durability)

PEMFC catalyst activity for ORR

Activity = TOF x $1.6\mathrm{x}10^{-19}$ x ASD

$(\mathrm{A.cm^{-3}})$ = $(\mathrm{e^{-}.site^{-1}.s^{-1}})$ X $(\mathrm{C.(e^{-})^{-1}})$ X $(\mathrm{site^{-1}.cm^{-3}})$



* H.A. Gasteiger and N.M. Markovic, **Science** (2009) 324:

Typical results achieved

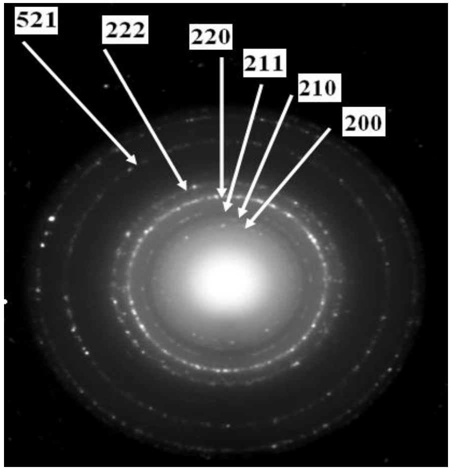
Fuel cell catalysts synthesized in the last 7 years:

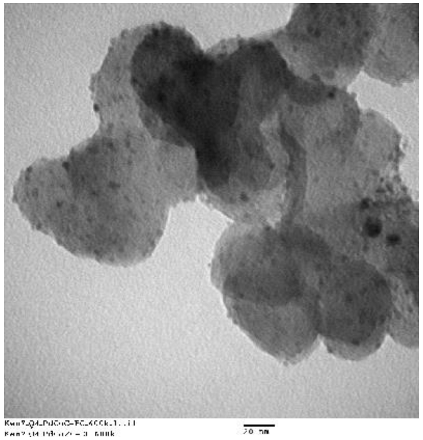
(1) Alloys ($PtBi_2$ Pt-Co/C, Pt-Ru-Ir-Sn/C, Pd-Co/C, Ir-Co/C, PtRu/C, PtPd/non-carbons)

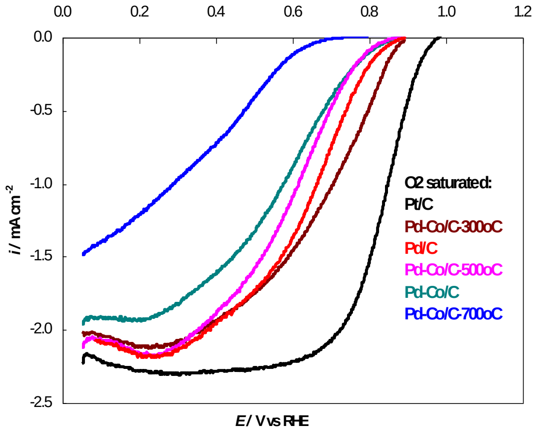
(2) Macrocycles (Co-TMPP/C, Co-PPY/C, Fe-N_4/C, Mo-N/C)

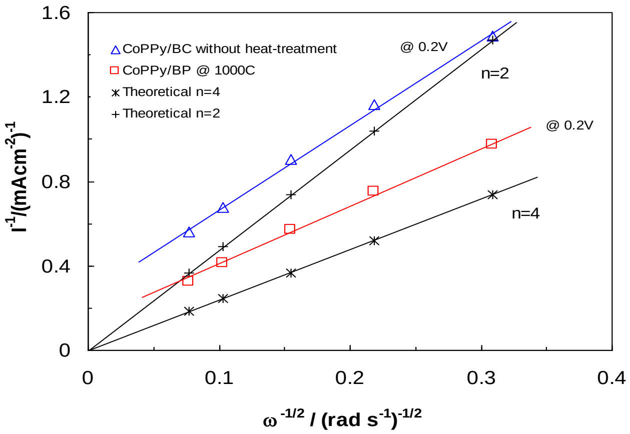
(3) Chalcogenides (Ir-Se/C, W-Co-Se/C)

(4) Mesoporous carbon supported and self-supported catalysts (Pt/MC, PtCo/MC, Fe-N/C)



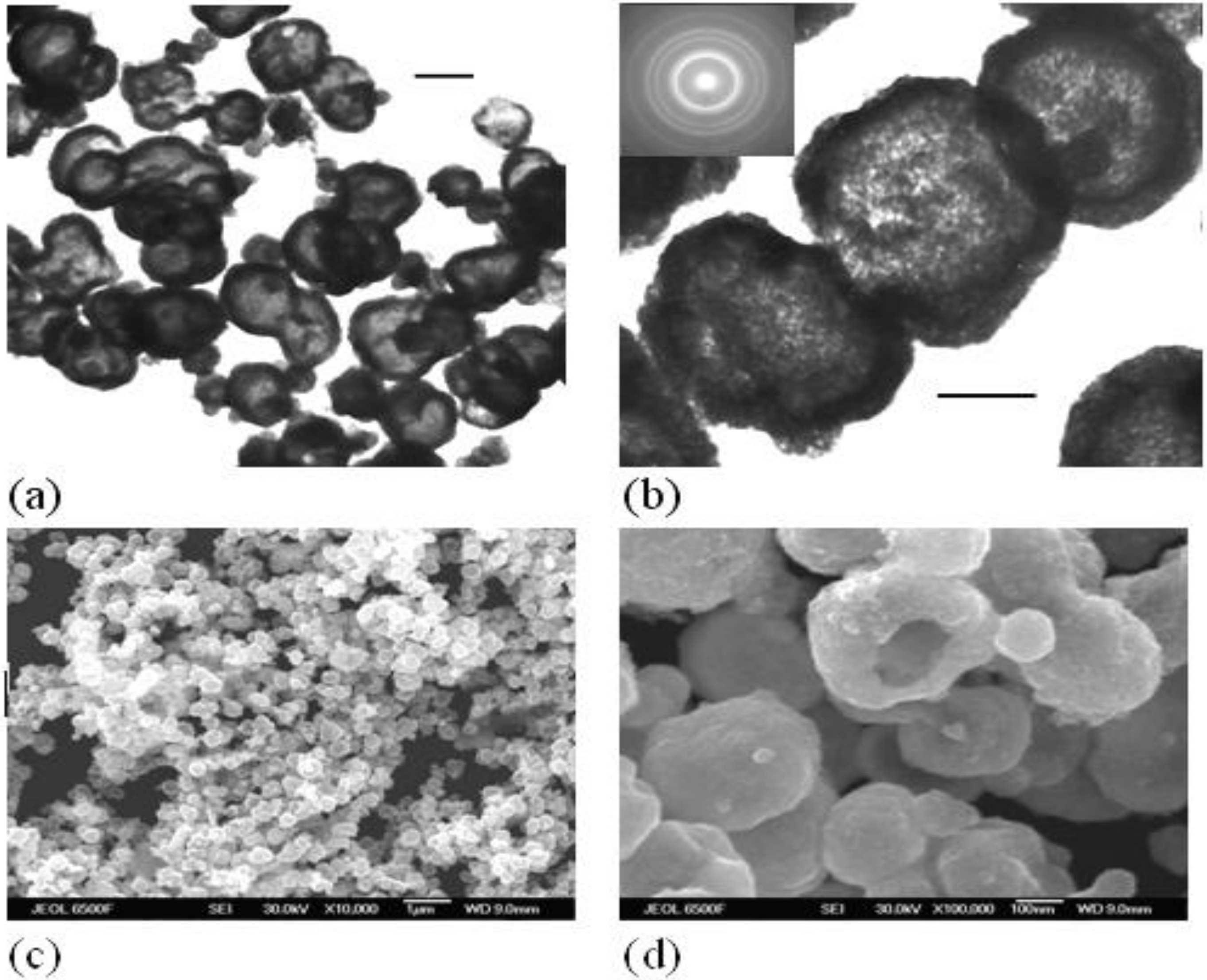




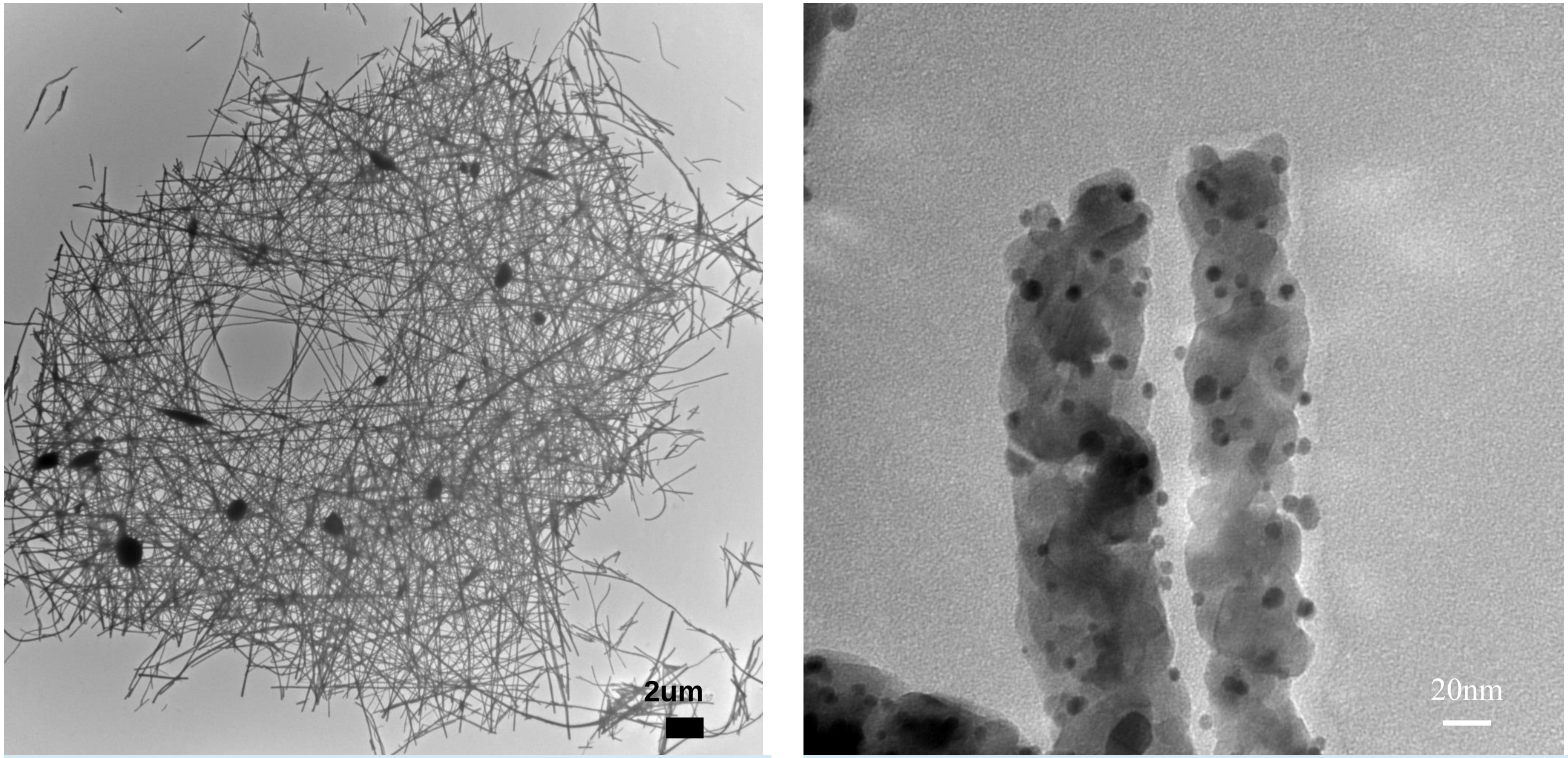


Typical results achieved

Hollow Pt-Co sphere catalysts

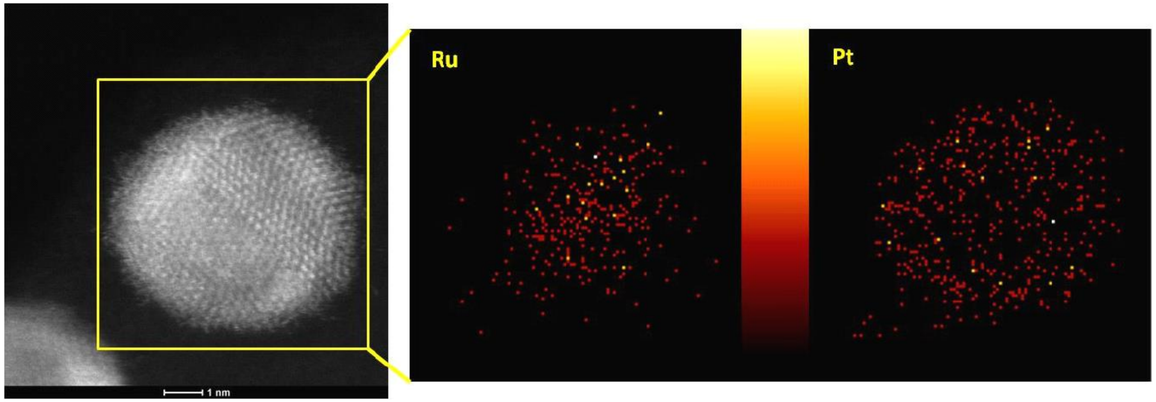


Typical results achieved

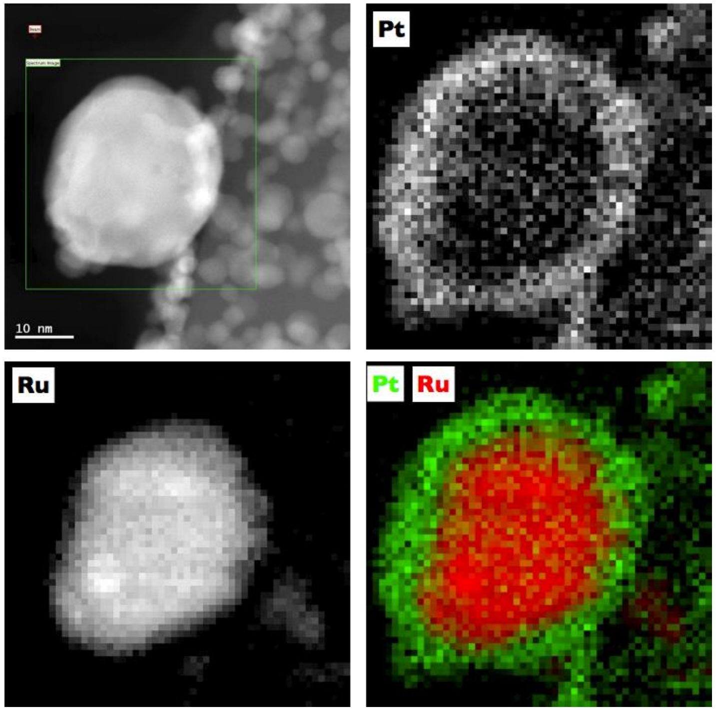


Ceramic nanofiber-supported Pt catalysts

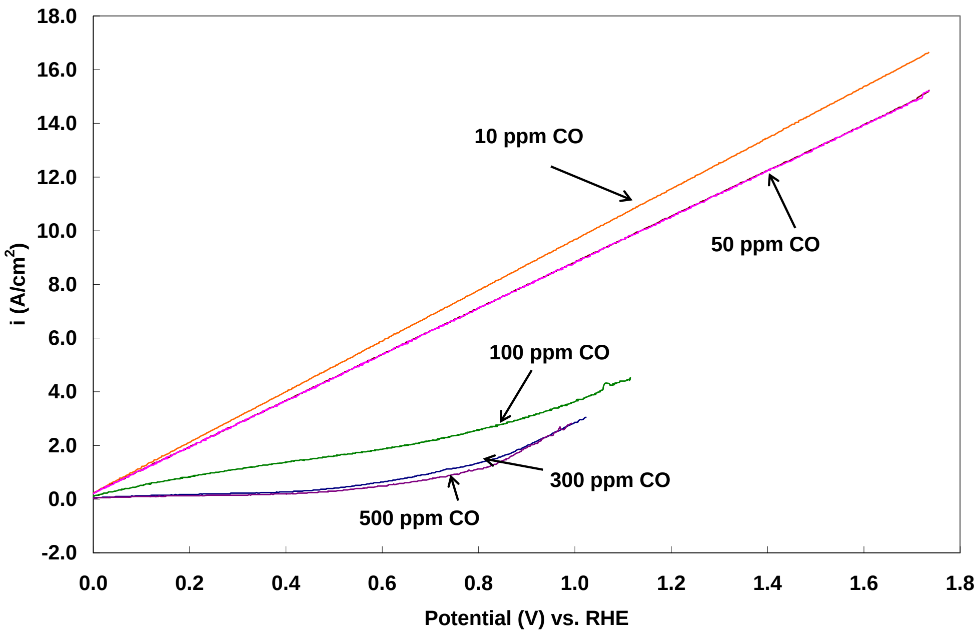
Typical results achieved (core-shell catalysts)



Carbon supported Ru@Pt core-shell catalyst



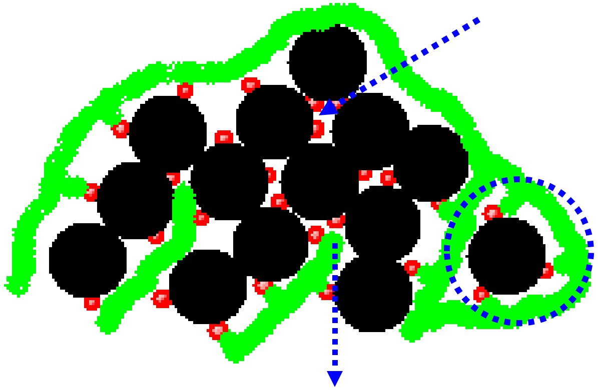
Ti_4O_7 supported Ru@Pt core-shell catalyst



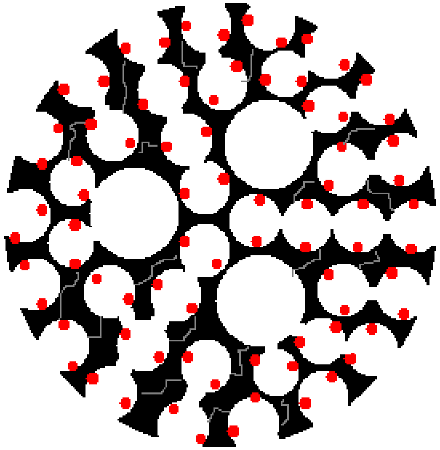
Carbon supported Ru@Pt core-shell catalyst induced CO tolerance in H_2 oxidation

Porous carbon sphere: A new catalyst support

Objective: *Improve catalyst performance through controlling carbon support structure*



Conventional Pt/C aggregate
(carbon particle aggregate)

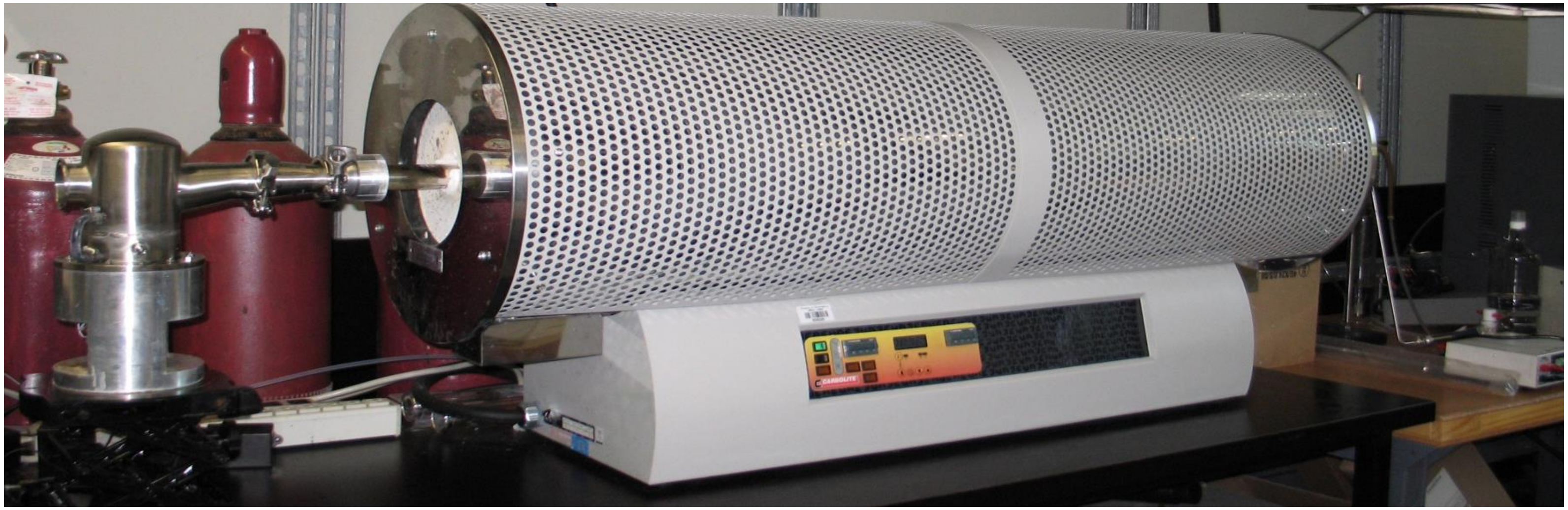


New Pt/C aggregate
(carbon pore aggregate)

Challenges: *1. How to controllable synthesis of such a carbon structure?*
2. How to deposit Pt nanoparticles into this carbon sphere?

Synthesis method

Template assisted ultrasonic spray pyrolysis
— a unique technique for porous materials
(Pending US Patent application)

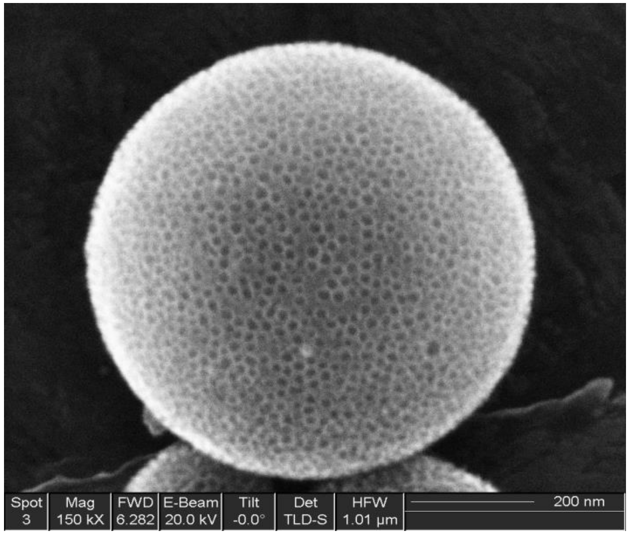


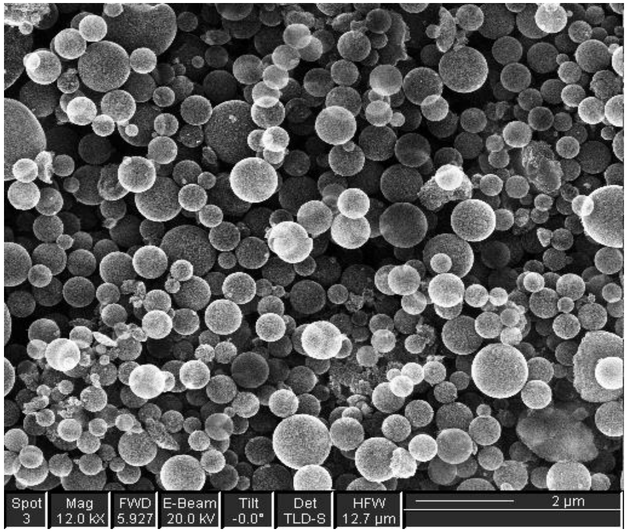
Advantages:

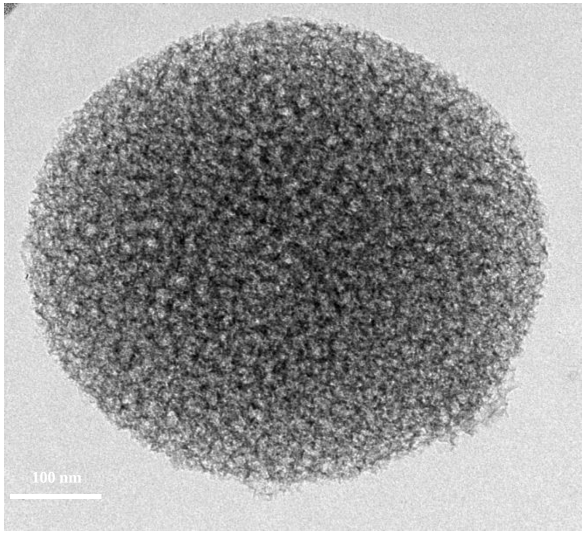
- **Spherical particle---facilitate electrode fabrication**
- **Controllable surface area---maximize the reaction activity**
- **Tuneable porosity---satisfy the needs of different reactions**
- **Scalability---grams per day at labs, kilograms per hour by industry**

Typical example achieved

Porous Carbon Sphere



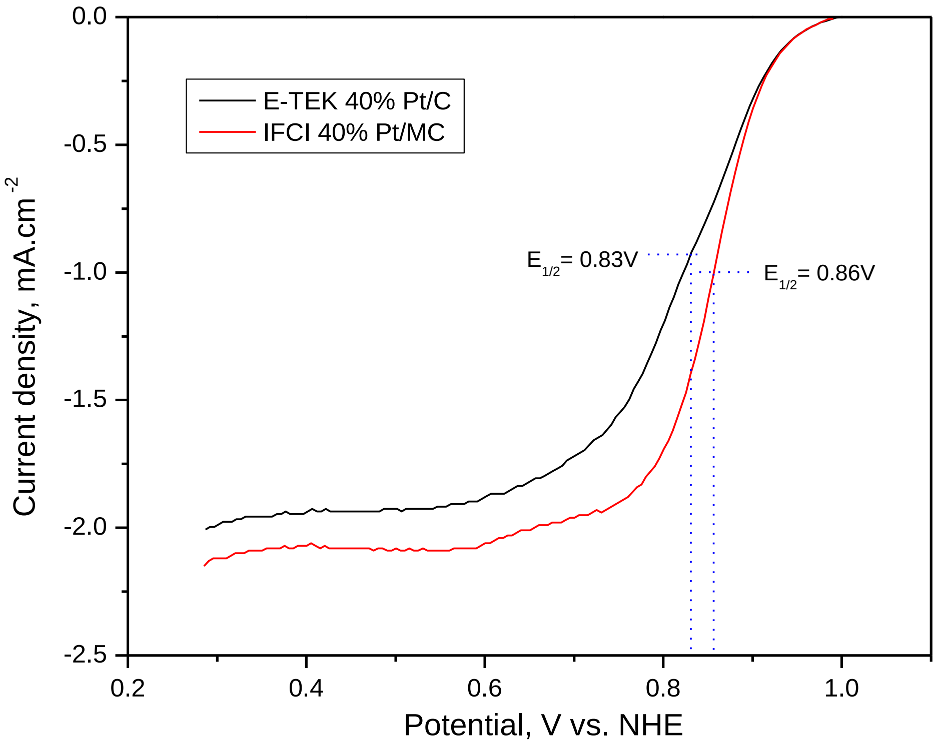




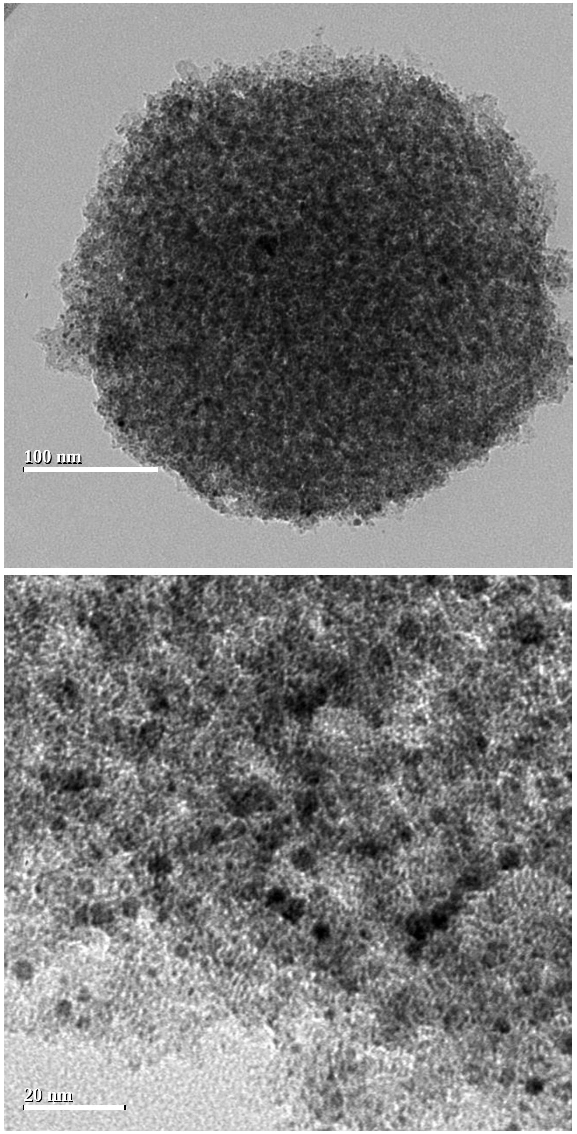
- Narrow particle size distribution (~1μm)
- Controllable specific surface area (200-2000 m^2/g)
- Controllable porosity (pore size: 1-100 nm, pore volume: 0.5-5.0 cm^3/g)

Typical example achieved

Porous Carbon Sphere Supported Pt Catalyst

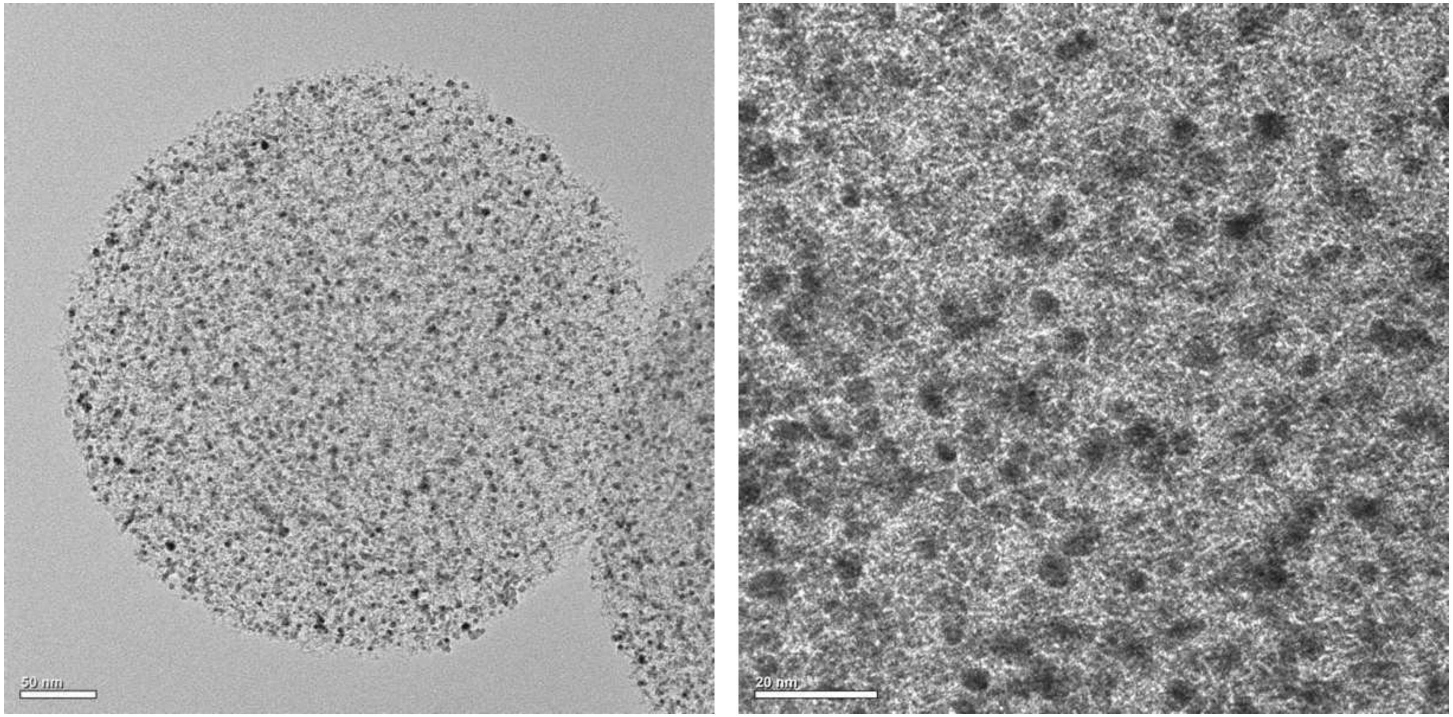


$$1/j = 1/j_k + 1/j_d + 1/j_f$$



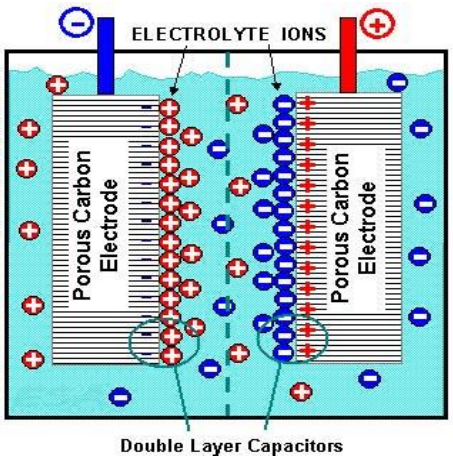
Alloy deposition by microwave-polyol method

Porous Carbon Sphere Supported Pt-Co alloy Catalyst

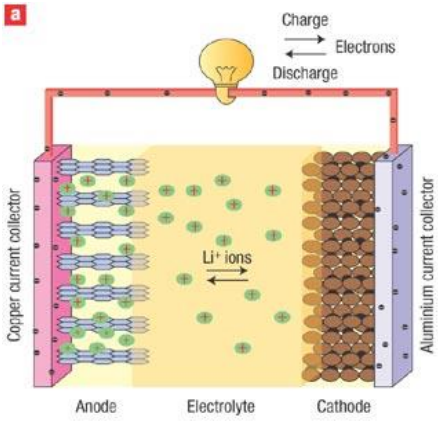


* This alloy catalyst has a double specific activity to a Pt catalyst.

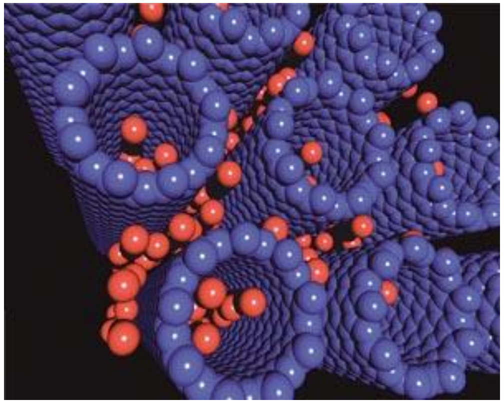
Other applications of porous carbon spheres



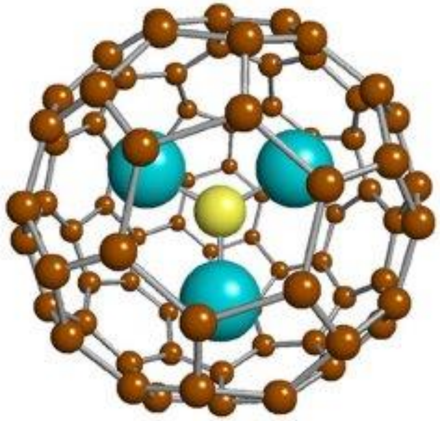
Supercapacitor



Lithium ion battery



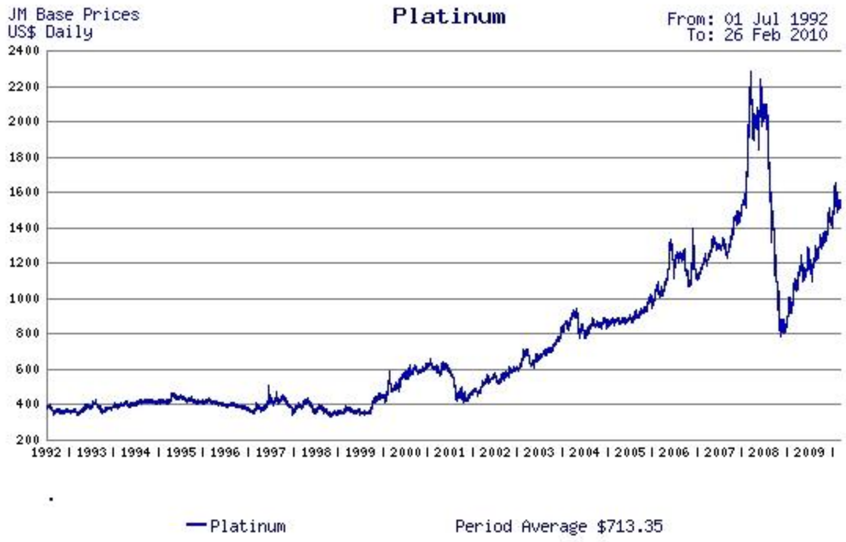
Hydrogen storage

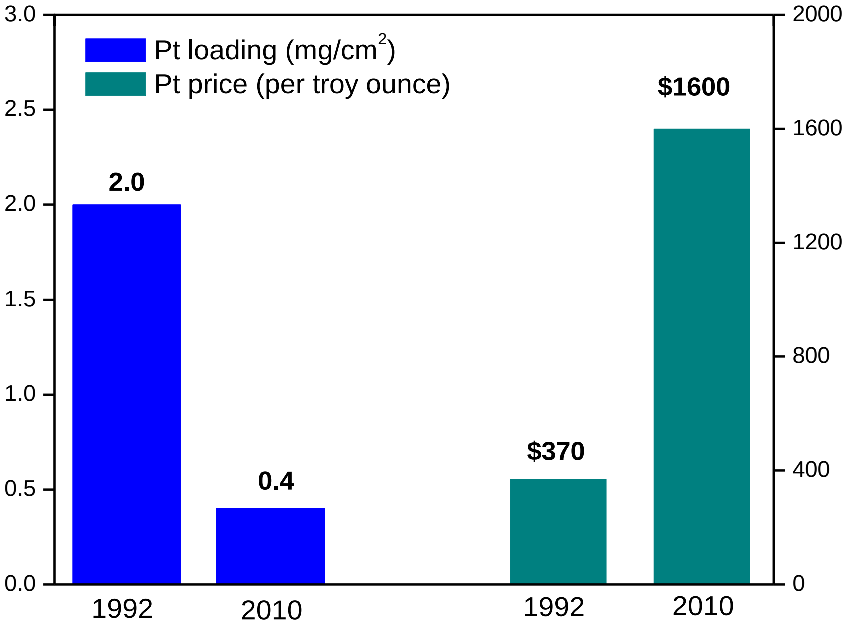


Drug delivery

Why we need to explore non-noble metal catalysts?

Pt loading reduction R&D Status



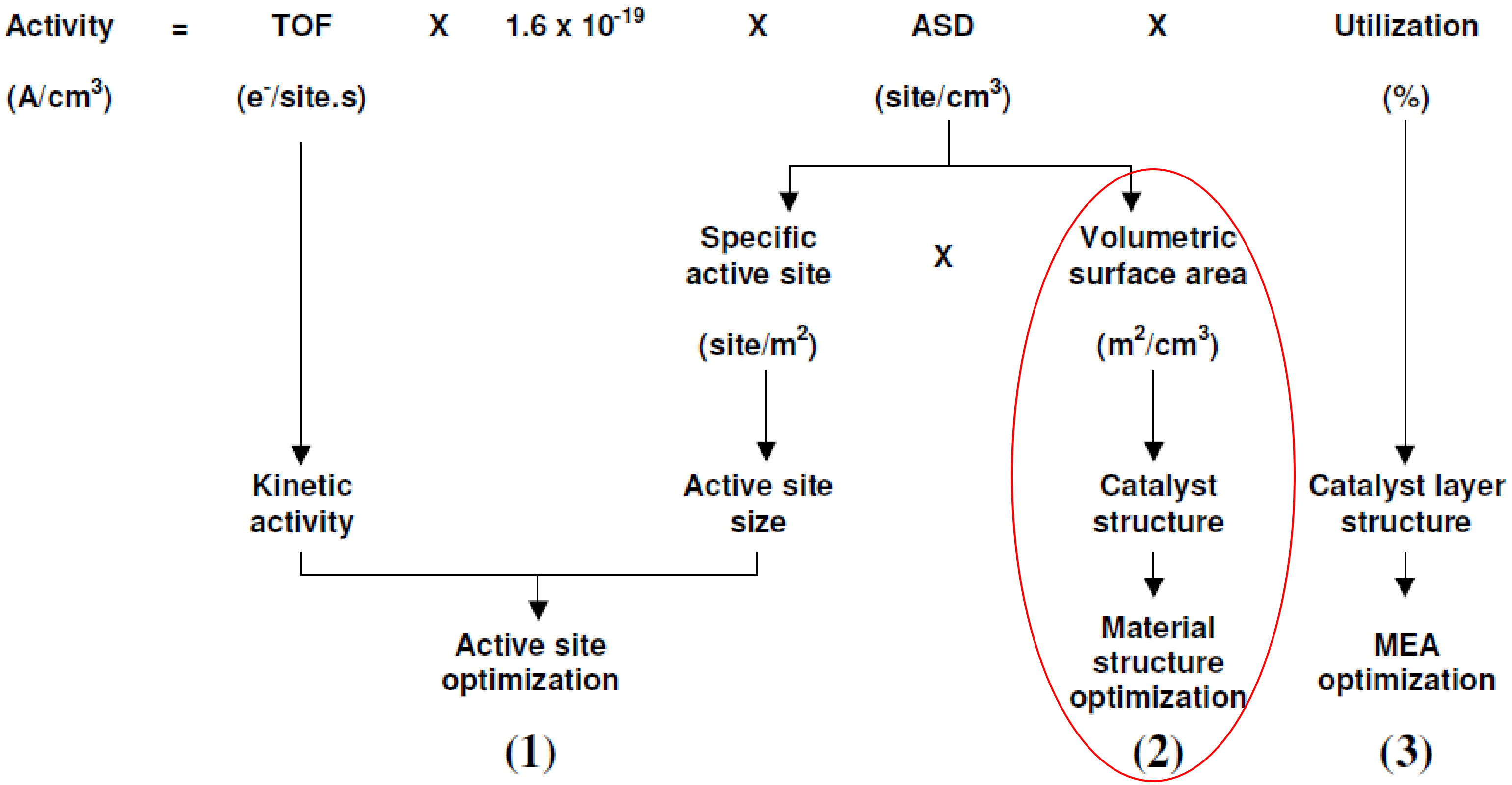


- ➢ ***Pt price increase offset the efforts of Pt loading reduction during the past 18 years!***

- ➢ ***Further low-Pt efforts face the high risk to loss performance and lifetime.***

Non-noble metal catalysts

Three ways to approach the success of non-noble metal catalysts



Activity = TOF X 1.6×10^{-19} X ASD X Utilization

(A/cm^3) (e$^-$/site.s) (site/cm^3) (%)

Specific active site X Volumetric surface area

(site/m^2) (m^2/cm^3)

Kinetic activity

Active site size

Catalyst structure

Catalyst layer structure

Active site optimization

(1)

Material structure optimization

(2)

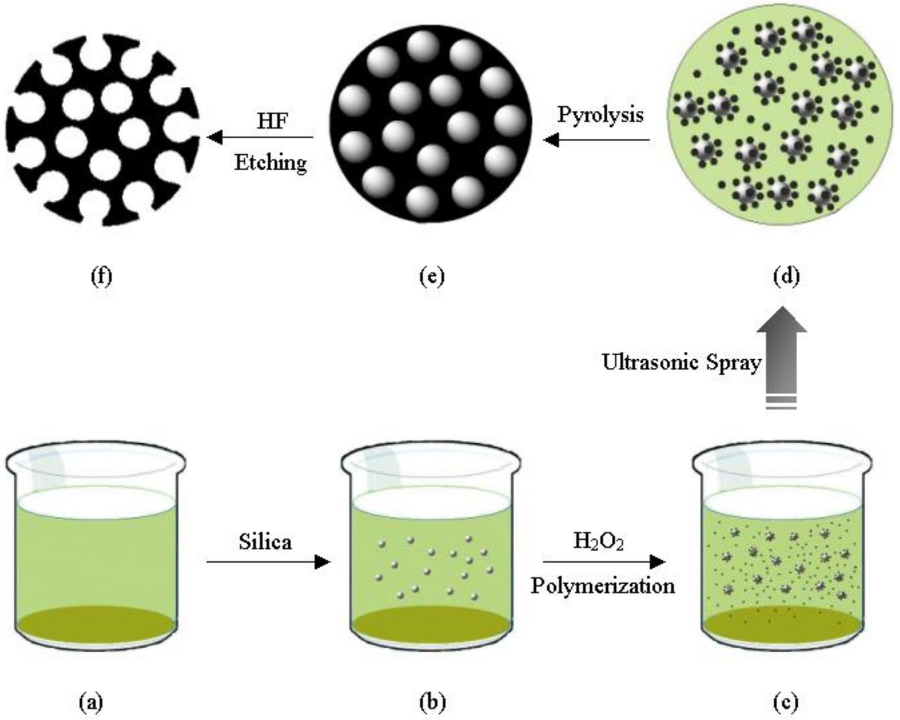
MEA optimization

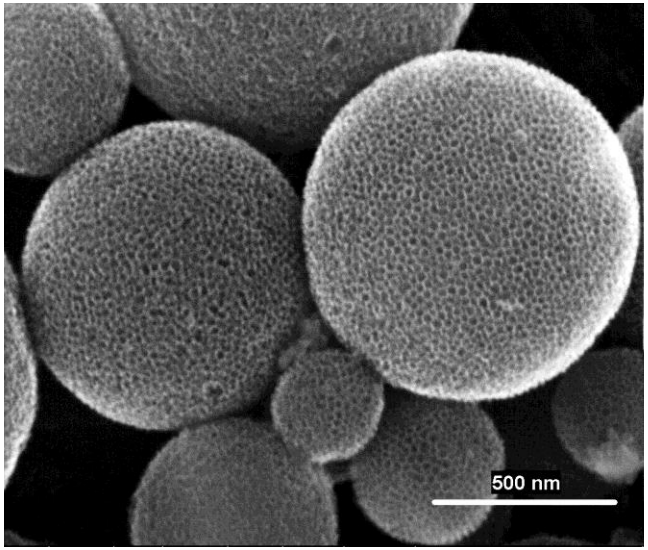
(3)

#. Volumetric surface area is a new concept, independent on active site mechanism.

Non-noble metal catalysts

Self-supporting strategy to prepare non-noble catalysts with high volumetric surface area

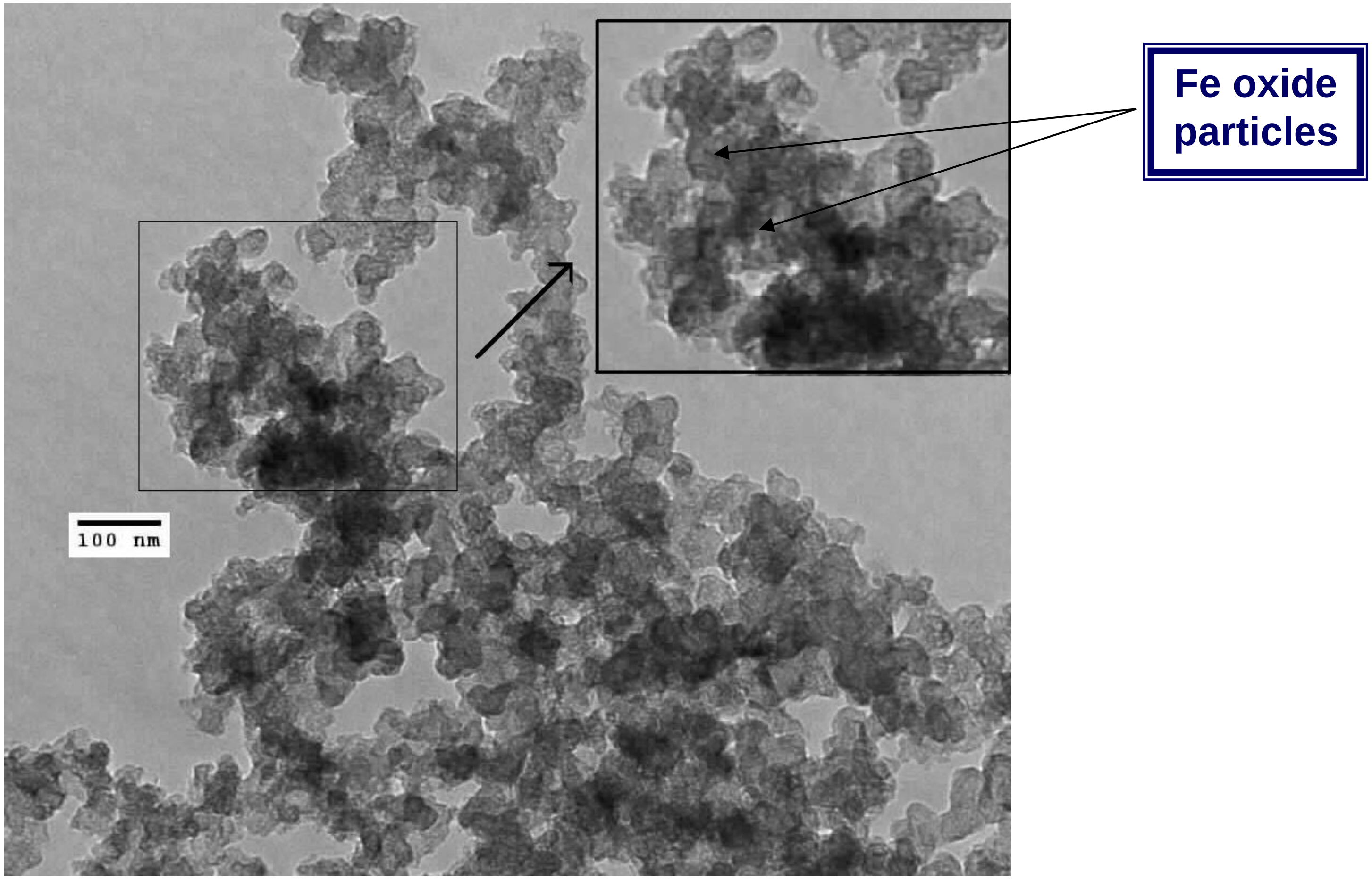




Synthesis process and morphology of self-supported iron-polypyrrole mesoporous catalyst

Non-noble metal catalysts

- **TEM micrograph of Fe-TPTZ/C after heat treatment at 800^{o}C**

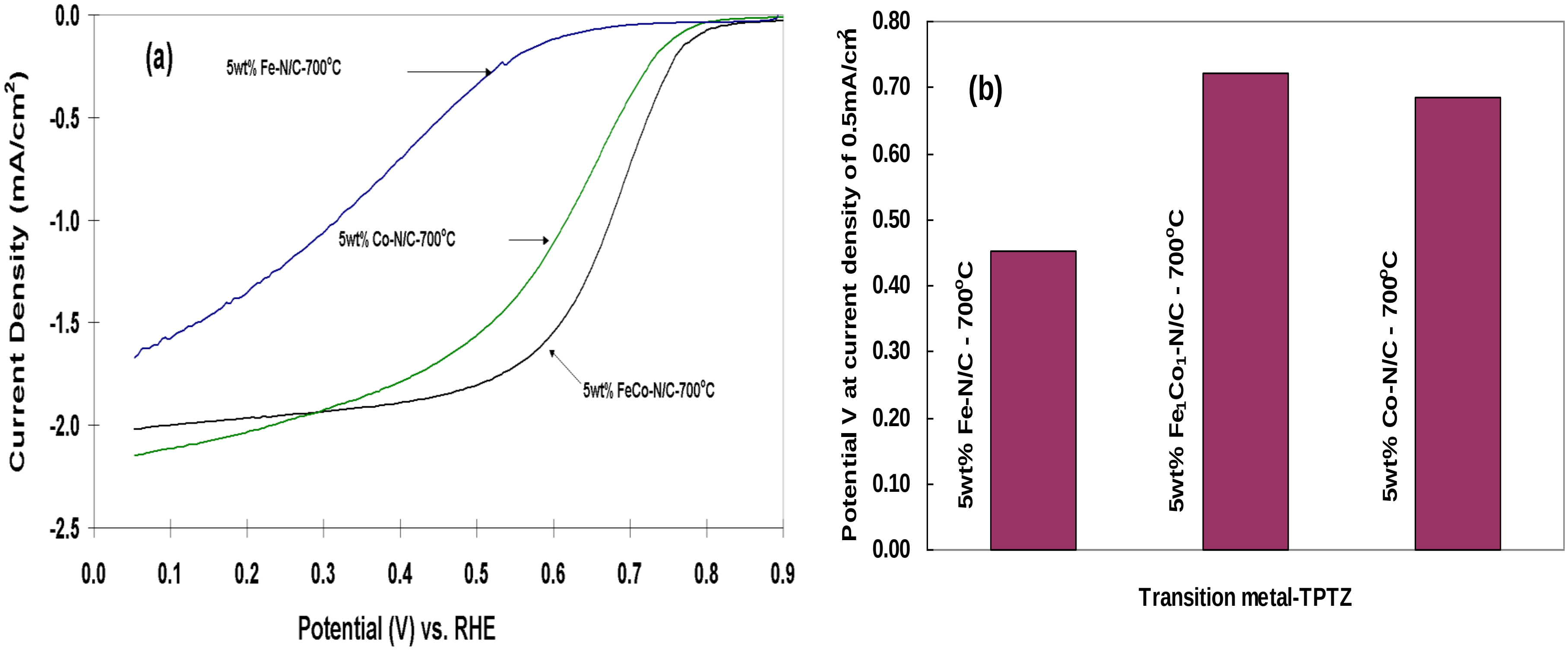


Fe oxide particles

(Mag.: 120K)

Non-noble metal catalysts

Electrochemical activity comparison (CoTPTZ, FeTPTZ, (Fe,Co)TPTZ)



❖ Enhanced activity of binary (Fe, Co)TPTZ compared to single Fe or Co-TPTZ

Comments on Future PEMFC Catalysts

- Supported Pt-based alloy catalysts should be the near future direction in order to meet the requirement of PEMFC early commercialization. However, non-carbon supported Pt alloy catalysts are the priority

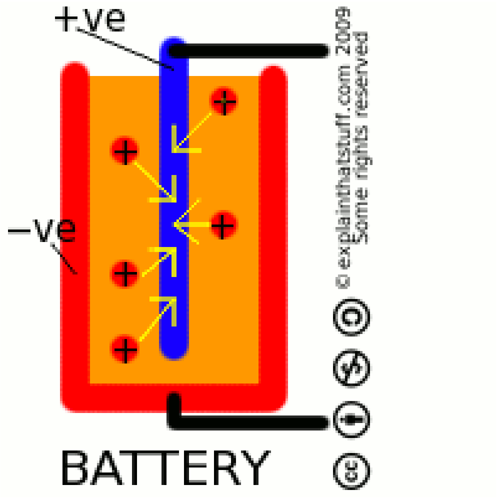
- Future PEMFCs seem may not only rely on Pt-based catalysts for commercialization (It is only a near- or mid-term or demo solution).

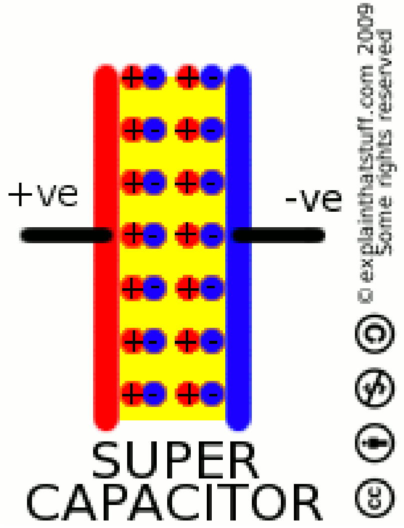
- Non-noble catalysts seem to be the necessary choice for PEMFCs in terms of sustainable commercialization.

- Understanding achieved on Pt-based catalysts is useful but will become history – New understanding for non-noble catalysts must be established.

Differences between supercapacitor and battery or fuel cell

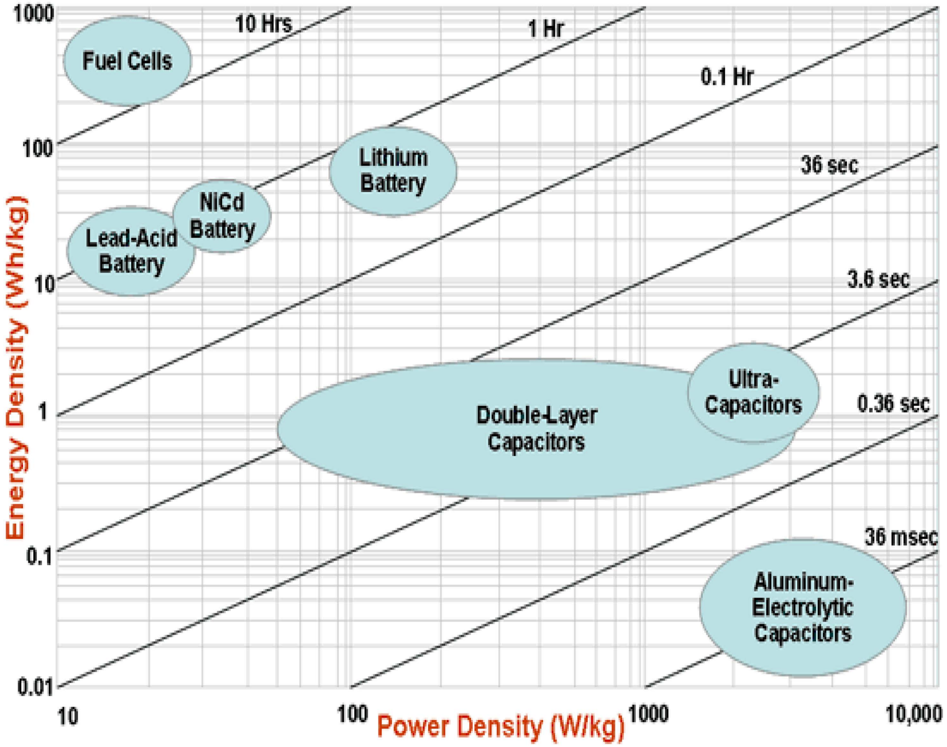
- **Supercapacitors have much higher power density and less energy density than batteries and fuel cells**
- **For double-layer supercapacitors, there is not Faradic process during charge and discharge process**
- **There is an intrinsic cell voltage increase or decrease with charging or discharging of a supercapacitor, while a battery has a constant cell voltage during the charging and discharge**
- **The charge and discharge times of supercapacitors are much shorter than batteries or fuel cells**
- **Cycle life of supercapacitor is much longer than batteries or fuel cells**
- **Electrode structures of supercapacitor are not changed during the charge/discharge processes**
- **Supercapacitors are much safe than batteries and fuel cells.**
- **Heat management in supercapacitors is much easier than batteries**





Advantages of supercapacitors

- Long cycle life (>100,000)
- Much High power density than batteries
- Wide operating temperatures
- Can be combined with other electrochemical energy conversion systems for hybrid applications
- When coupled with battery or fuel cell, the lifetime of such a device can be significantly improved (~5 times)
- Ideal for powering vehicle accelerations
- Regenerative braking (fast recharge of the supercapacitor during braking, impossible for Li-ion batteries)
- Stop-and-go applications (very high cyclability)
- Heat management is much easier than batteries and fuel cells
- Environmentally Friendly Solution



Source US Defence Logistics Agency

Challenges and solutions for supercapacitors

Challenges

1. Low energy density
2. High production cost

Solutions

1. Materials with high surface area and high capacitance (nanostructure with suitable pores plus electro-active materials such as metal oxides)
2. High cell voltage (non-aqueous electrolytes)

$C=\varepsilon A/d$

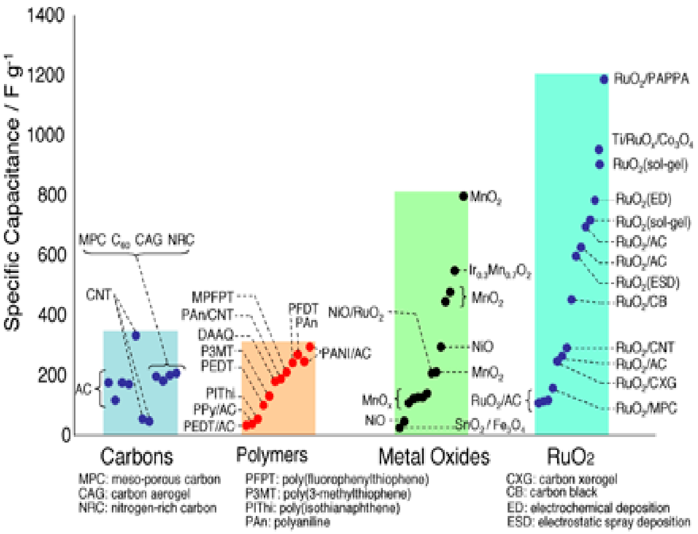
C: capacitance; A: electrode surface area

$E=1/2\ CV^2$

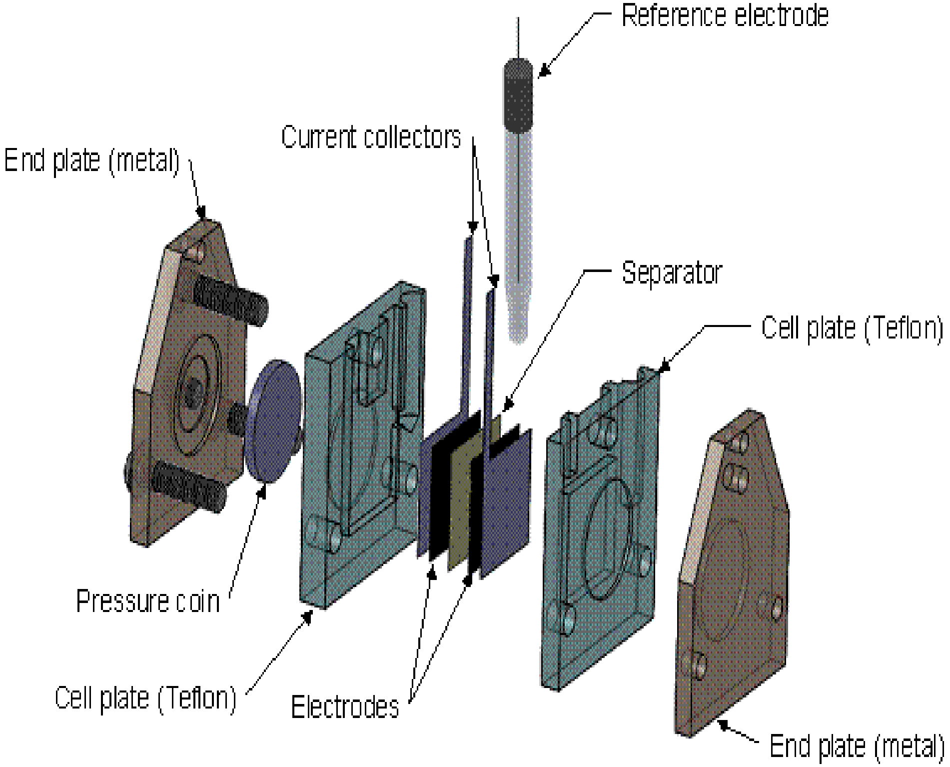
E: maximum energy stored; V: cell voltage

$P=V^2/4R$

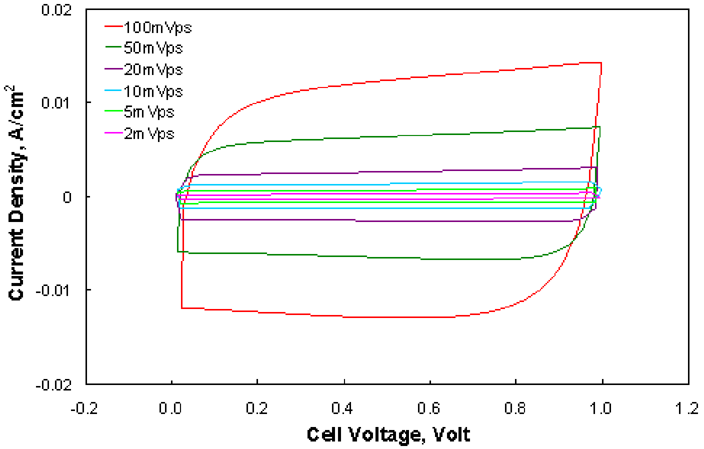
P:delivered power; R: ESR



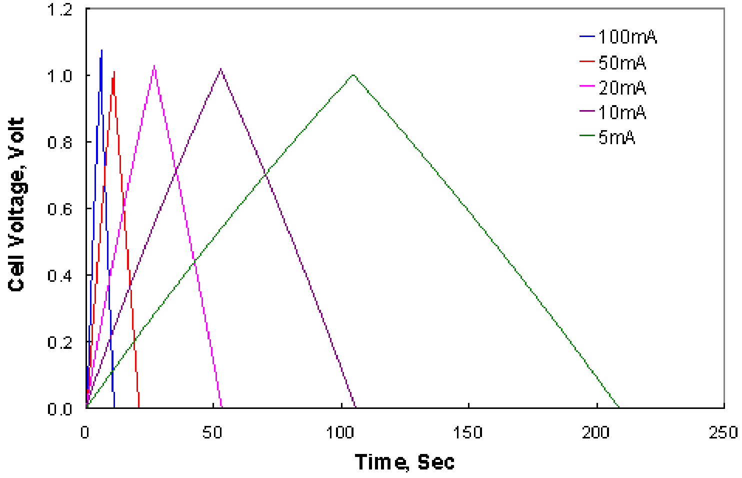
Supercapacitor test cell design and validation



Test cell design



Cyclic voltammograms

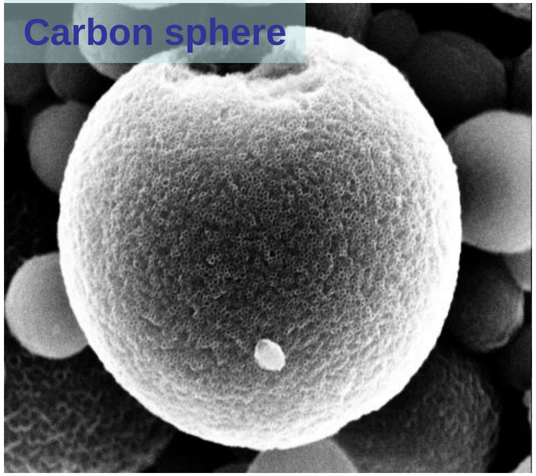


Charging-discharging curves

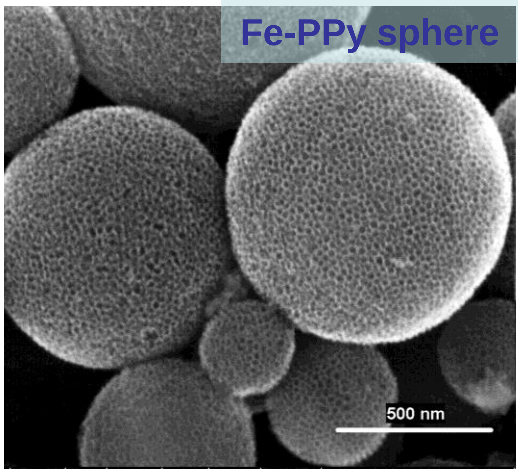
Typical Results for supercapacitors

High Surface Area Porous Materials

- Up to 2000 m^2/g
- 1-100nm pores



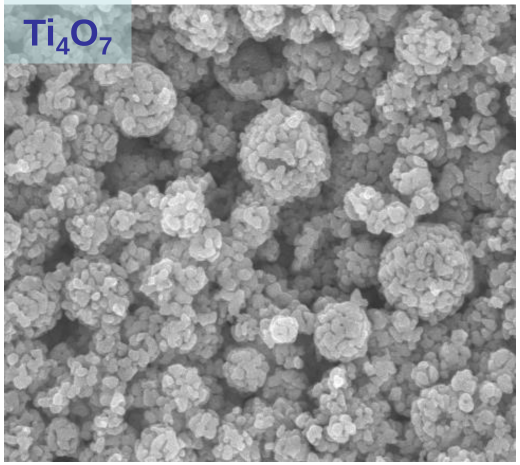
Carbon sphere



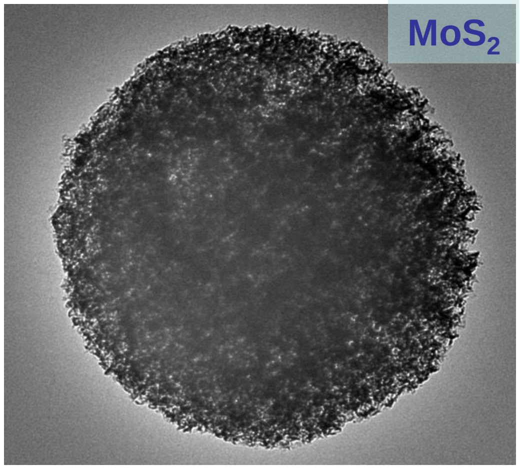
Fe-PPy sphere

- Self supported
- High active sites

- 188 m^2/g
- conductive



Ti_4O_7

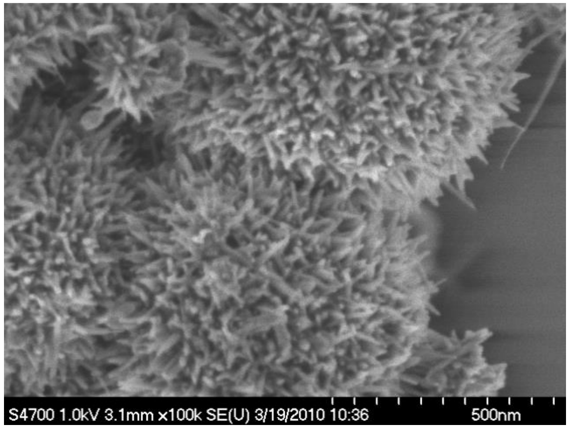


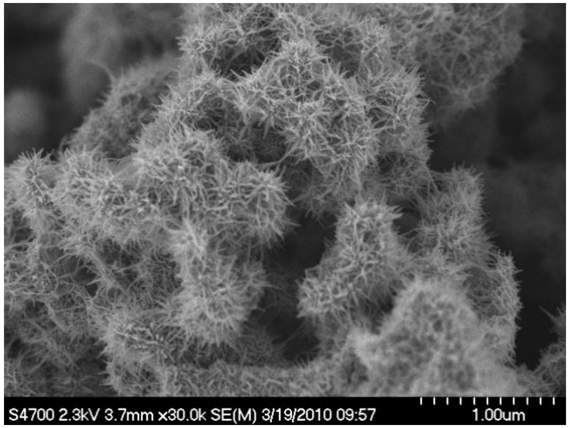
MoS_2

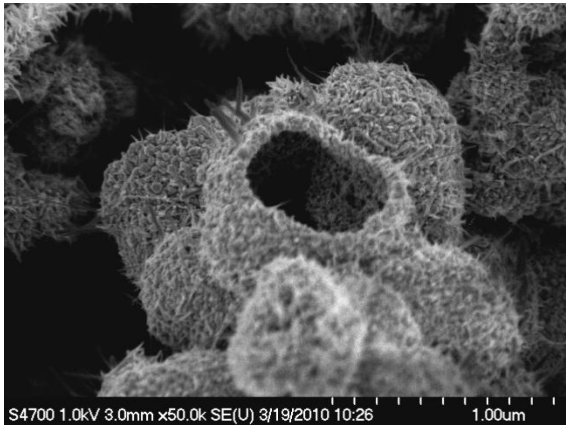
- Self supported
- 250 m^2/g

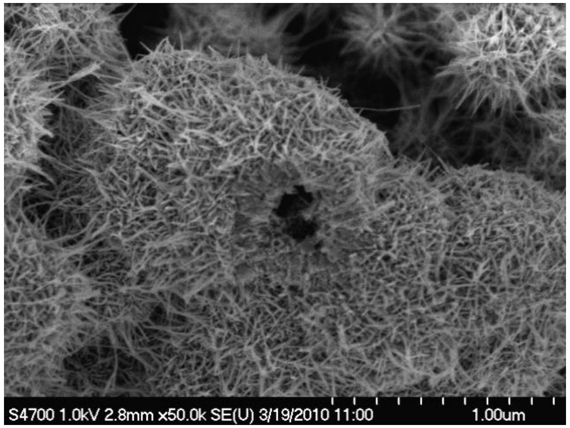
Typical Results for supercapacitors

Next Generation Supercapacitor Materials





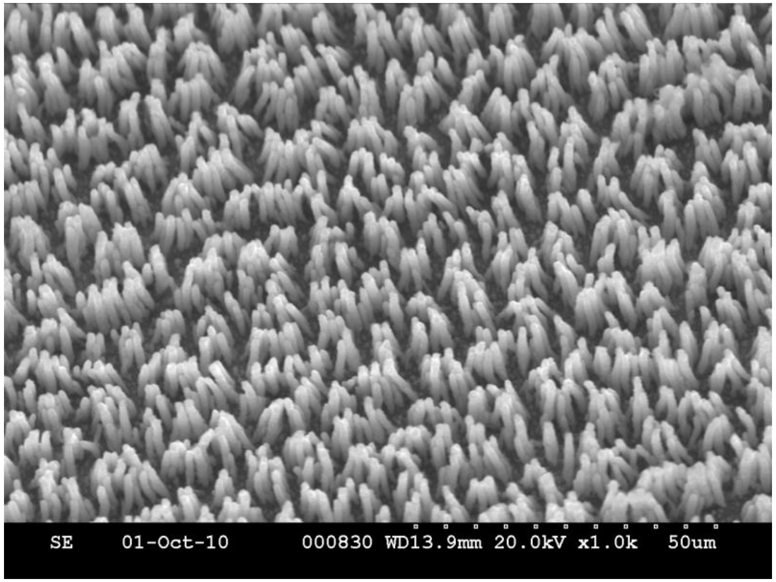




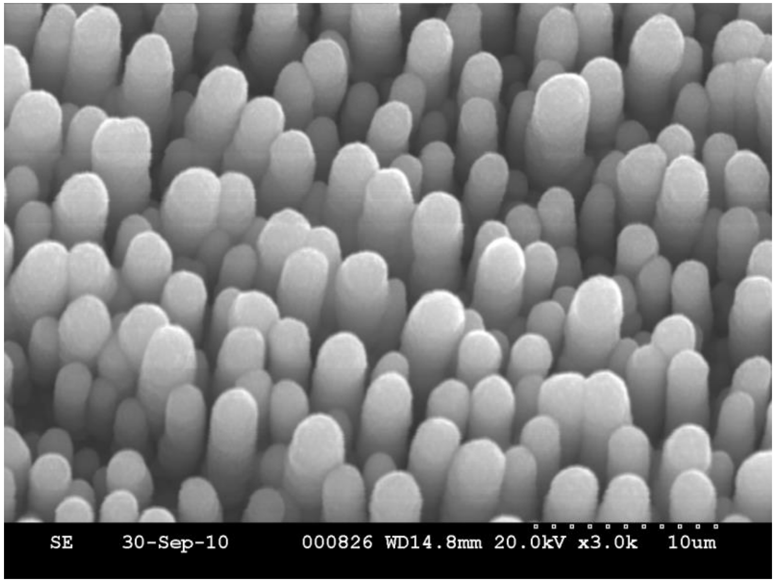
- γ-MnO_2 phase
- Well-formed shell shape with nano-fibrous features on the surface
- ~300 nm particle size

Typical Results for supercapacitors

Anodic deposition of MnO_2 on stainless steel current collector



50°C and 30 mA cm^{-2}

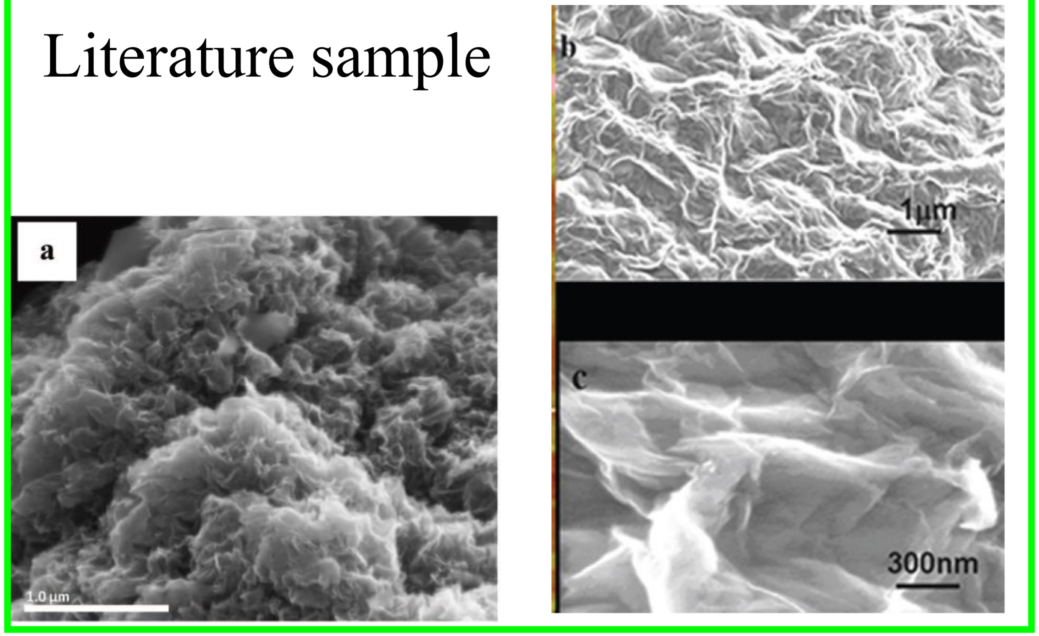


50°C and 15 mA cm^{-2}

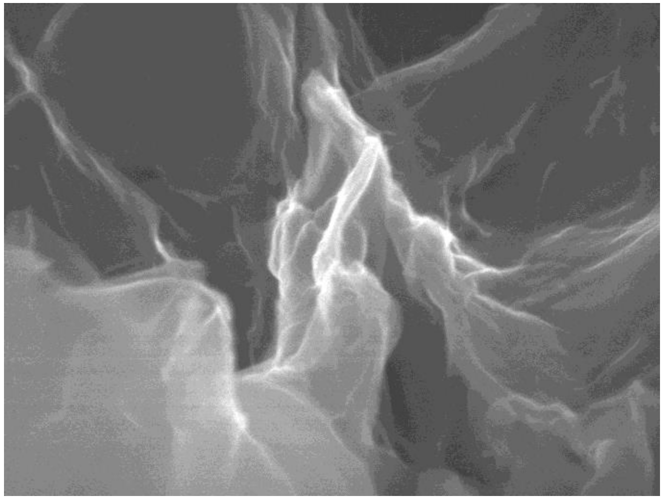
Typical Results for supercapacitoirs

Synthesis and characterize graphene-based carbon material

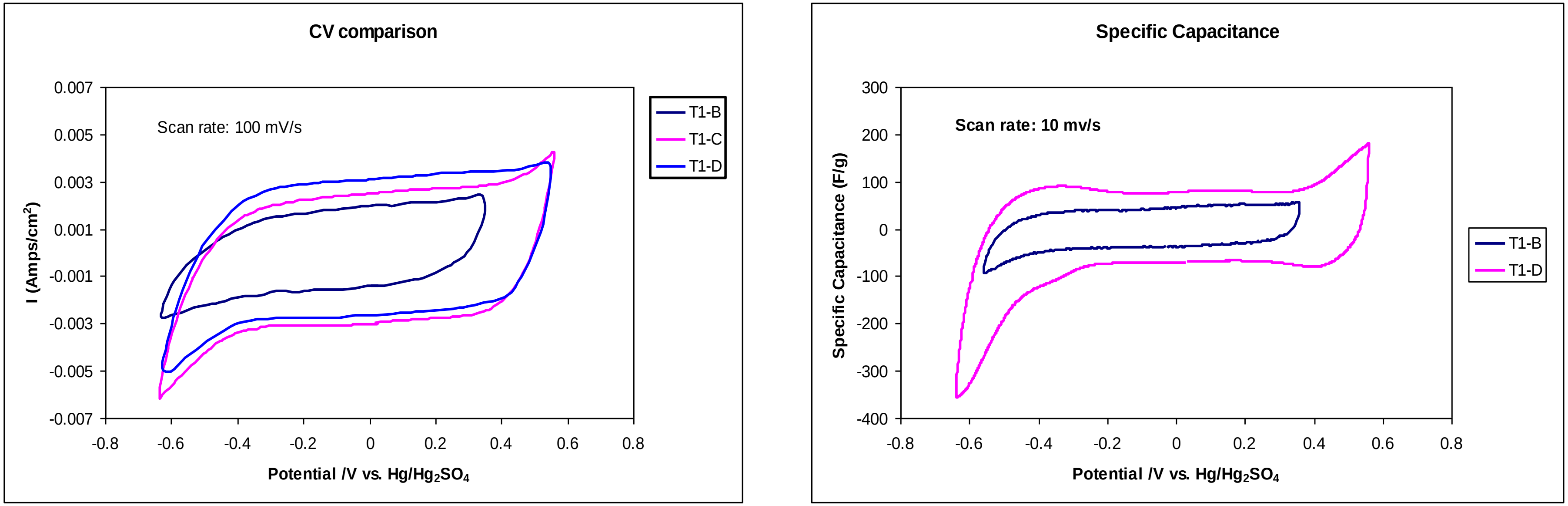
Literature sample



Our sample



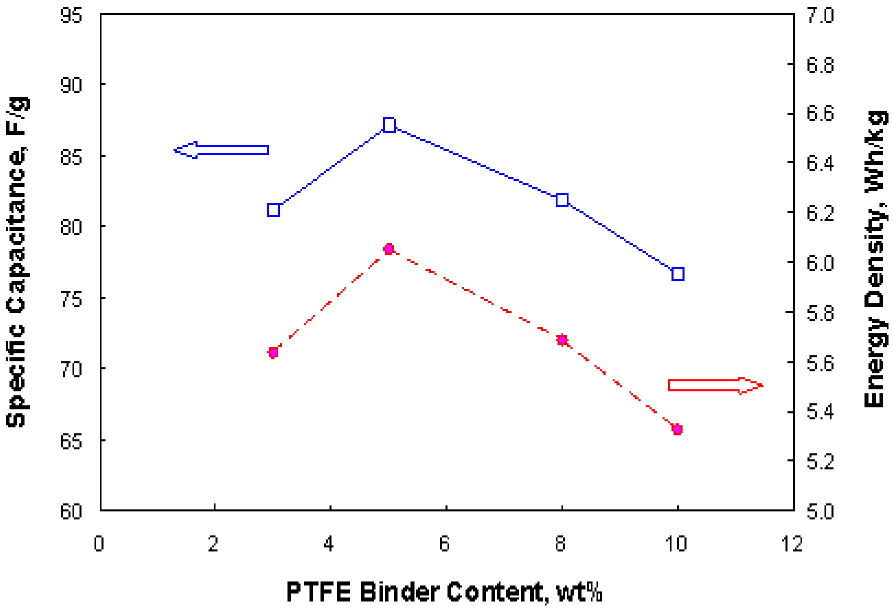
Material specific capacitances



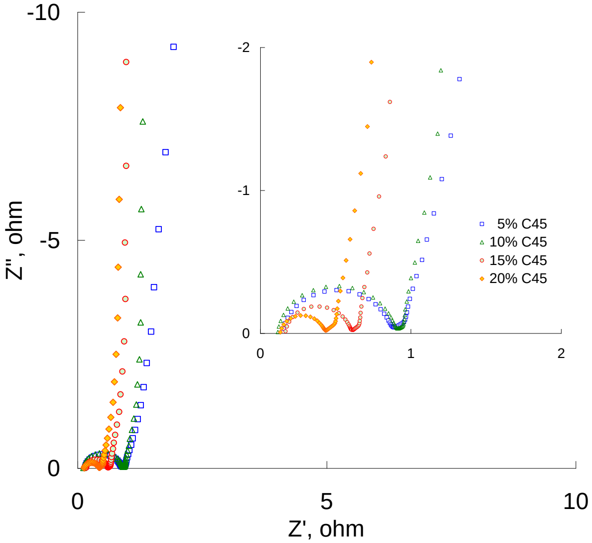
Cyclic voltammograms for MnO$_x$ electrode materials

- Obtained α-phase by solution method
- BET surface area reached to 223 m^2/g
- Well developed CV curve indicates the good charge behaviour at high scan rate
- 100 -300 F/g specific capacitance has been reached

Supercapacitor electrode layer optimization



PEFE content effect



AC impedance at different conducting carbon contents

Optimized electrode layer (0.5 M Na_2SO_4 aqueous solution):

- **15 wt% of Super C45**
- **5 wt% of PTFE**
- **100 μm of electrode layer thickness**

Key points for supercapacitors:

- Electrochemical supercapacitors have high power density, long cycle life, and are environmentally Friendly energy devices, proven to be the best complements to batteries and fuel cells;

- When coupled with battery or fuel cell, the lifetime of such a device can be significantly improved (~5 times)

- Supercapacitors are Ideal for powering vehicle accelerations, and can regenerate braking (fast recharge of the supercapacitor during braking, impossible for Li-ion batteries)

- Breakthrough in both electrode and electrolyte materials is necessary to increase supercapacitors' energy density in order to match with batteries and fuel cells

- If supercapacitor's energy density can be higher than 150 Wh/kg, it would be able to replace other batteries

Ballard Fuel Cell Scooter

Thank You for Your Attention!