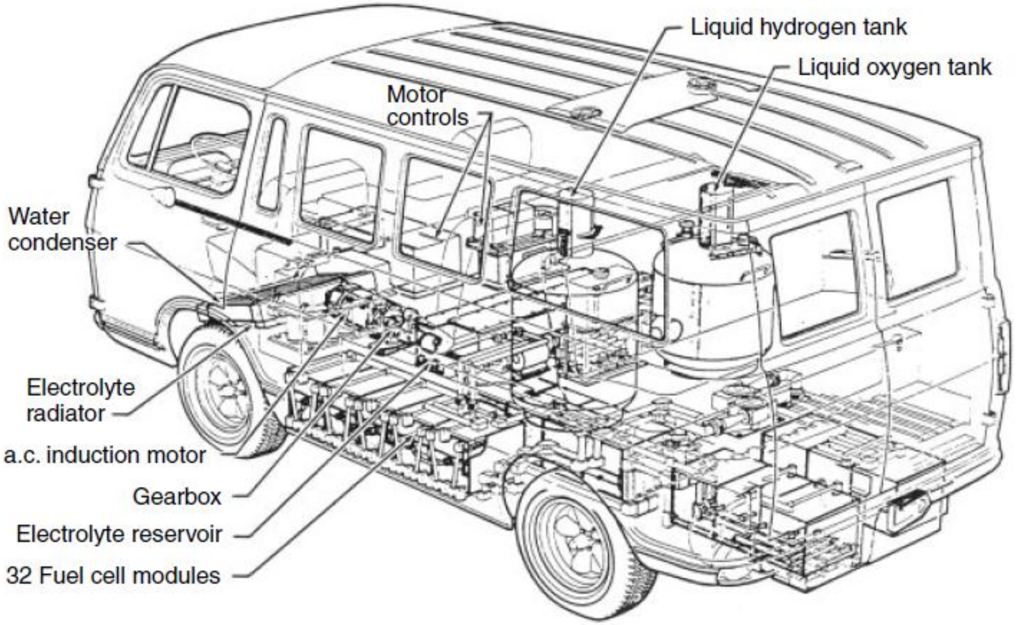
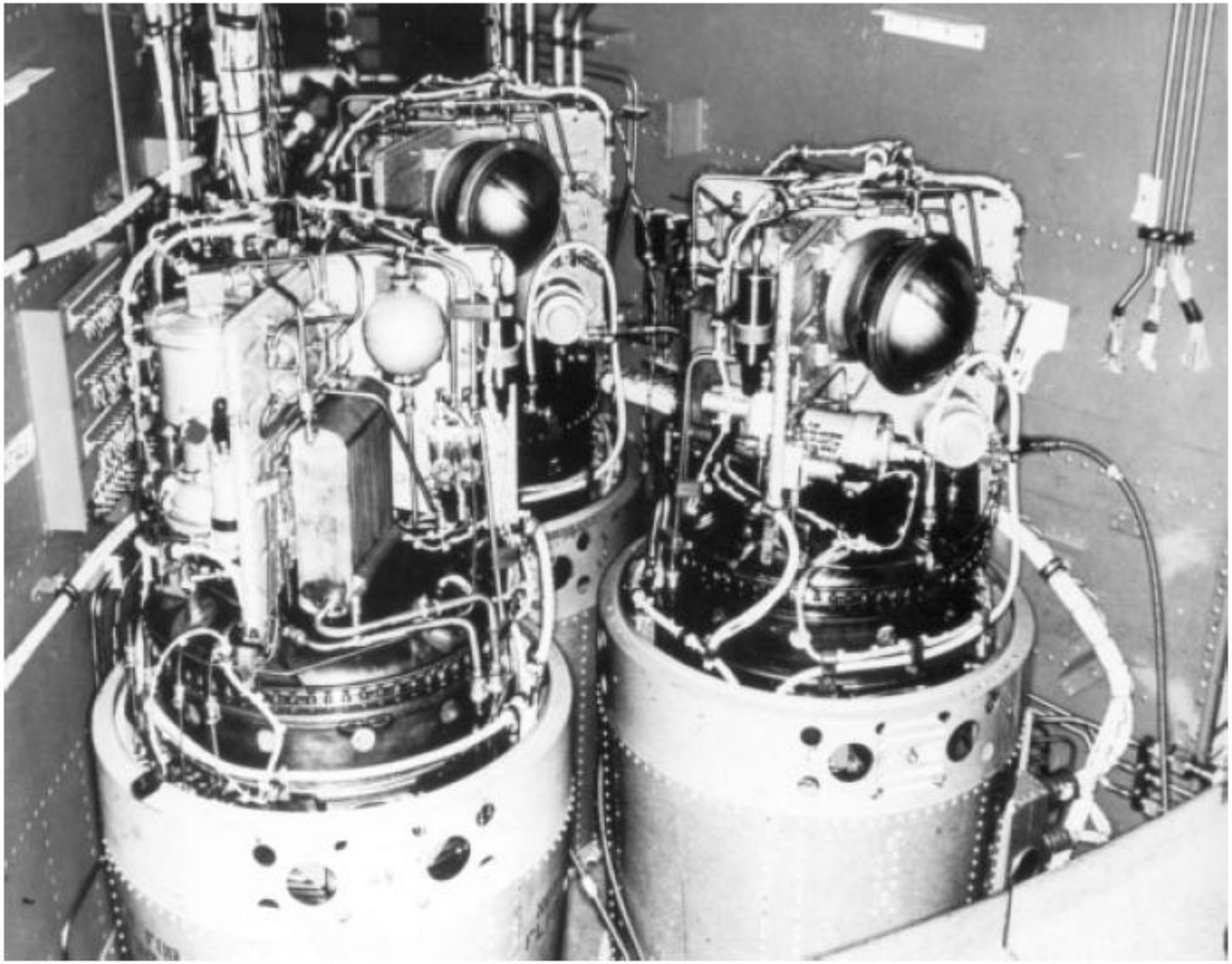
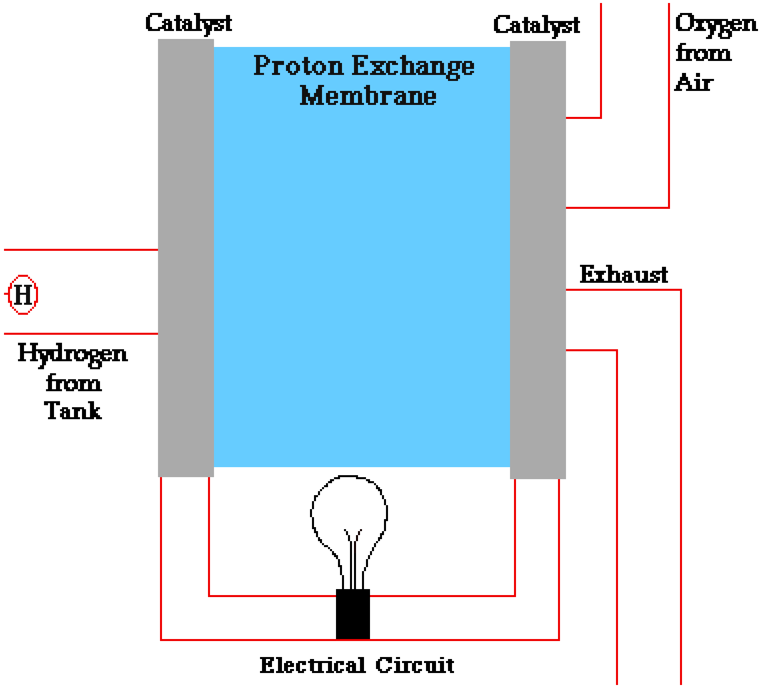
FUEL CELLS


Liquid hydrogen tank
Liquid oxygen tank
Motor controls
Water condenser
Electrolyte radiator
a.c. induction motor
Gearbox
Electrolyte reservoir
32 Fuel cell modules




Catalyst
Catalyst
Oxygen from Air
Proton Exchange Membrane
Exhaust
H
Hydrogen from Tank
Electrical Circuit

Fuel cell

A fuel cell is an electrochemical device that produces electricity without combustion by combining hydrogen and oxygen to produce water and heat.

Discovered German Scientist G H Shoenbein

First developed by William Grove

In 1839, Grove was experimenting on electrolysis (the process by which water is split into hydrogen and oxygen by an electric current), when he observed that combining the same elements could also produce an electric current

1930s -1950s Francis Thomas Bacon, a British scientist, worked on developing alkaline fuel cells.

He demonstrated a working stack in 1958.

The technology was licensed to Pratt and Whitney where it was utilized for the Apollo spacecraft fuel cells.

Advantages over conventional energy sources

They produce zero or very low emissions, especially Green House Gases (GHGs) depending on the fuel used.

Have few moving parts and thus require minimal maintenance, reducing life cycle costs of energy production.

Modular in design, offering flexibility in size and efficiencies in manufacturing

Can be utilized for combined heat and power purposes, further increasing the efficiency of energy production

Working Principle

A fuel cell is a device that uses hydrogen (or hydrogen-rich fuel) and oxygen to create electricity by an electrochemical process.

A single fuel cell consists of an electrolyte sandwiched between two thin electrodes (a porous anode and cathode)

Hydrogen, or a hydrogen-rich fuel, is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions (protons)

At the cathode, oxygen combines with electrons and, in some cases, with species such as protons or water, resulting in water or hydroxide ions, respectively

The electrons from the anode side of the cell cannot pass through the membrane to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell. This movement of electrons is an electrical current.

The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell

Still, a single fuel cell produces enough electricity for only the smallest applications. Therefore, individual fuel cells are typically combined in series into a fuel cell stack. A typical fuel cell stack may consist of hundreds of fuel cells.

Fuel cells are classified primarily by the kind of electrolyte they employy. This determines the kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors.

There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications.

Classification of Fuel Cells

Based on the type of Electrolyte

1. Alkaline Fuel cell (AFC)
2. Phosphoric Acid Fuel cell (PAFC)
3. Polymer Electrolytic Membrane Fuel Cell (PEMFC)
   Solid Polymer Fuel Cell (SPFC) and
   Proton Exchange Membrane Fuel cell (PEMFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Solid Oxide Fuel Cell (SOFC)

Based on Types of Fuel and oxidant

1. Hydrogen (pure)-Oxygen (pure) fuel cell
2. Hydrogen rich gas-air fuel cell
3. Ammonia –air fuel cell
4. Synthesis gas- air fuel cell
5. Hydro carbon (gas)- air fuel cell

Based on operating temperature

Alkaline Fuel Cells (AFC)

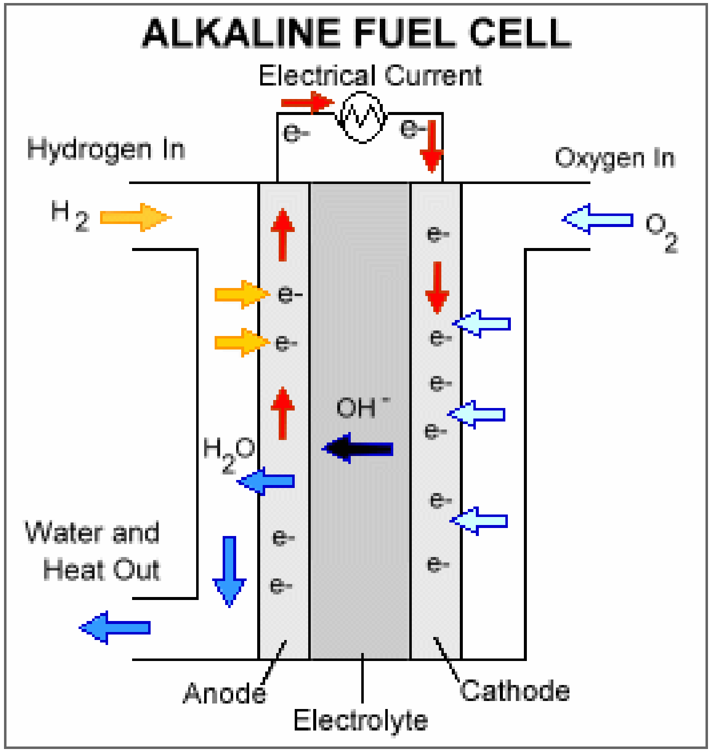
The alkaline fuel cell uses an alkaline electrolyte such as 40% aqueous **potassium hydroxide**. In alkaline fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.

It was originally used by NASA on space missions. NASA space shuttles use Alkaline Fuel Cells. Alkaline fuel cells (AFCs) were one of the first fuel cell technologies developed, and they were the first type widely used in the U.S. space program to produce electrical energy and water onboard spacecraft. These fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode. High-temperature AFCs operate at temperatures between 100ºC and 250ºC (212ºF and 482ºF). However, more-recent AFC designs operate at lower temperatures of roughly 23ºC to 70ºC (74ºF to 158ºF).

AFCs are high-performance fuel cells due to the rate at which chemical reactions take place in the cell. They are also very efficient, reaching efficiencies of **60 percent** in space applications.

The disadvantage of this fuel cell type is that it is easily **poisoned by carbon dioxide (CO2).** In fact, even the small amount of CO2 in the air can affect the cell's operation, making it necessary to purify both the hydrogen and oxygen used in the cell. CO2 can combine with KOH to form potasium carbonate which will increase the resistance.
This purification process is costly. Susceptibility to poisoning also affects the cell's lifetime (the amount of time before it must be replaced), further adding to cost.

Cost is less of a factor for remote locations such as space or under the sea. However, to effectively compete in most mainstream commercial markets, these fuel cells will have to become more cost effective. AFC stacks have been shown to maintain sufficiently stable operation for more than 8,000 operating hours..



Anode Reaction: $2H_2$ + 4OH- »» $4H_2O$ + $4e^-$
Cathode Reaction: O2 + $2H_2O$ + $4e^-$ »» 4OH-

Molten Carbonate Fuel Cells (MCFC):

The molten carbonate fuel cell uses a **molten carbonate salt as the electrolyte.** It has the potential to be fuelled with coal- derived fuel gases, methane or natural gas. These fuel cells can work at up to 60% efficiency

In molten carbonate fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.

Molten carbonate fuel cells (MCFCs) are currently being developed for natural gas and coal-based power plants for electrical utility, industrial, and military applications. MCFCs are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide (LiAlO2) matrix. Since they **operate at extremely high temperatures of 650ºC** and above, nonprecious metals can be used as catalysts at the anode and cathode, reducing costs.

Unlike alkaline, phosphoric acid, and polymer electrolyte membrane fuel cells, MCFCs don't require an external reformer to convert more energy-dense fuels to hydrogen. Due to the high temperatures at which they operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming, which also reduces cost.

Although they are more resistant to impurities than other fuel cell types, scientists are looking for ways to make MCFCs resistant enough to impurities from coal, such as sulfur and particulates.

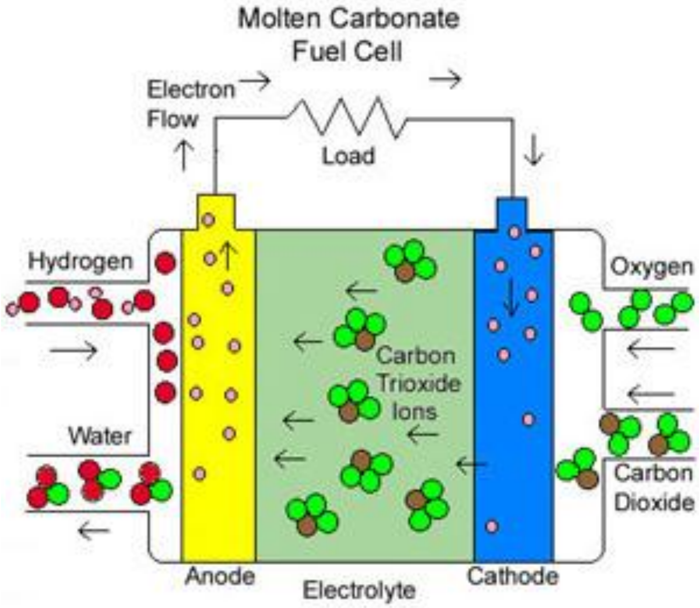
The primary disadvantage of current MCFC technology is durability. The high temperatures at which these cells operate and the corrosive electrolyte used accelerate component breakdown and corrosion, decreasing cell life.

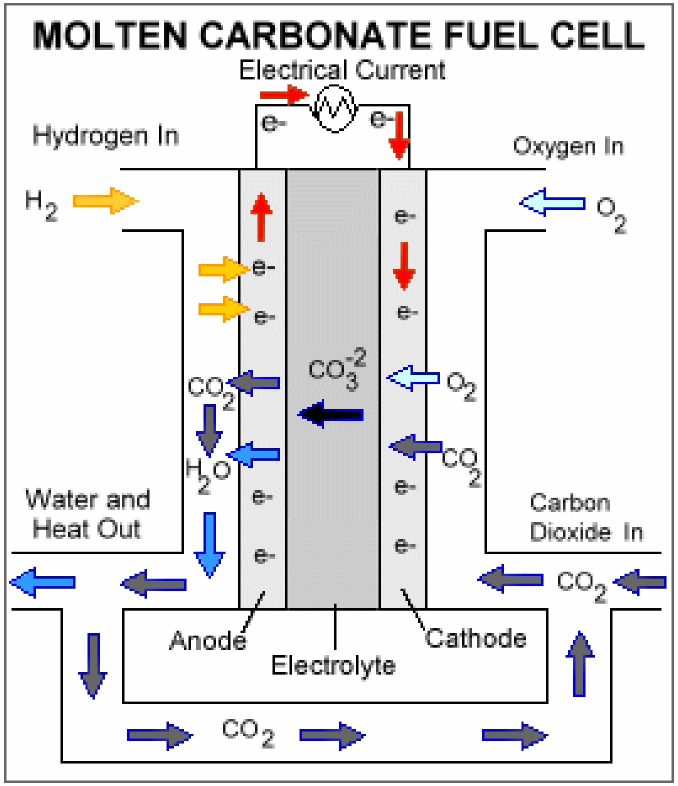
Scientists are currently exploring corrosion-resistant materials for components as well as fuel cell designs that increase cell life without decreasing performance.

Anode Reaction: $CO_3^{-2} + H_2 \rightarrow H_2O + CO_2 + 2e^-$

Cathode Reaction: $CO_2 + ½O_2 + 2e^- \rightarrow CO_3^{-2}$

Overall Cell Reaction: $H_2 + ½O_2 \rightarrow H_2O$



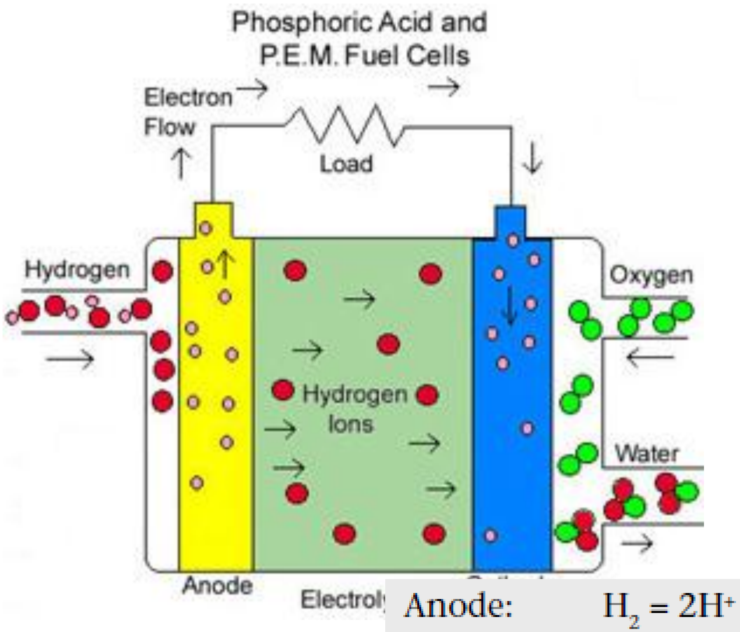


Phosphoric Acid Fuel Cells (PAFC):

A phosphoric acid fuel cell (PAFC) consists of an **anode and a cathode made of a finely dispersed platinum catalyst on carbon** and a silicon carbide structure that holds the phosphoric acid electrolyte.

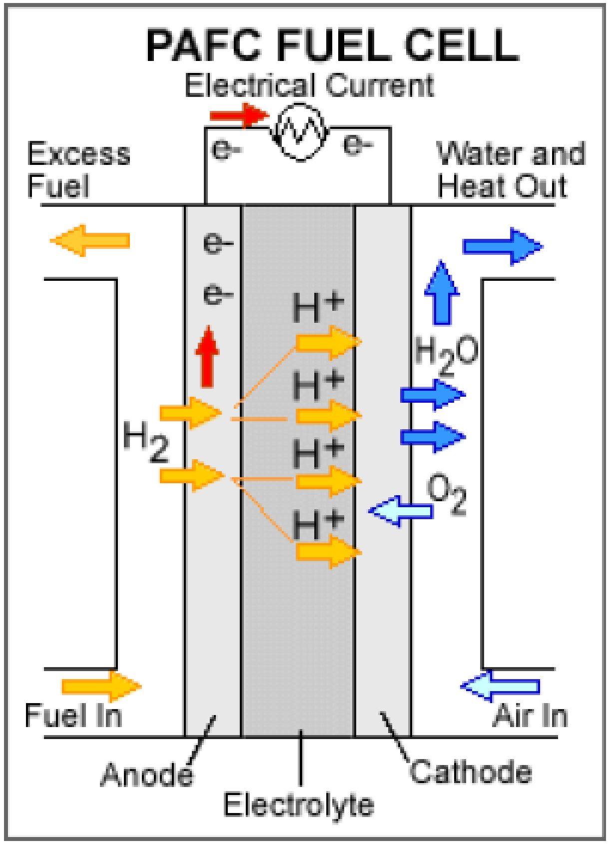
In phosphoric acid fuel cells, protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.

This is the most commercially developed type of fuel cell and is being used to power many commercial premises



Anode: $H_2 = 2H^+ + 2e^-$

Cathode: $^1/_2\, O_2 + 2H^+ + 2e^- = H_2O$



Phosphoric acid fuel cells use liquid phosphoric acid as an electrolyte—the acid is contained in a Teflon-bonded silicon carbide matrix—and porous carbon electrodes containing a platinum catalyst.

The phosphoric acid fuel cell (PAFC) is considered the "first generation" of modern fuel cells. It is one of the most mature cell types and the first to be used commercially, with over 200 units currently in use.

This type of fuel cell is typically used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses

PAFCs are more tolerant of impurities

They are 85 percent efficient when used for the co-generation of electricity and heat, but less efficient at generating electricity alone (37 to 42 percent).

PAFCs are also less powerful than other fuel cells, given the same weight and volume. As a result, these fuel cells are typically large and heavy. PAFCs are also expensive.

Like PEM fuel cells, PAFCs require an expensive platinum catalyst, which raises the cost of the fuel cell.

Polymer electrolyte membrane (PEM) fuel cells (PEMFC)

In polymer electrolyte membrane (PEM) fuel cells, protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.

Polymer electrolyte membrane (PEM) fuel cell uses a polymeric membrane as the electrolyte, with platinum electrodes.

These cells operate at **relatively low temperatures**

These cells are the best candidates for cars, for buildings and smaller applications. Polymer electrolyte membrane (PEM) fuel cells—also called proton exchange membrane fuel cells—deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst.
They **only hydrogen, oxygen from the air**, and water to operate and do not require corrosive fluids like some fuel cells. They are typically fueled with pure hydrogen supplied from storage tanks or onboard reformers

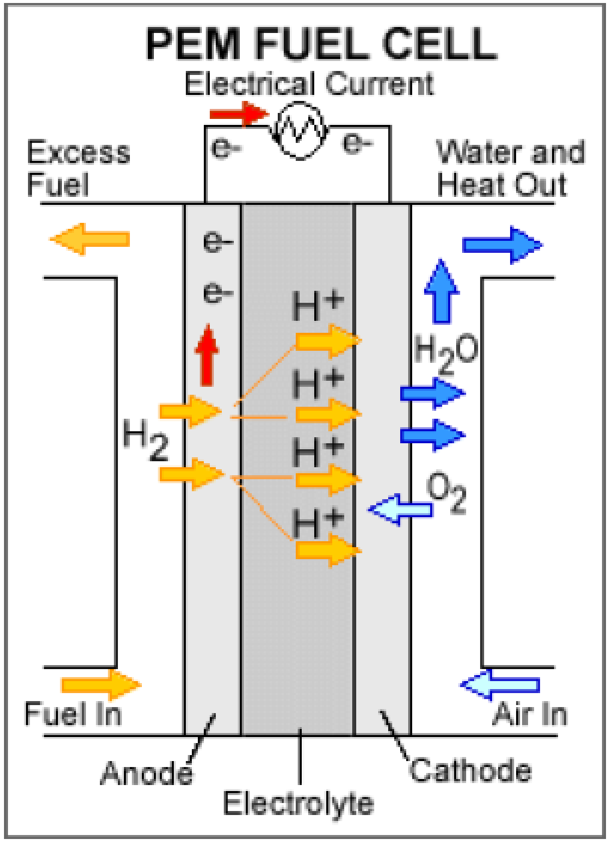
Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80°C (176°F).

Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability.

However, **it requires that a noblemetal catalyst (typically platinum)** be used to separate the hydrogen's electrons and protons, adding to system cost.

The **platinum catalyst is also extremely sensitive to CO poisoning**, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost.

Developers are currently exploring platinum/ruthenium catalysts that are more resistant to CO.



Anode: $H_2 = 2H^+ + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$

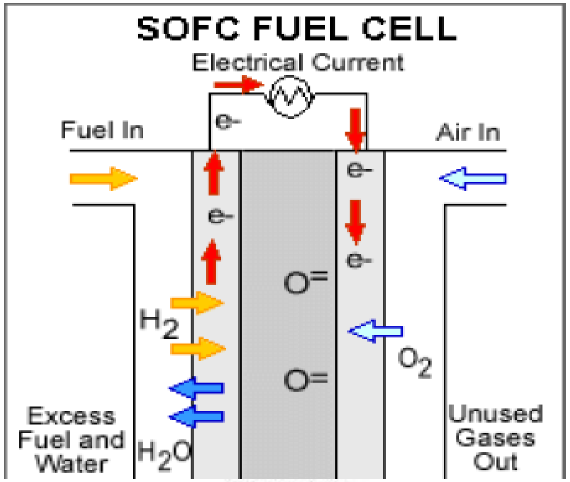
Solid Oxide Fuel Cells (SOFC)

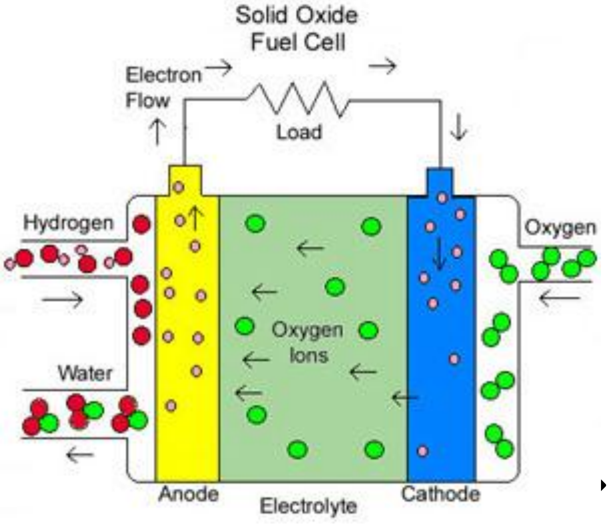
Work at higher temperatures

They use a solid ceramic electrolyte, such as **zirconium oxide stabilised with yttrium oxide,** instead of a liquid and operate at 800 to 1,000°C. In solid oxide fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.

Efficiencies of around 60 per cent and are expected to be used for generating electricity and heat in industry and potentially for providing auxiliary power in vehicles.

Since the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration typical of other fuel cell types.





$2H_2O + 4e^-$

Cathode Reaction: $O_2 + 4e^- \rightarrow 2O^{-2}$

Overall Cell Reaction: $2H_2 + O_2 \rightarrow 2H_2O$

High temperature operation removes the need for precious-metal catalyst, thereby reducing cost.

They are not poisoned by carbon monoxide (CO), which can even be used as fuel.

Sulphur resistant

This allows SOFCs to use gases made from coal.

Scientists are currently exploring the potential for developing lower-temperature SOFCs operating at or below 800ºC that have fewer durability problems and cost less.

Regenerative Fuel Cells (RFC):

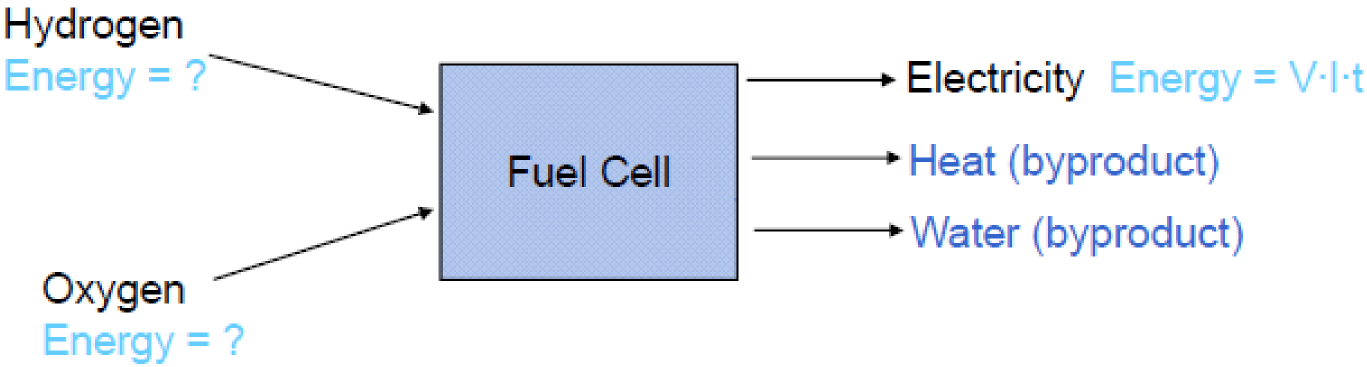
This class of fuel cells produces electricity from hydrogen and oxygen, but can be reversed and powered with electricity to produce hydrogen and oxygen; effectively storing energy or electricity

Table I. Classification of fuel cells

Fuel Cell Type	Electrolyte Used	Operating Tempearture	Electrode Reactions	
Polymer Electrolyte	Polymer Membrane	60-140°C	Anode:	$H_2 = 2H^+ + 2e^-$
			Cathode:	$^{1}/_{2}\, O_2 + 2H^+ + 2e^- = H_2O$
Direct Methanol	Polymer Membrane	30-80°C	Anode:	$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$
			Cathode:	$^{3}/_{2}\, O_2 + 6H^+ + 6e^- = 3H_2O$
Alkaline	Potassium Hydroxide	150-200°C	Anode:	$H_2 + 2\ OH^- = H_2O + 2e^-$
			Cathode:	$^{1}/_{2}\, O_2 + H_2O + 2e^- = 2\ OH^-$
Phosphoric Acid	Phosphoric Acid	180-200°C	Anode:	$H_2 = 2H^+ + 2e^-$
			Cathode:	$^{1}/_{2}\, O_2 + 2H^+ + 2e^- = H_2O$
Molten Carbonate	Lithium/Potassium Carbonate	650°C	Anode:	$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$
			Cathode:	$^{1}/_{2}\, O_2 + CO_2 + 2e^- = CO_3^{2-}$
Solid Oxide	Yittria Stablized Zirconia	1000°C	Anode:	$H_2 + O^{2-} = H_2O + 2e^-$
			Cathode:	$^{1}/_{2}\, O_2 + 2e^- = O^{2-}$

Basic energy conversion of a fuel cell can be described as:

Chemical energy of fuel = Electrical energy + Heat energy



Hydrogen
Energy = ?

Oxygen
Energy = ?

Fuel Cell

Electricity Energy = V·I·t

Heat (byproduct)

Water (byproduct)

The input energy is that produced during reactions at the electrodes.

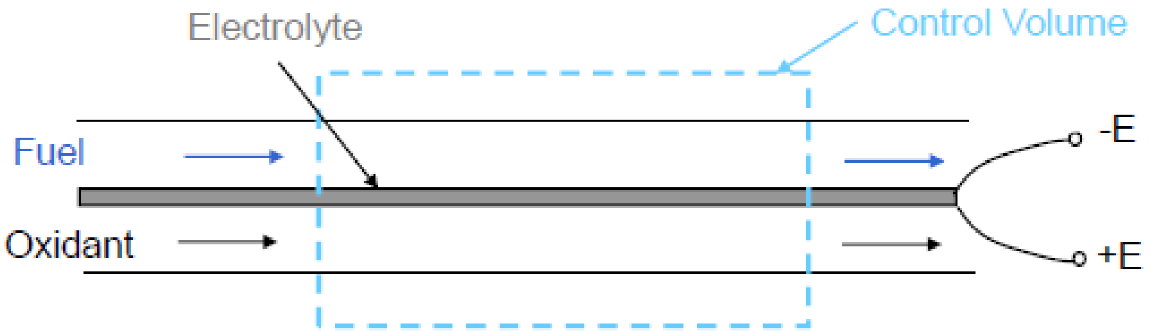
Performance

One measure of the energy conversion efficiency of a fuel cell is the ratio of the actual voltage at a given current density to the maximum voltage obtained under no load (open circuit) conditions.

η = On load voltage / theoretical open circuit voltage

Thermodynamic Analysis: 1st Law

It is usually formulated by stating that the change in the internal energy (ΔH) of a closed system is equal to the amount of heat supplied (Q) to the system, minus the amount of work (W) performed by the system on its surroundings.



=> $\Delta H = Q - W$

Defining the work term

Electrical work is, in general, described by the relation: $W = EI\Delta t$ where E is the cell voltage and I is the current

In a fuel cell reaction, electrons are transferred from the anode to the cathode, generating a current.

The amount of electricity ($I\Delta t$) transferred when the reaction occurs is given by NF, where

N = number of electrons transferred

F = Faraday's constant = 96,493 coloumbs

So the electrical work can be calculated as: $W = NFE$ (Work done on the surrounding)

The First Law then becomes: $\Delta H = Q - NFE$

Thermodynamic Analysis: 2nd Law

Consider the fuel cell to be ideal for now, meaning that it is reversible and thus behaves as a perfect electrochemical apparatus :

“ If no changes take place in the cell except during the passage of current, and all changes which accompany the current can be reversed by reversing the current, the cell may be called a perfect elctrochemical apparatus.”

Heat transferred during a reversible process was expressed as:

$$Q = T\,\Delta S \qquad (1)$$

T = absolute temperature, Δ*S* = change in entropy

Combining the First and Second Law analysis, we get

$$\Delta H = T\Delta S - NFE \qquad (2)$$

$$NFE = -(\Delta H - T\Delta S) \qquad (3)$$

Gibbs Free Energy is given by $G = H - TS$

Or $\Delta G = \Delta H - (T\,\Delta S - S\,\Delta T)$

$$\Delta G = \Delta H - T\,\Delta S \qquad (4)$$

As there is no change in temperature $\Delta T = 0$

Eqn (2) becomes $NFE = -\Delta G$)

Max efficiency = NFE/ΔH

Physical Interpretation of $dG = dH - TdS$

dH represents the total energy of the system.

TdS represents the “unavailable” energy (that which cannot be converted to useful work).

Therefore G represents the “free” energy or the energy available to do useful work.

Fuel Cell Efficiency

Since fuel cells use materials that are typically burnt to release their energy, the fuel cell efficiency is described as the ratio of the electrical energy produced to the heat that is produced by burning the fuel.

From the basic definition of efficiency: η = W / Qin

Hydrogen fuel cell:
Oxidation half reaction $2H_2 \longrightarrow 4H^+ + 4e^-$
Reduction half reaction $O_2 + 4H^+ + \longrightarrow 4e^- \; 2H_2O$

Energy formation (KJ/mole)
-ΔHo = 286 -ΔGo = 237

The maximum efficiency of the fuel cell would be 83%.

Classification of Losses in an Actual Fuel Cell

Activation Losses: These losses are caused by the slowness of the reaction taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons.

Ohmic Losses: The voltage drop due to the resistance to the flow of electrons
through the material of the electrodes. This loss varies linearly with current density.

Concentration Losses: Losses that result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used.

Fuel Crossover Losses: Losses that result from the waste of fuel passing through the electrolyte and electron conduction through the electrolyte. This loss is typically small, but can be more important in low temperature cells.

Applications of 0D, 1D, 2D and 3D NSMs

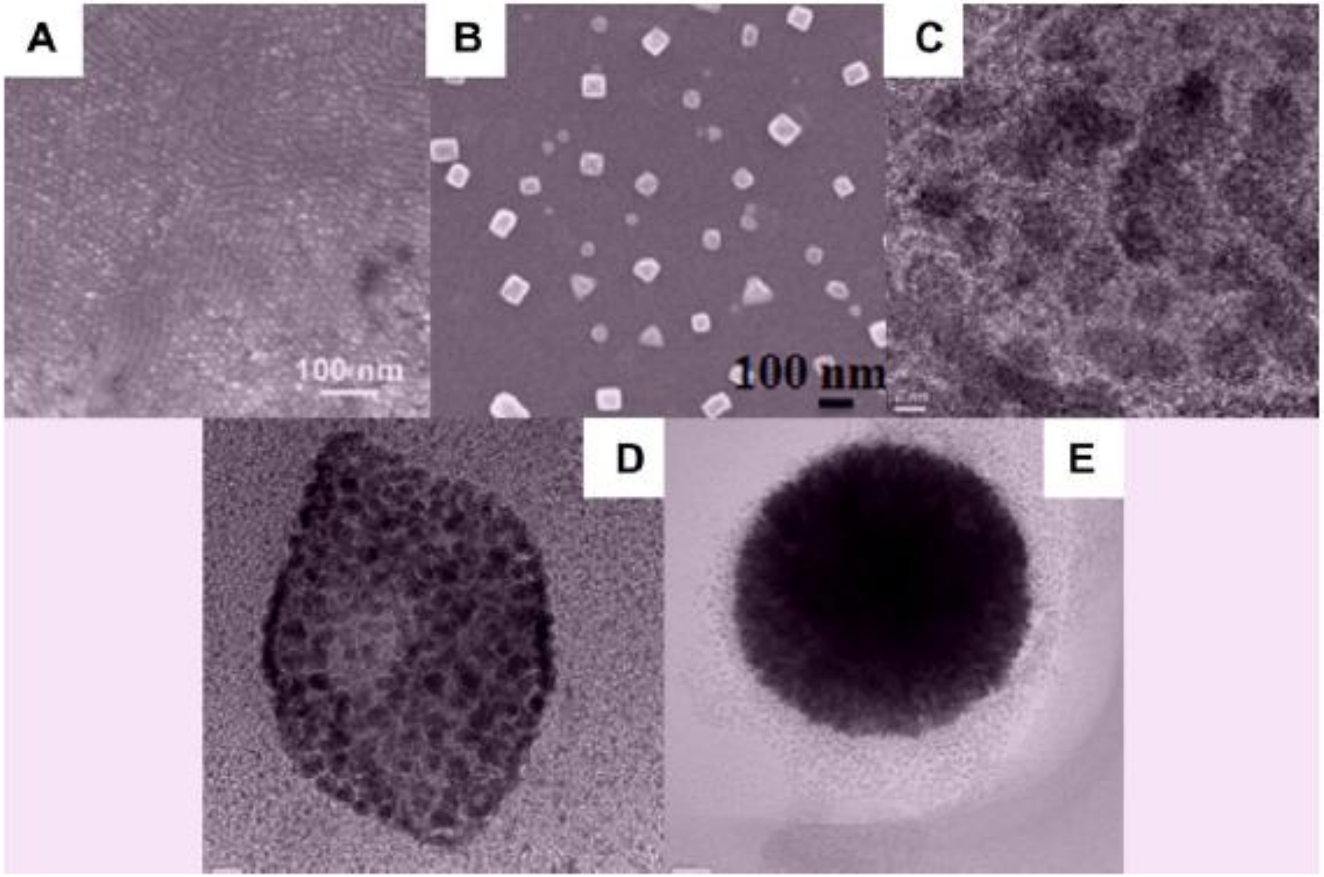
The main active components are fuel electrode (anode), oxidant electrode (cathode). The proton conducting solid membrane used as electrolyte, is sandwiched between the anode and cathode electrodes

Although the technology of such fuel cells was developed to an extent, some problems remain unclear and only their solution can result in wide-scale commercialization of fuel cells, especially as the efficient current sources for portable devices. The most important problem is the <u>development of efficient catalysts</u>, which would provide the long-term operation of fuel cells without sacrificing their characteristics.

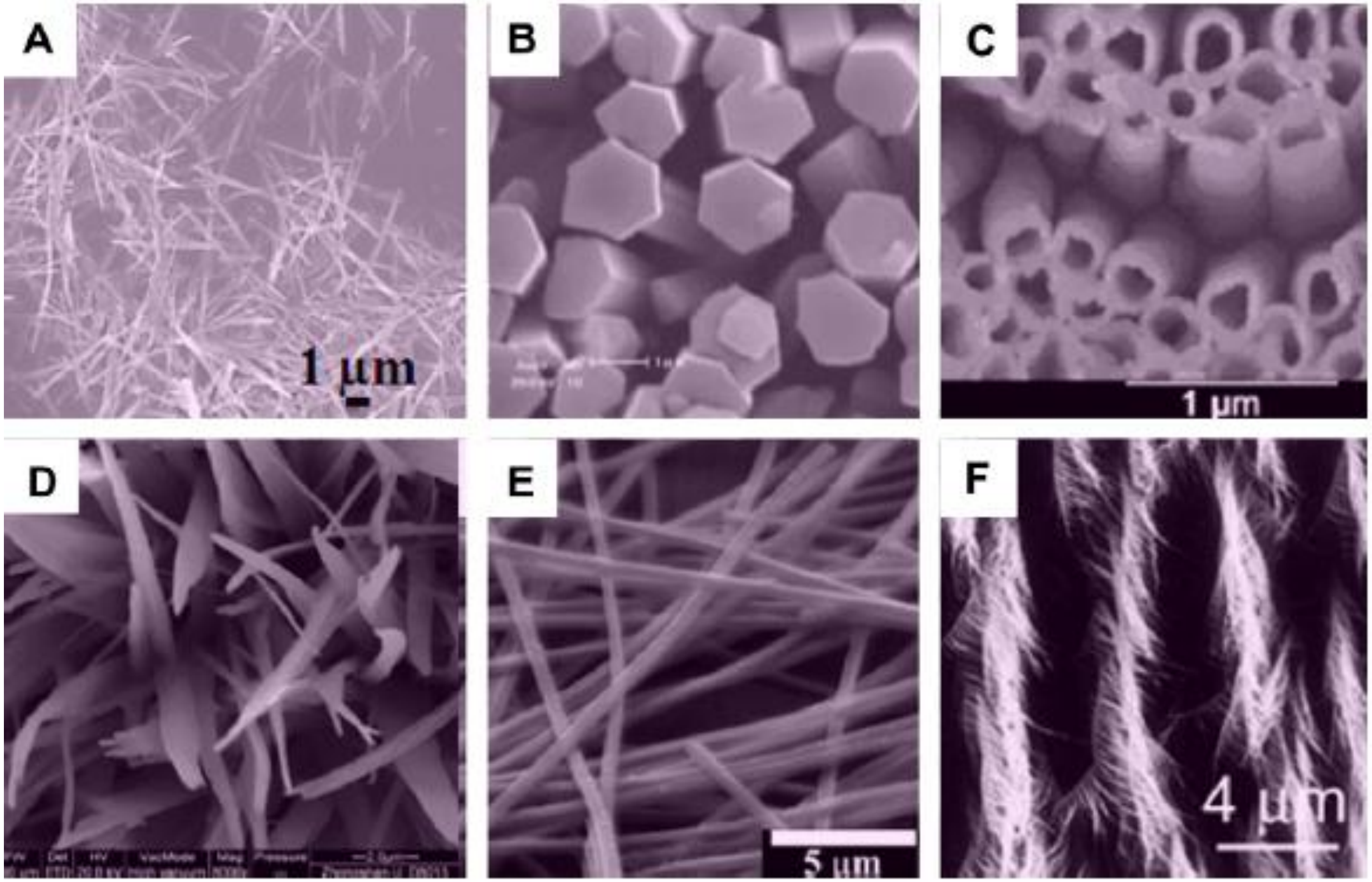
The CO poisoning intrinsic to Pt based cathodes pose a further barrier to fuel cell devices. Hence it is important to open up new methods for making low cost and effective electrocatalysts.

It is well known that the catalytic activity attainable depends significantly on the size of the Pt catalysts and their support. However, there are two routes to overcome this problem. First, the direct synthesis of novel 0D, 1D, 2D, and 3D NSMs (Pt or Pt alloy catalysts) with high surface area for fuel cell devices. Secondly, the synthesis of novel NSMs with high surface area as a support of Pt or Pt alloys catalysts for fuel cell devices.

(SEM) and (TEM) image of different types of 0D NSMs, which is synthesized by several research groups. (A) Quantum dots [20], (B) nanoparticles arrays, (C) core–shell nanoparticles, (D) hollow cubes, and (E) nanospheres.

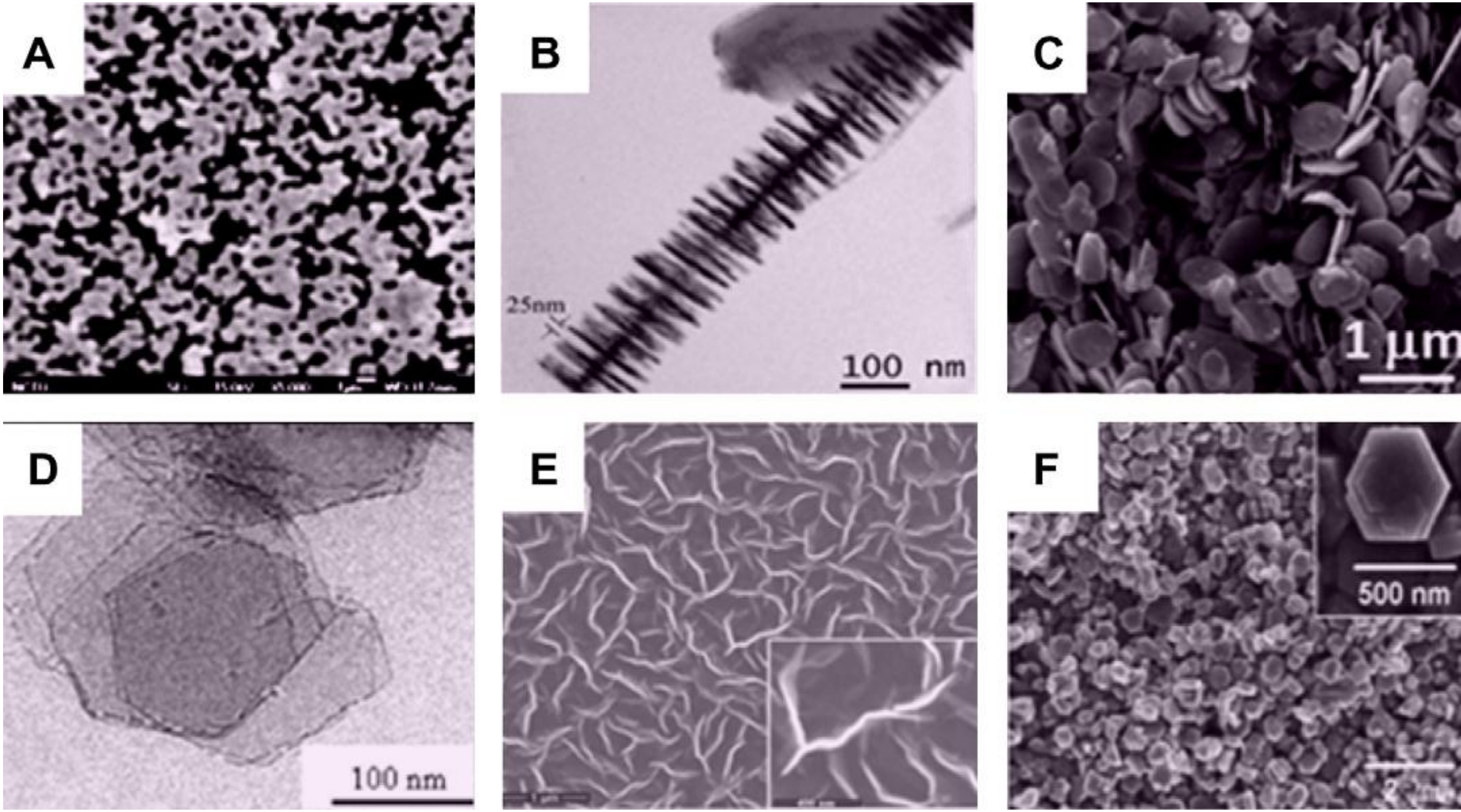


SEM image of different types of 1D NSMs, which is synthesized by several research groups. (A) Nanowires, (B) nanorods , (C) nanotubes , (D) nanobelts , (E) nanoribbons, and (F) hierarchical nanostructures



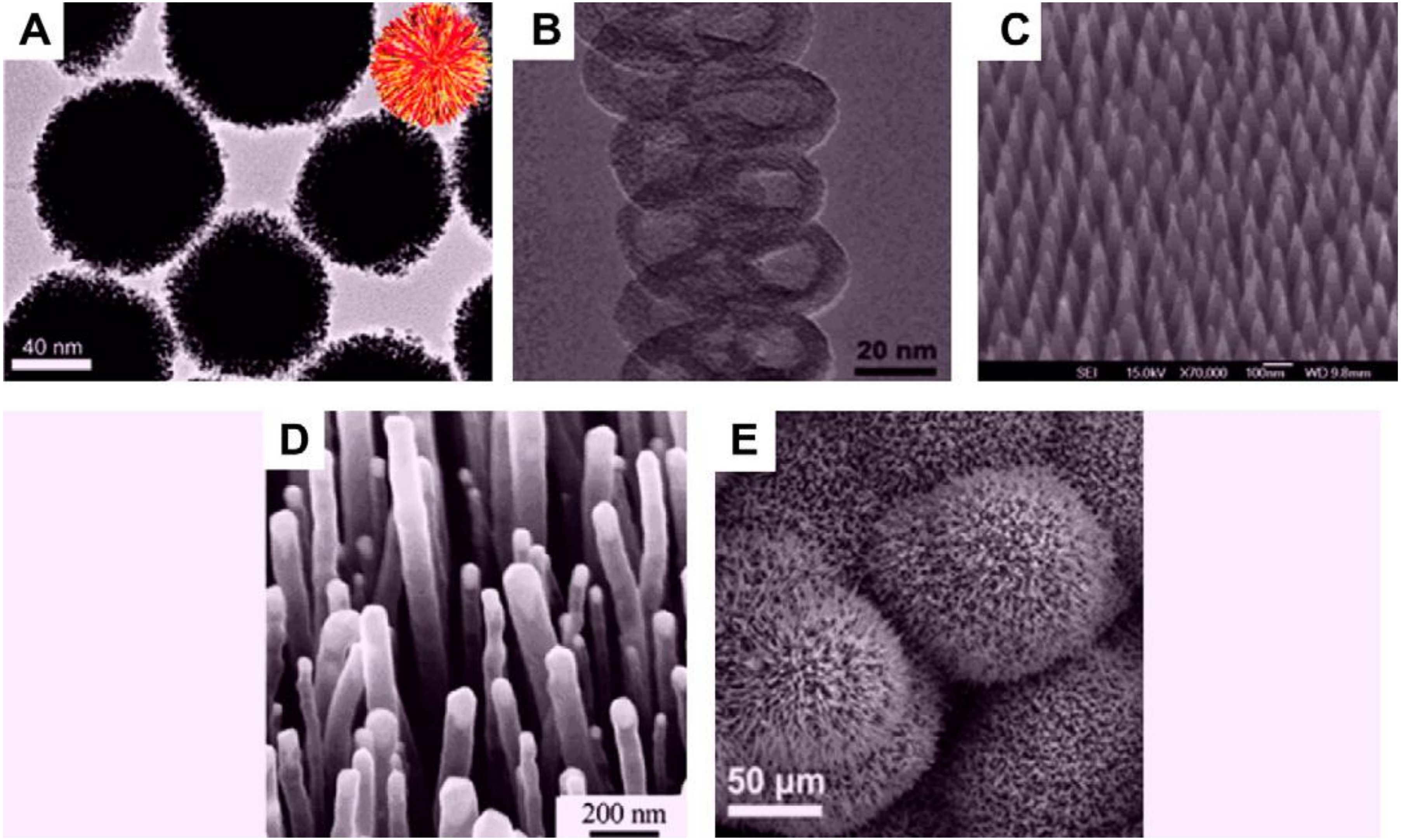
SEM and TEM image of different kinds of 2D NSMs, which is synthesized by our and several research groups.

(A) Junctions (continuous islands), (B) branched structures , (C) nanoplates , (D) nanosheets, (E) nanowalls , and (F) nanodisks



Typical SEM and TEM image of different kinds of 3D NSMs, which is synthesized by several research groups.

(A) Nanoballs (dendritic structures), (B) nanocoils , (C) nanocones, (D) nanopillers , and (E) nanoflowers



During the past decade, the clusters stabilizing Pt nanoparticles have attracted a considerable interest as catalysts for low temperature fuel cell devices, such as polymer electrolyte fuel cells (PEMFCs)and direct methanol fuel cells (DMFCs). The clusters stabilizing Pt nanoparticles are formed in order to maximize the active number of surface versus the inactive number of Pt bulk atoms. However, one of the major problems associated with the clusters stabilizing Pt catalysts are their stability in the acid environment of DMFCs and PEMFCs. This is because of after only 100 h of testing the reaction rate dropped to half in such fuel cell devices. During this process the CO-ads species were continuously formed, which strongly absorbs to the clusters stabilizing Pt active sites to poison the fuel cell performance devices.

Due to these problems of the clusters stabilizing Pt nanoparticles, researchers decided to investigate the bimetallic clusters and colloids with nanometer-scale dimensions for fuel cell device applications.
There are two main reasons for using the **bimetallic clusters and colloids with nanometer-scale dimensions**, firstly, because they may serve as models for studying the formation of different alloy catalysts.
Secondly, it is possible to save precious metal, such as Pt, by optimizing the synthetic conditions so that only very thin surface layers occur . In **most cases, Pt and Pt-based alloy nanoparticles are used in the form of small nanoparticles**, since small size offers high surface area which is especially crucial for catalysis and fuel cell applications

A very recent report by Tiwari et al. showing perfect Pt nanocubes had much higher electrocatalytic activity and stability for methanol and ethanol oxidation than other nanostructures such as truncated **Pt nanocubes, truncated Pt** (cubes + tetrahedra) and spherical Pt nanoparticles.

Wang et al. reported the controlled synthesis of dendritic Au@Pt core–shell nanomaterials.

Chen et al. synthesized the Co–Pt catalyst with a hollow sphere structure via a very simple thermolytic reaction. The Co–Pt hollow sphere catalyst showed the high surface area with a comparison to the pure Pt nanoparticle catalyst and Co–Pt nanoparticles . In addition, the Co–Pt hollow sphere catalyst showed enhanced electrocatalytic activity for methanol oxidation with a comparison to the pure Pt nanoparticle catalyst and Co–Pt nanoparticles at the same Pt loading.

1D NSMs

In the last few years, attention has been shifted towards the synthesis of 1D NSMs because of their fundamental importance and potential applications in fuel cells. To date, 1D NSMs (such as nanowires, nanorods, nanobelts, and nanotubes) have been most extensively studied because of their simplicity in preparation and its improved catalytic properties as compared to bulk metallic materials

Ksar et al. fabricated the Pd nanowires in a hexagonal mesophase (as soft templates) by electron beam irradiation. They also reported that the average lengths of the Pd nanowires are controlled by the amount of co-surfactant that assists the reduction/growth processes. In addition, the electrochemical studies indicated that the Pd nanowires had a very good electrocatalytic activity and stability for ethanol oxidation.

Liu et al. prepared the nanoporous Pt–Co alloy nanowires by dealloying electrodeposited by dealloying Pt-Co nanowires and examined their electrochemical properties Pt–Co nanowires (15 h) had a superior tolerance against CO poisoning.

In addition, nanoporous Pt–Co alloy nanowires exhibit an enhanced electrocatalytic activity toward methanol oxidation (in comparison to state-of-the art Pt/C and PtCo/C catalysts).

2D NSMs

2D NSMs such as junctions (continuous islands), branched structures, nanoprisms, nanoplates/ nanosheets, nanowalls, and nanodisks are an especially promising form of nanoscale with a rare combination of extremely high specific surface area, exceptional thermal/electrical conductivity and stability

The utilization of 2D NSMs as a support to anchor catalyst nanoparticles and facilitate electron transport opens up interesting new possibilities for designing and building of next generation catalysts for fuel cells. In addition, 2D NSMs can avoid aggregation and maintain high specific surface areas; these factors are important in increasing the accessibility of adsorbates to reactive sites

Li et al. fabricated the **close-packed Au nanoprism thin films on the indium tin oxide coated glass substrates**. Au nanoprism are single crystalline, whose basal surfaces are atomically flat {111} planes and lateral surfaces are {110} planes. A small amount of Pt or Pd was deposited onto the Au nanoprism thin film electrodes and studies their catalytic properties. They noticed that the Pt on Au nanoprism exhibited greatly **enhanced catalytic activity toward the oxidation of methanol** and much better **CO poison resistance than commercial Pt-based catalysts**

Wong's group have synthesized **Pd nanoplates array onto Au substrate** by electrochemical process.

the Pd nanoplate's array electrode shows extraordinary electro-catalytic activity towards the **oxidation of methanol**

Choi and Woo prepared **a 2D Pt–Ru nanowire** network using a SBA-15 nanoreactor and showed that this nanostructured material displayed a **higher performance than commercial Pt–Ru (JM) in DMFC.**

2D continuous Pt island network on a flat Si substrate by Tiwary group

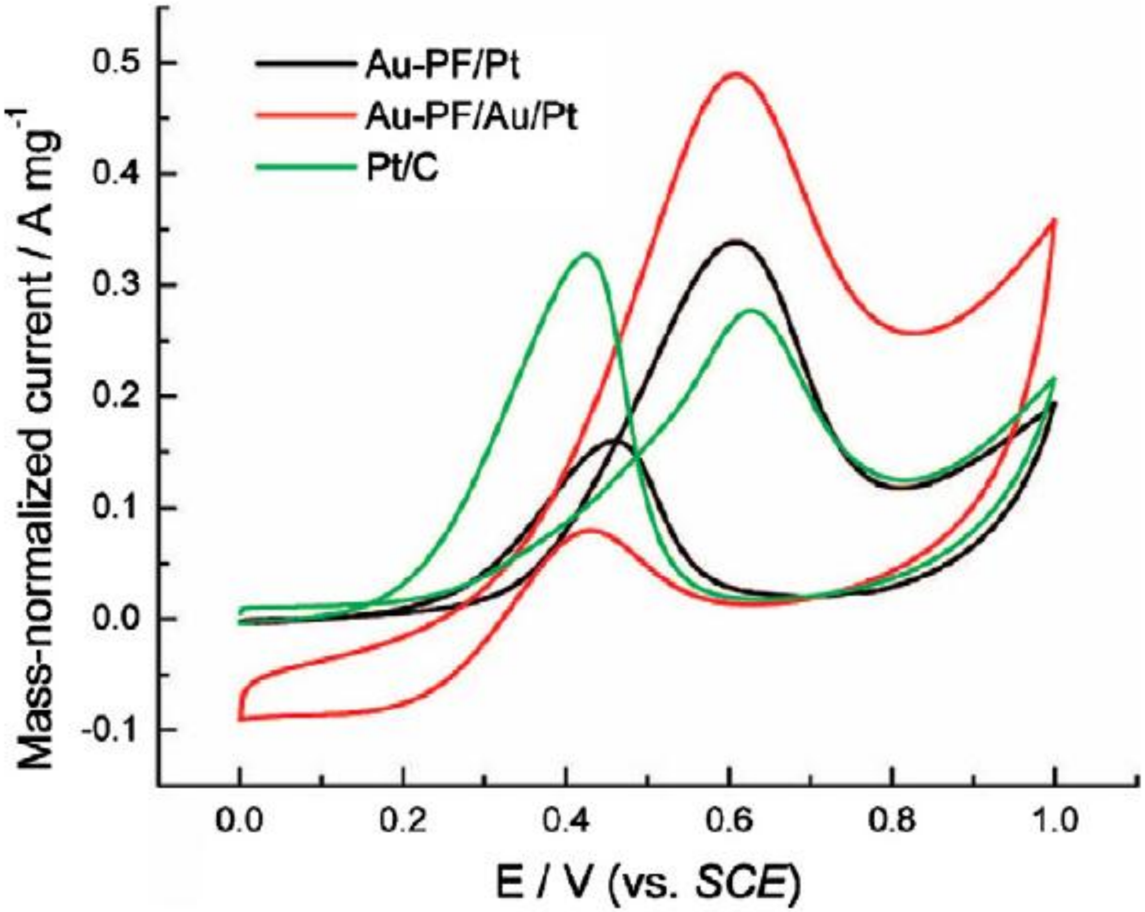
This catalyst structure on the Si substrate has better electroactivity toward methanol oxidation than the blanket Pt/Si and the Ru decorated Pt film/Si electrodes. Recently many material scientists and engineers have fabricated 2D graphene nanosheets as catalyst supports for DMFCs

The electrochemical results of methanol oxidation indicate that Pt–Ru/graphene nanosheets display excellent catalytic activity over that of Pt–Ru/Vulcan. These results indicate that graphene nanosheets could significantly increase the electrochemical active surface area resulting in better catalyst utilization.

3D NSMs

Compared to 0D, 1D, and 2D NSMs, the 3D NSMs hold a unique morphology, which are expected to provide a larger surface area and to facilitate the transport of reactants and products effectively, so that electrochemical performance can be greatly improved.

Several research groups have fabricated 3D Pt nanoflowers as a catalyst for fuel cell applications. Tong et al. prepared 3D Pt nanosheets perpendicular to a boron-doped diamond (BDD) hybrid film surface, synthesized by double template method



CVs of commercial Pt/C catalyst, Au–PF/Pt and the Au–PF/Au/Pt electrodes in a 0.1 mol dm3 HClO4 + 0.4 mol dm3 CH3OH solution at a scan rate of 50 mV s1.

Zhang et al.   prepared 3D Pt nanoflowers via a template-free, direct electrodeposition method.
This electrochemical experiment demonstrates that Pt nanoflowers have superior performance in aspects of electrocatalytic activity and stability towards the oxidation of methanol.

Energy Storage

Energy is useful only if available when and where it is wanted.

Carrying energy to *where* it is wanted is called *distribution* or *transmission*;

Keeping it available until *when* it is wanted is called *storage*

Since the use of renewable energy supplies constitutes a diversion of a continuing natural *flow* of energy, there are problems in matching supply and demand in the time domain, i.e. in matching the *rate* at which energy is used.

This varies with time on scales of months (e.g. house heating in temperate climates), days (e.g. artificial lighting) and even seconds (e.g. starting motors)

In contrast to fossil fuels and nuclear power, the primary input power of renewable energy sources is outside our control

we have the choice of either *matching the load* to the availability of renewable energy supply or *storing the energy* for future use.

Energy can be stored in many forms, i.e. chemical, heat, electric, potential or kinetic energy.

Electrical storage: batteries and accumulators

A device that has electricity both as input and output is called an (electrical) accumulator or (electrical) storage battery. Batteries are an essential component of most autonomous power systems (especially with photovoltaic and small wind turbine generation), of standby and emergency power systems, and of electric vehicles.

The lead acid battery

Although many electrochemical reactions are reversible in theory, few are suitable for a practical storage battery, which will be required to cycle hundreds of times between charging and discharging currents of 1–100A or more. The most widely used storage battery is the lead acid battery

As in all electrochemical cells, there are two electrode ‘plates’ immersed in a conducting solution (electrolyte).

In this case the electrodes are in the form of grids holding pastes of lead (Pb) and lead dioxide respectively; the pastes are made from powders to increase surface area in ‘spongy’ form.

Electrodes shaped as tubes give added mechanical strength and resist ‘shedding’ , and so are suitable for deep discharge

The electrolyte is sulphuric acid, which ionises as follows:

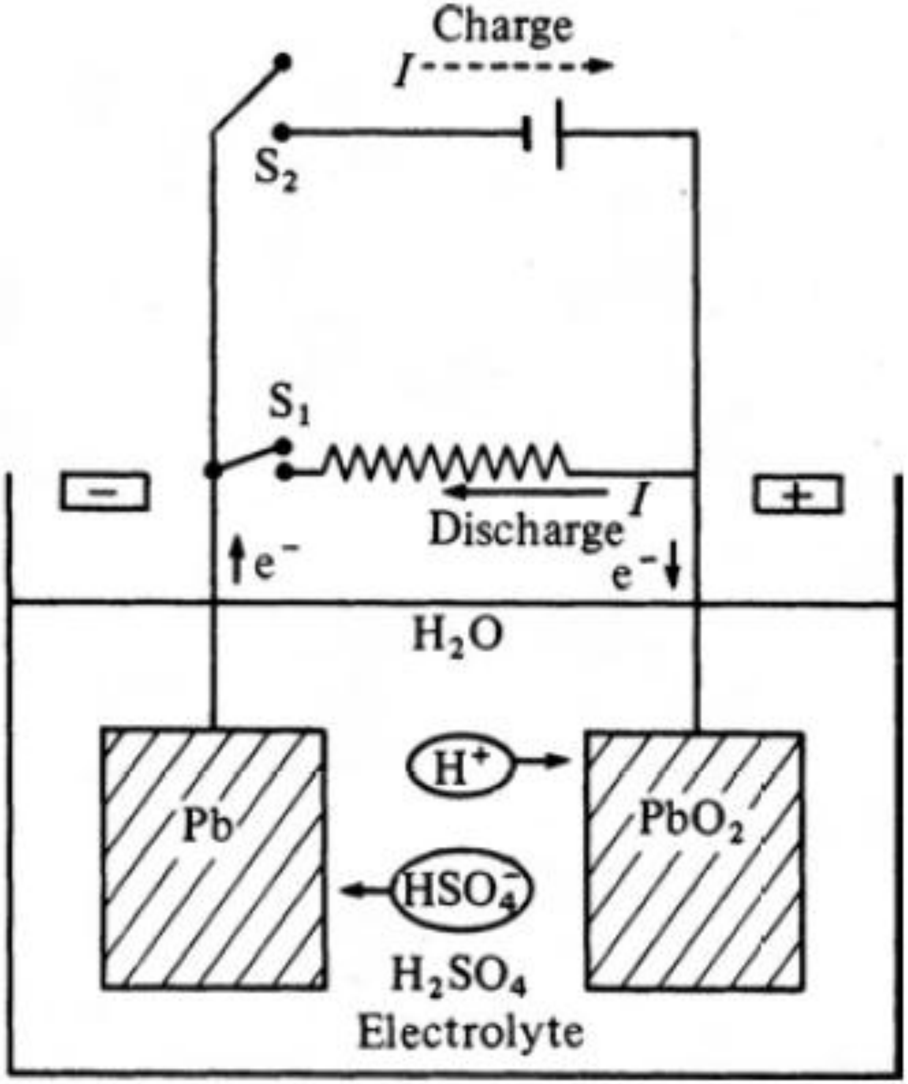
$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

During *discharge*, the reaction at the negative electrode is

$$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$$

The electrons so liberated travel through the external circuit to the positive electrode, where they contribute to the reaction:

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$


Charge
I
S₂
S₁
−
+
I
Discharge
e⁻
e⁻
H₂O
H⁺
Pb
PbO₂
HSO₄⁻
H₂SO₄
Electrolyte

The electrical current through the solution is carried by H^+ and HSO^{-4} ions from the sulphuric acid electrolyte, which themselves take part in the plate reactions.

Transportable ‘gelled cells’ have this electrolyte immobilised in pyrogenic silica, with the fibrous glass mat separator giving open gas paths for the release of hydrogen and oxygen in overcharge.

Although this makes them relatively expensive, they are safer to use and transport, since there is no danger of spilling highly corrosive sulphuric acid, and are ‘maintenance free’.

The theoretical cell-EMF at standard conditions for

Pb/PbSO4/H2SO4/PbSO4/PbO2 is cell = +1.92V

The actual cell EMF depends on the concentration of reagents, and can be calculated by standard electrochemical methods. In general, the open-circuit voltage of a cell differs by only a few per cent from the theoretical cell voltage

In particular, lead acid batteries are produced at open-circuit potential difference of 2.0V per cell.

In the specific case of the lead acid battery, the main reasons for the ‘underachievement’ are:

A working battery necessarily contains non-active materials, e.g. the case, the separators (which prevent the electrodes short-circuiting) and the water in which the acid is dissolved. Moreover, the acid concentration must not be too large, since the battery would then discharge itself. Since the mass of actual battery contents exceeds the mass of the active ingredients, the energy density based on the mass of the whole battery is less than the theoretical value based on the active mass alone.

However, this factor is not of great importance for stationary batteries.

The reactions cannot be allowed to go to completion. If all the lead were consumed by reaction there would be no electrode left for the reverse reaction to operate, i.e. the battery could not be cycled.

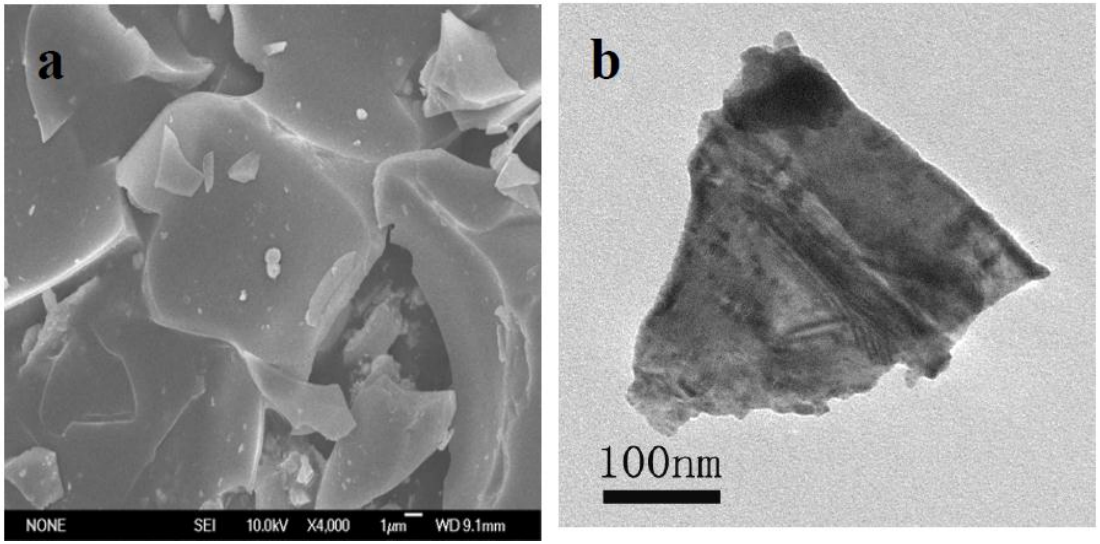
Similarly, if the concentration of H2SO4 is allowed to reduce too much, the electrolyte ceases to be an adequate conductor.

In practice, many battery types should not be allowed to discharge more than about 50% of total potential stored energy, or they may be ruined. However, specially designed batteries do allow ‘deep discharge’ beyond 50%.

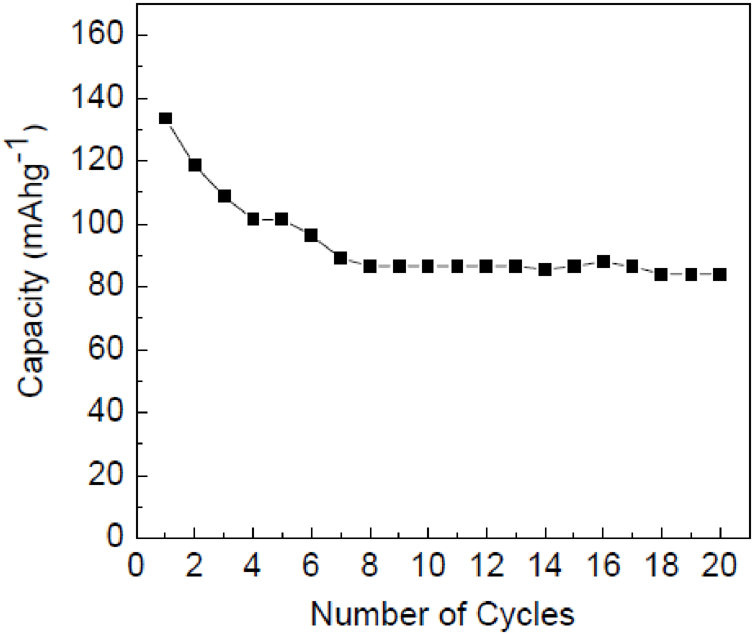
The other main factor limiting the life of even a well-maintained battery is self-discharge of the positive electrode. This is particularly acute in vehicle SLI (Starting, Lighting and Ignition) batteries in which the grid is not pure Pb but usually a lead–antimony–calcium alloy. Electrode plates with antimony are physically stronger and better able to stand the mechanical stresses during motion.

Development of improved lead acid batteries still continues, producing a variety of models with performance optimised for different applications, in terms of reliability, long life, cost, power/weight ratio, etc. Key developments over the last few decades include polypropylene for inert leak-proof enclosures, ‘absorbent glass mat’ technology for plate separators, valve regulated lead acid batteries

SEM (a) and TEM (b) image of nanostructured lead oxide PbO

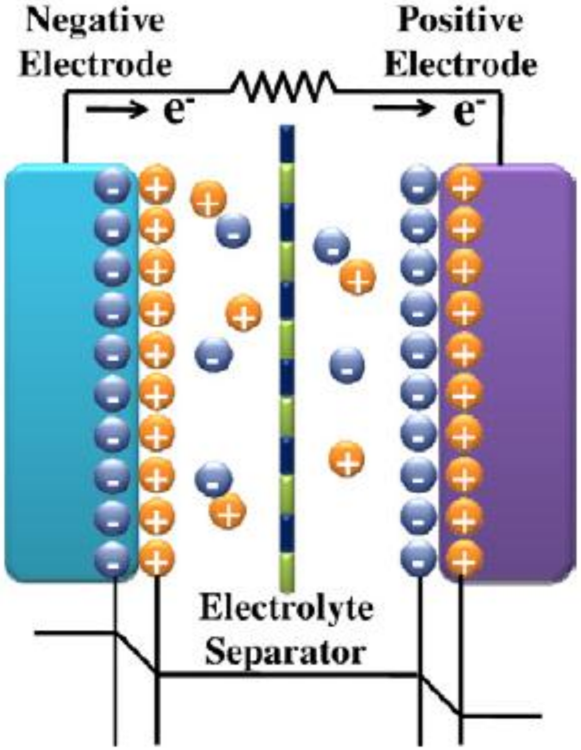


discharge capacity *v.s.* cycle number for the nanostructured lead oxide



Supercapacitors

Supercapacitors represent an important component for energy storage devices, particularly for short-acting high power batteries. Batteries suffer from a relatively slow power delivery or uptake, faster and higher-power energy storage systems are needed in a number of applications, and this role has been given to the supercapacitors



The highest performance supercapacitors are currently based on NSMs, given that increased electrode surface area improves the capacitance. It is the reason why so many researchers have been involved in working on different kinds of NSMs.

In brief, supercapacitors are formed by two polarizable electrodes, a separator and an electrolyte. They utilize double layer capacitance where the ions of the electrolyte are adsorbed on the charged electrode, resulting in a Helmholtz layer

The Helmholtz double layer thickness is defined as half the diameter of the adsorbed solvated ions at the electrode/solution interface

The power density of supercapacitors is lower than that of batteries. Therefore, the development of supercapacitors aims to improve the power density and significantly reduce cost. These electrochemical devices are also known as ultracapacitors, pseudo capacitors, and double layer capacitors.

0D and 1D NSMs

Initially researchers synthesized NSMs with zero-dimensional atomic clusters (quantum dots) for supercapacitors. Atomic clusters, nanoparticles, filaments and similar spatially confined molecula systems are defined as zero modulation dimensionality (0D or more correctly quasi-zero dimensional) and possess an aspect ratio from one to infinity. Atomic clusters are spherical and composed of several thousands atoms. However, the possibility of designing atomic clusters is no very promising at present.

Two major problems still exist in the synthesis of atomic clusters. First, it is difficult to produce mass-selected clusters in large quantities.

Secondly, to make atomic cluster materials, one has to consider other cluster–cluster interactions and make sure that this would not lead to coalescence of clusters that would change its original physical and chemical characteristics.

However, well-controlled and mass-producible atomic clusters will likely increase with more advanced research and their applications in the future.

many research groups have found that electrode-active materials
with nanoscale crystalline particle size usually show better discharge life due to their high specific surface areas. Additionally, nanoscale particles dramatically change surface reaction rates, causing a dramatic improvement in power density when compared to conventional capacitor. As a result, researchers have tried to develop some transition metal oxides nanoparticles, such as hydrous IrO2, SnO2 , amorphous RuO2 , hydrous and anhydrous crystalline RuO2 nanoparticles , for supercapacitor applications due to their high pseudocapacitance charge-storage mechanism

The charge-storage mechanism of metal oxides {XO_2 (X = Ir, Ru, Sn, Mn, etc.)} as proposed is based on the novel concept of redox (oxidation–reduction) reactions associated with the surface reac-tion and the insertion of metallic cations, for instance, H+, Li+, Na+, K+ into the metal oxides. The simple
reaction on charge-storage mechanism can be written as follows:

$$XO_2 + {}_nC^+ + {}_ne^- \rightarrow XO_{2-n}(OC)_n$$

Where X and C+ represent the metal and proton or alkalimetal cation, respectively

The supercapacitive behavior of various metal oxides, such as RuO_2 , IrO_2 , NiOx MnO_2 Ni_3(-Fe$(CN)_6)_2(H_2O)$ and SnO_2 have already been evaluated. Among these materials, RuO_2 (specific capacitance 720 F g1) and IrO_2 (specific capacitance 550 F g1) have been recognized as the most promising candidates for supercapacitor electrodes due to their very large specific capacitance values. The weakness of these nanoparticles are their low specific surface area; therefore one of the key-issues to address increasing their specific surface area.

1D NSMs are able to solve the problem of specific surface area and thus improve the utilization of electrode active materials.

Most recently, 1D MnO_2 nanorods , Co_3O_4 nanorods, polyaniline nanowires , singleand multi-walled carbon nanotubes , Li4Ti5O_{12} with nanotubes/nanowires , MnO_2 nanobelts , and c-MnO_2 nanoneedles have been used.

These 0D and 1D NSMs still do not resolve the fundamental limitations of the materials for next generation electrochemical supercapacitors. In addition, high material cost limits the commercial use, so it is urgent to look for a substitute materials to replace RuO_2.

2D NSMs

2D NSMs dramatically change surface reaction rates and electrical transport throughout the material, causing a dramatic improvement in specific power density when compared to conventional capacitor.

Recent reports by various groups have shown that 2D NSMs (such as nanosheets, nanobelts, nanowalls, nanofibers, and nanoplates) enhance the average specific capacitance

A direct synthesized single-crystalline Ni(OH)2 hexagonal nanoplates on lightly oxidized graphene nanosheets exhibit a high specific capacitance of 1335 F g1 at a charge and discharge current density of 2.8 A g1 and 953 F g1 at 45.7 A g1 with remarkable cycling ability .

Fabricated PANI nanobelts onto a conducting substrate via an electrochemical route. These PANI nanobelts on conducting substrate showed large capacitances of 873 F g1 at 10 mV s1 and excellent stability over 1000 cycles.

Recently, Wu et al. prepared composite films of chemically converted graphene (CCG) and PANI nanofibers (PANI-NFs) and applied them as electrodes for supercapacitors. They found that the conductivity of the composite film is about 10 times that of a PANI-NF film. This conductive composite film showed a large electrochemical capacitance (210 F g1) at a discharge rate of 0.3 A g1.

Moreover, the electrochemical capacitances are much higher than those of supercapacitors based on pure CCG or PANI-NF films, mainly due to the synergic effect of both components. This means 2D NSMs exhibit high specific capacitance and remarkable rate capability as well as promise for applications in supercapacitors with both high energy and power densities. The weakness of these 2D NSMs are their low specific surface area, therefore, present research and development for these materials are focusing on increasing their specific surface area.

3D NSMs

3D NSMs may not only improve surface reaction rates, chemical stability, and electrical transport,but also greatly enhance the specific surface area throughout the material, causing a dramaticimprovement in storage capacity when compared with the 2D based supercapacitors

Recently, Liu et al. prepared hybrid supercapacitor electrodes by coaxially coating manganese oxide on a vertically aligned carbon nanofiber array . These ordered core–shell nanostructures have a very large surface area, which is 10 times higher than that of the flat surface. This large surface area offers a highly conductive and robust core for reliable electrical connection to the MnO2 shell, which ensures the rapid completion of the redox reactions and offer easy electrolyte access to a large-volume of active electrode materials. The specific capacitance value of core–shell nanostructure in a 0.10 M Na2SO4 aqueous electrolyte is 365 F g1.

Kim et al. synthesized 3D vertically aligned CNTs onto
conductive carbon papers and applied them as electrodes for supercapacitors. Remarkable supercapacitor properties were obtained by using the directly integrated, naturally patterned, and vertically aligned CNTs. The specific capacitance, energy, and power density were 200 F g1, 20Wh kg1, and 40 kW kg1 respectively

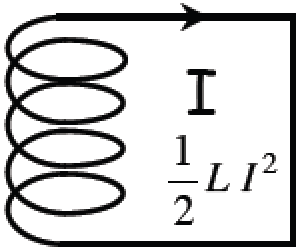
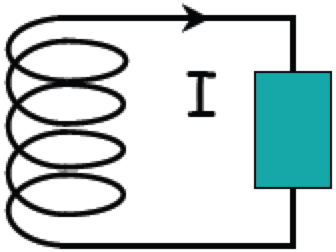
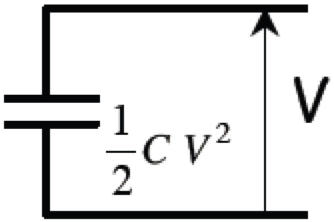
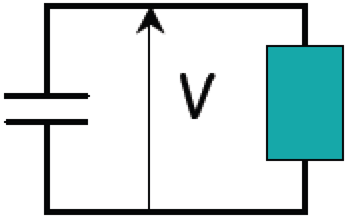
Hence, the 3D nanostructured electrode materials that boost high surface area exhibit good chemical stability, and have an ordered macro-porous structure increases the electrode/electrolyte interfacial area and facilitate ion transfer in the system with improved storage capacity. Moreover, we believe that 3D NSMs are able to resolve fundamental limitations of materials for next-generation scaling of advanced supercapacitors devices.

Superconducting electromagnetic energy storage (SMES)

A superconducting electromagnetic energy storage (SMES) system is a device for storing and very quickly discharging large quantities of electric power, e.g. 10MW for <1 s.

It stores energy in the magnetic field created by the flow of DC in a coil of superconducting material that has been cryogenically cooled to ∼4K).

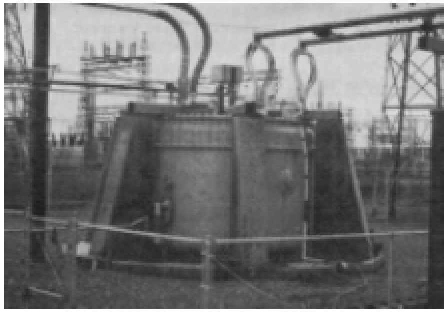
At these very low temperatures, certain materials have essentially zero resistance to electric current and can maintain a DC current for years without appreciable loss.

	Storage	Discharge	τ	Source
SMES			$\frac{L}{R}$	Current
Capacitor			RC	Voltage

SMES systems have been in use for some years to improve industrial power quality and to provide a premium quality service for those electricity users who are particularly vulnerable to voltage fluctuations. An SMES recharges within minutes and can repeat the charge/discharge cycle thousands of times without any degradation of the magnet.

Although there have been proposals to use SMES more generally for storing large amounts of electrical energy, the cost appears to be prohibitive

First SC device in a grid



P_{max}	10 MW
f	0.35 Hz
W_{max}	30 MJ
W_{exch}	9.1 MJ
I_o - V_o	5 kA - 2.2 kV
$Ø_{magnet}$	2.7 m

BPA SMES on the grid installed in 1979

(transmission stabilization, low frequency power oscillation damping)

One year operation. Cryogenic problems and other solution to damp the oscillations.

Some HTS SMES

Organ.	Country	Year	Data	SC	Application
Chubu	Japan	2004	1 MVA, 1 MJ	Bi-2212	Voltage stability
CAS	China	2007	0.5 MVA, 1 MJ	Bi-2223	
KERI	Korea	2007	0.6 MJ	Bi-2223	Power, voltage quality
DGA CNRS	France	2007	0.8 MJ	Bi-2212	Pulse appl. Electric gun
KERI	Korea	2011	2.5 MJ	YBCO	Power quality
Chubu	Japan	2012	MJ class	YBCO	Grid stabilization

Li–ion batteries

Li-ion batteries consist of a three primary functional components. The main components of a Li-ion battery device are the positive electrode, negative electrode and the electrolyte, for which a variety of materials may be used.

Generally, the most useful material for the positive electrode is one of three materials: lithium cobalt oxide, lithium iron phosphate, or a spinel such as lithium MnO_2.

On the other hand, the most common materials for the negative electrode are carbon based compounds and lithium- containing alloys.

Upon charging, lithium ions are extracted from the positive electrode material and inserted into the negative electrode material. Upon discharging, the reverse process takes place. Common batteries should exhibit three characteristics: (a) high energy and power capacity, (b) high charging rate, and (c) long lifetime (cycling stability). Although Li-ion batteries are available commercially, the performance of Li-ion batteries is limited by the current electrode and electrolyte materials. For future generations of rechargeable Li-ion batteries, not only for applications in portable electronic devices but especially for clean energy storage and use in hybrid electric vehicles, further improvements of materials are essential. We need to find new, efficient and effective ways to improve the physical and chemical characteristics of the materials for use in electrochemical Li-ion batteries

One avenue that is opening up is that of NSMs for electrochemical Li-ion batteries devices. However, the selection of NSMs for use as negative electrode, positive electrode, and electrolyte, as well as their voltage, capacity, life, and safety abilities in electrochemical Li-ion battery devices can dramatically improve. Recently, great efforts have been made toward the development of improved electrolyte, negative and positive electrodes materials

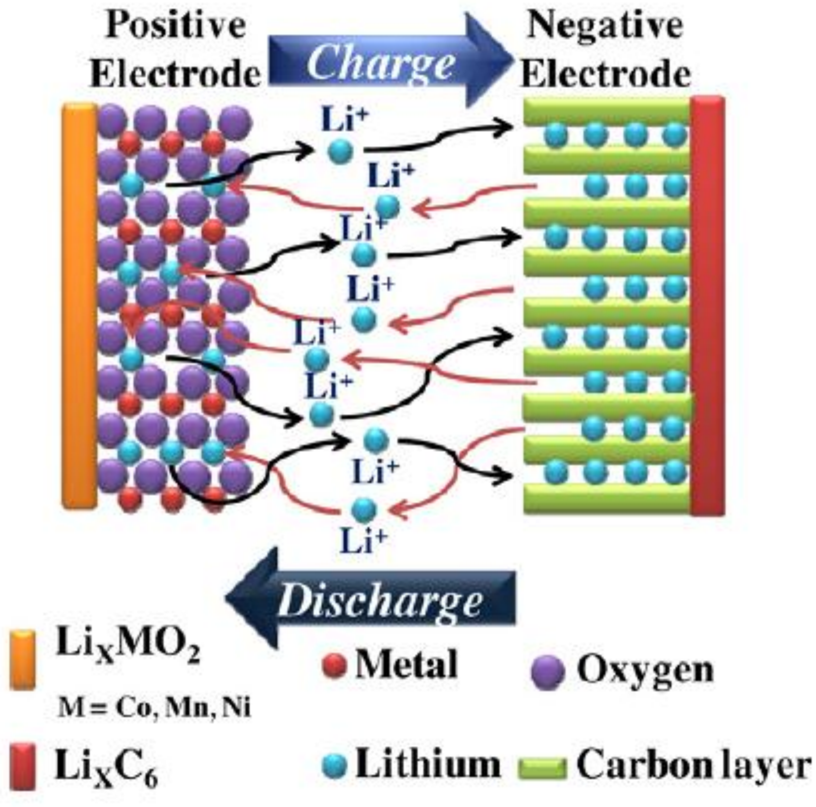
It has been demonstrated that the morphology of nanostructures can be optimized to achieve higher energy and charge densities in electrochemical Li-ion battery devices. Therefore, nanoarchitecture is another consideration that can be optimized for further improvement. In this regard, research on . NSMs is expanding rapidly into the assembly of nanoparticles in 0D and 1D structures.

Recently, some research groups have tried to synthesize 0D nanoparticles to avoid the problem of poor Li+ ion diffusivity and electron conductivity, which would eliminate either metal doping or carbon coating.

0D nanoparticles with high-crystallinity are particularly advantageous when the aim as above mentioned is to achieve faster lithium-ion diffusion. They also display a better rate capability, which indicates its possible use in electrochemical Li-ion battery devices.

However, 0D NSMs are not very stable and very difficult to make in large quantities. Various efforts have been implemented to synthesize novel 0D NSMs but have been met with very limited success in the improvement of electrochemical Li-ion battery device performance.

Due to this, researchers have fabricated new 1D NSMs that will make electrochemical Liion battery devices more efficient due to their unique mechanical, thermal, electrical properties and structural versatility. Various efforts have been made by the scientific community to fabricate novel 1D NSMs such as nanotubes, nanorods, and nanobelts . The figure bekow shows the schematic diagram of a Li+ ion pathway in 1D NSMs.



They also constructed a full cell composed of a LiCoO2 cathode and a car-bon–silicon core–shell nanowire anode. Significantly, using these core–shell nanowires they achieved high mass loading and an area capacity of 4mA h cm2.

Importantly, the capacity of a Li-ion full cell consisting of a cathode of LiCoO2 and anode of Si nanotubes shows a higher capacity than commercially available graphite even after 200 cycles. However, a new problem arose for 1D NSMs are low surface area and slow diffusion rates. Due to low surface area, slow diffusion rates and poor conductivity, 1D NSMs show the poor energy density and poor rate capacities. Consequently, improvement in surface area to volume ratio, diffusion rates and conductivity is necessary.

2D NSMs

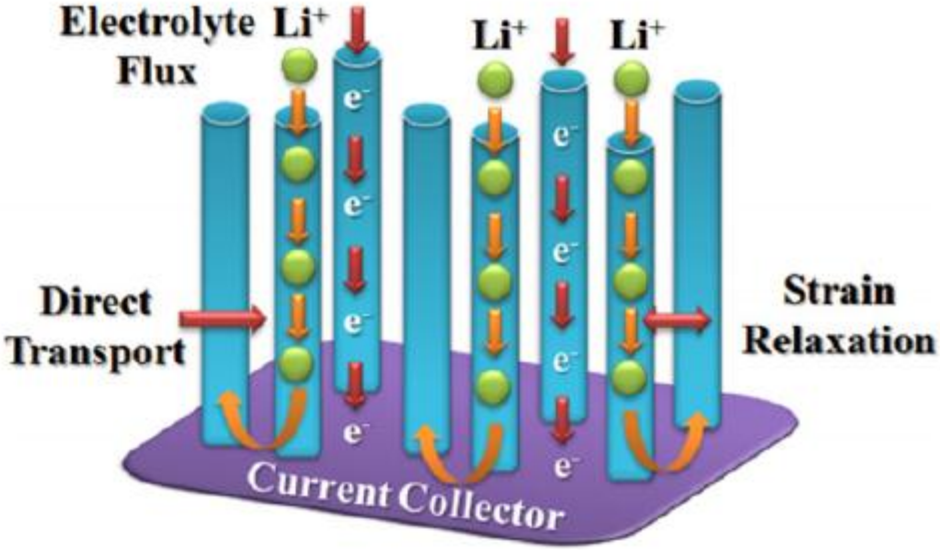
2D NSMs are a useful approach to improve the electrode performances in higher overal capacity, high-rate capability, and longer cycling life. 2D NSMs normally exhibit small crystalline size, high surface area, large surface-to-volume ratio, and favorable structura stability over 1D, and 0D NSMs. The development of a 2D nanostructure gives the right structure necessary for a fast mass transport, for instance.

Recently, Zhou et al. synthesized a Si/TiSi2 heteronanostructure on Ti foil in a CVD chamber with $TiCl_4$, SiH_4 and H_2 as precursors. The Si/TiSi2 heteronanostructure was used as an anode material for Li+ batteries. In this heteronanostructure, Si nanoparticles acts as an active component to store and release Li+ while TiSi2 serves as the inactive component to support Si and to facilitate charge transport. The Si/TiSi2 heteronanostructures show fast and superior charge/discharge capacities.

3D NSMs

In order to further achieve higher energy and charge densities in electrochemical Li-ion battery devices, 3D nanostructured electrodes may be needed. As 3D NSMs electrode have a higher surface area, larges surface-to-volume ratio, and more favorable structural stability over 2D, 1D, and 0D NSMs. The 3D NSMs can be flooded with electrolyte, ensuring a high specific surface area in contact with the electrode and hence a high flux of Li+ ion across the interface.

The nanowalls between the NSMs, of equal dimensions throughout, ensure very short diffusion paths for Li ions on intercalation and deintercalation, and hence homogeneous rates of transports.


Electrolyte
Flux
Li⁺
Li⁺
Li⁺
e⁻
Direct
Transport
Strain
Relaxation
Current Collector

An excellent reversible capacity was obtained for these MnO_2/CNT nanotube array electrodes. The coaxial MnO_2/carbon nanotube arrays offer the following advantages: (a) presence of carbon nanotube improves the electrical conductivity

(b) homogeneous electrochemical accessibility and better ionic conductivity is achieved by avoiding agglomerative binders and other additives

(c) well-directed coaxial alignment provides a better conductive path

(d) MnO_2/CNT hybrid nanostructures offer a unique dual-binding mechanism of lithium storage (insertion–deinsertion in the case of carbon nanotubes and formation and decomposition of Li_2O in the case of MnO_2 nanotubes).

The use of 3D NSMs is increasing rapidly in the field of Li-ion battery devices because of their substantial advantages in terms of mass transport. Transport in 3D NSMs typically encompasses shorter transport length for Li+ ions and electrons, better electrode–electrolyte contact area, and great merits to permit reproducible Li+ insertion and extraction. This verifies their promising application as electrode materials for Li-ion batteries.

Hydrogen Storage

- Physical storage of H_2
  - Compressed
  - Cryogenically liquified
  - Metal Hydride
  - Carbon nanofibers
- Chemical storage of hydrogen
  - Sodium borohydride
  - Ammonia
  - Methanol
  - Alkali metal hydrides

- Physical storage of H_2
- Chemical storage of hydrogen
- New emerging methods

The current hydrogen market is, dominated by uses for oil refining, food production, metals treatment, and fertilizer manufacture. Power production uses relatively little of the hydrogen, perhaps on the order of 10-20 million kilograms per year in the US, or about 0.1% of the total

ENERGY CONTENT FOR VARIOUS FUELS [3]

Fuel	Chemical formula	State	Energy per unit mass (MJ/kg)	Energy per unit volume (MJ/m^3)
Gasoline	$C_{5-10}H_{12-22}$	liquid	47.4	34.9
LPG	$C_{3-4}H_{8-10}$	liquid	48.8	24.4
LNG	$\sim CH_4$	liquid	50.0	~ 230.0
Methanol	CH_3OH	liquid	22.3	18.1
Ethanol	C_2H_5OH	liquid	29.9	23.6
Liquid Hydrogen	H_2	liquid	141.9	10.1
Hydrogen	H_2	Gaseous	141.9	0.013
Natural gas	$\sim CH_4$	Gaseous	50.0	0.040

Hydrogen Storage Technologies

Gaseous Hydrogen

The most traditional way of storing hydrogen is in the gaseous form in pressure vessels. Since hydrogen behaves very much like an ideal gas in the ambient temperature (and the temperatures below) it satisfies the ideal gas law $PV = nRT$,

where n is the amount of hydrogen in moles and R is the gas constant

Gaseous hydrogen can be stored either in aboveground portable or stationary containers or in different kinds of earth caves.

For a given volume and temperature the energy density of storage is increased when increasing the pressure of storage vessel. The only problem of this is the safety features and regulations that limit the allowable pressure.

One of the best properties of pressure vessels is that they do not leak. The losses of the storage capacity are thus virtually non-existent . Some leaks may occur through connectors but with proper fittings and regulators these leaks can be minimized.

The most common hydrogen storage systems can withstand the pressure of 20 MPa, while light weight composite cylinders can withstand the pressure up to 80 MPa . When hydrogen is stored at such high pressures, very thick wall tank has to be used.

Compressed

- Volumetrically and Gravimetrically inefficient, but the technology is simple, so by far the most common in small to medium sized applications.

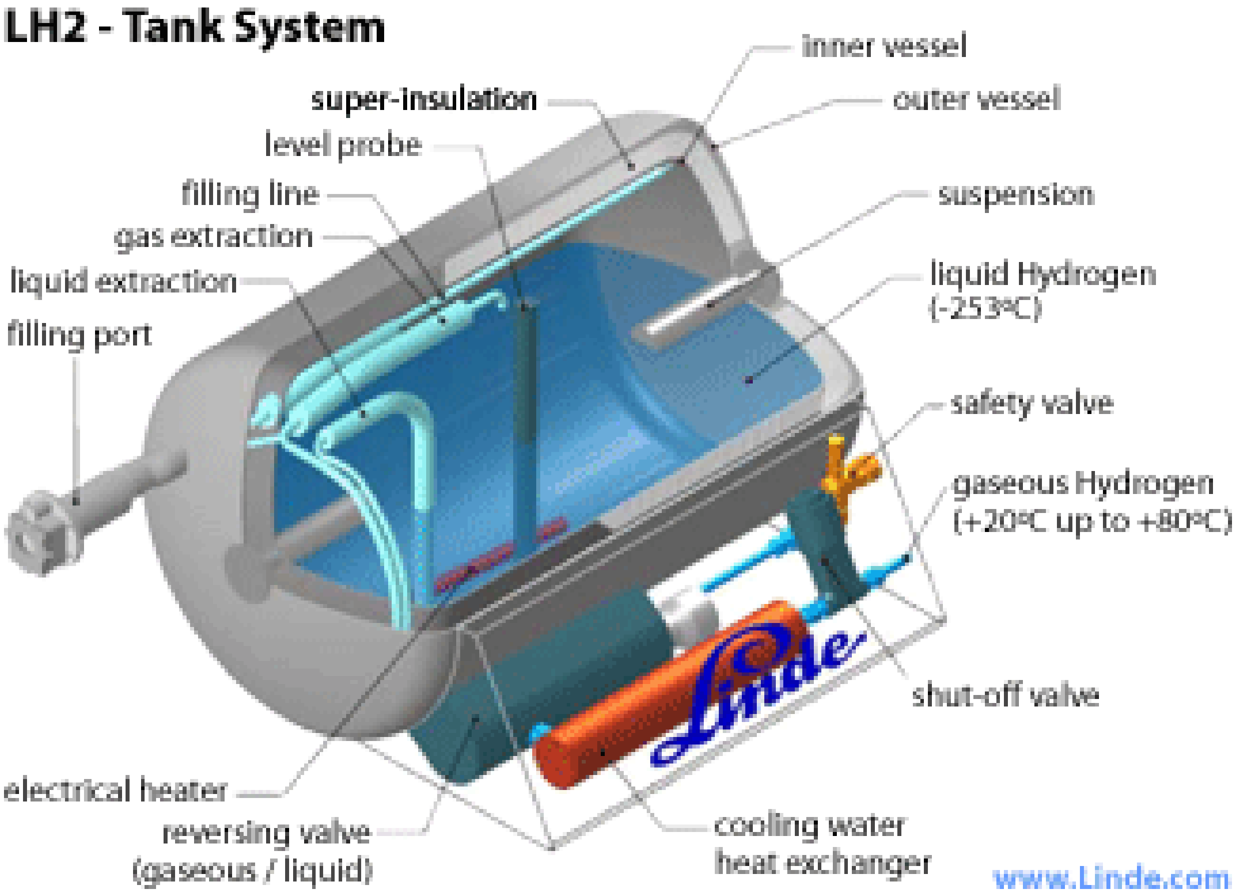
1. Research on material embrittlement, using new *ad hoc* fracture mechanics techniques.
2. Development of stronger and lower cost construction materials, especially carbon fibers.
3. Development of an efficient and clean (without oils) high pressure compressor.

Liquid H2 (Cryogenic)

Cryogenic hydrogen, usually simply referred to as liquid hydrogen (LH_2), has a density of 70.8 kg/m3 at normal boiling point (-253C). (Critical pressure is 13 bar and critical temperature is –240°C). The theoretical gravimetric density of LH_2 is 100%, but only 20 wt. % H_2 of this can be achieved in practical hydrogen systems today

On a volumetric basis the same respective values are 80 kg/m3 and 30 kg/m3. This means that liquid hydrogen has a
much better energy density than the pressurized gas solutions mentioned above. However, it is important to recall that about a 30-40% of the energy is lost when LH_2 is produced. The other main disadvantage with LH_2 is the boil off losses during dormancy, and the fact that a super insulated cryogenic container is needed.

Liquid (Cryogenic)



- Gravimetrically and volumetrically efficient but very costly to compress

Hydrogen in the liquid form is used widely as a principal fuel in space programs due to its high volumetric density (70.8 kg/m3)

Liquid hydrogen has been demonstrated in commercial vehicles (particularly by BMW)

The main R&D tasks are

1. Develop more efficient liquefaction processes.
2. Lower costs and improve the insulated containers.
3. Develop systems that automatically capture the boil off and re-liquefy the fuel

Metal Hydrides

- Technically a chemical reaction, but acts like a physical storage method
- Hydrogen is absorbed like in a sponge.
- Operates at 3-30 atm, much lower than for compressed gas tanks
- Comparatively very heavy, but with good volumetric efficiency, good for small storage, or where weight doesn’t matter

Metal hydrides are composed of metal atoms that constitute of a host lattice and hydrogen atoms that are trapped in interstitial sites, such as lattice defects. The trap site can be a vacancy or a line defect. In the case of a line defect, a string of hydrogen atoms may accumulate along the defect. Such a string increases the lattice stress, especially if two adjacent atoms recombine to form molecular hydrogen.

Since adsorption of hydrogen increases the size of lattices , the metal is usually ground to a powder

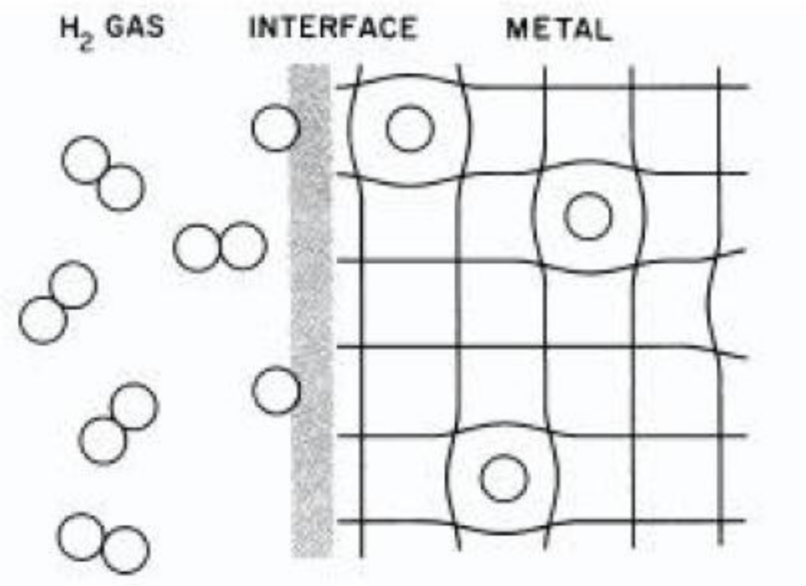
There are two possible ways of hydriding a metal, direct dissociative chemisorption and electrochemical splitting of water. These reactions are, respectively

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x ,$$

and

$$M + \frac{x}{2} H_2O + \frac{x}{2} e^- \leftrightarrow MH_x + \frac{x}{2} OH^- ,$$

where *M* represents the metal. In electrochemical splitting there has to be a catalyst, such as palladium, to break down the water



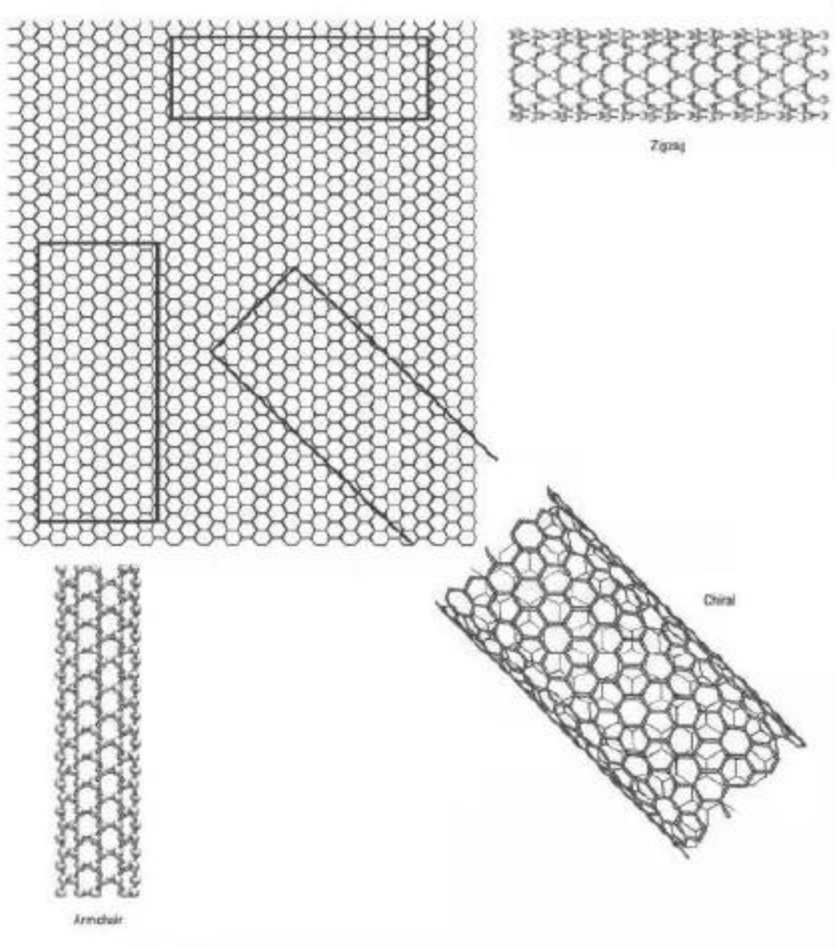
As a hydrogen molecule approaches the metal surface, weak van Der Waal's forces begin to act upon it drawing it closer. The molecule reaches the potential well *Ep* at distance *zp*, and very large forces would be required to force it any closer the surface in a molecular form. However, the dissociation energy of hydrogen molecule is exceeded by the chemisorption energy. Thus the hydrogen molecule dissociates and individual hydrogen atoms are attracted to the surface by chemisorptive forces and they reach the potential well E_{CH}. From this point sometimes even the ambient temperature's thermal energy is enough to increase the vibrational amplitude of hydrogen atoms which can thus reach and enter the metal surface

Metal and hydrogen usually form two different kinds of hydrides, a-phase and b- phase hydride. In a-phase there is only some hydrogen adsorbed and in b-phase the hydride is fully formed. For example, Mg_2Ni forms hydrides of $Mg_2NiH_{0.3}$ and $Mg2NiH_4$

A study of nano-scaled particles shows that when the metal grains are in the range of 5 to 50 nm, the kinetics of both absorption and desorption is improved by an order of magnitude because of improved thermal conductivity

Hydrogen is a highly reactive element and is known to form hydrides and solid solutions with thousands of metals and alloys

Hydrogen in Carbon Structures

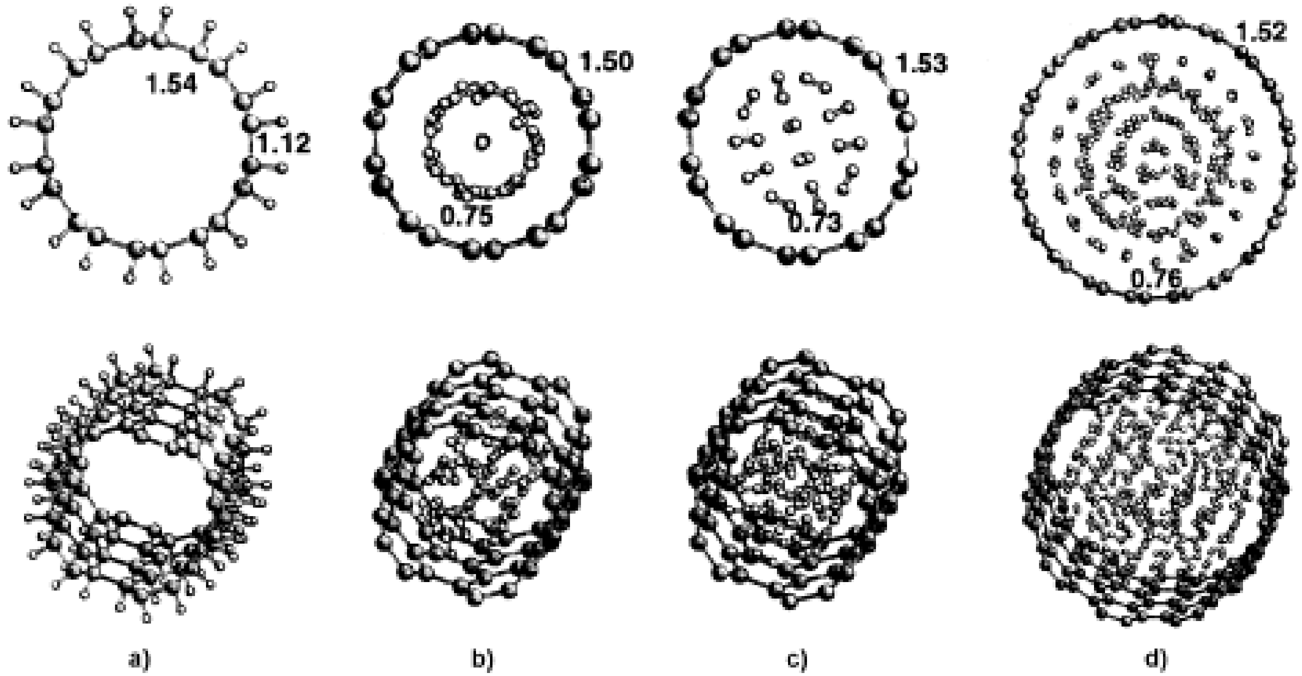


Hydrogen can be stored into the nanotubes by chemisorption or physisorption. The methods of trapping hydrogen are not known very accurately but density functional calculations have shown some insights into the mechanisms .

Calculations indicate that hydrogen can be adsorbed at the exterior of the tube wall by H-C bonds with a H/C coverage 1.0 or inside the tube by H-H bonds with a coverage up to 2.4 as shown in Figure .

The adsorption into the interior wall of the tube is also possible but not stable. The hydrogen relaxes inside the tube forming H-H bonds.

The numbers in the figure tell the bond lengths in 10-10 m.



Hydrogen adsorption in a nanotube. a) exterior adsorption with H/C coverage 1.0, b) interior adsorption with coverage 1.0, c) interior adsorption with coverage 1.2, d) interior adsorption with coverage 2.4

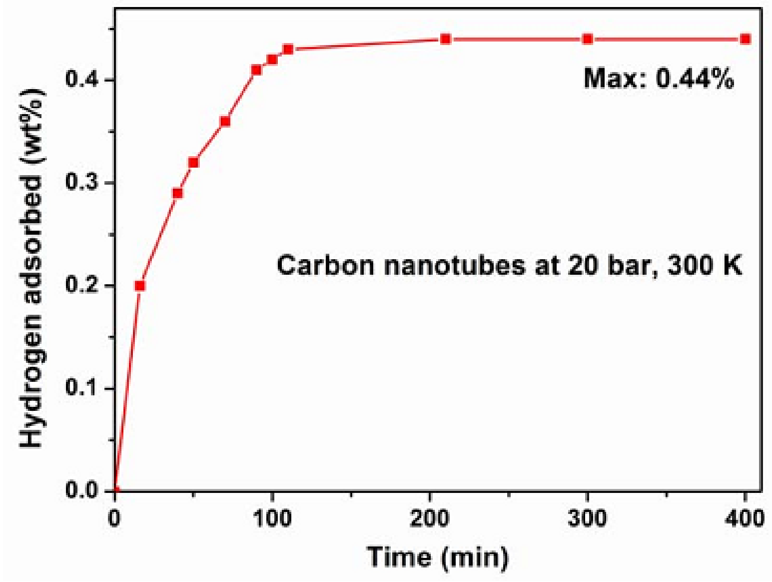
Multi-walled nanotubes, in which two or more single tubes are rounded up each other with van Der Waal’s attraction, can adsorb hydrogen between the single-wall nanotubes.

The hydrogen causes the radius of the tubes to increase and thus makes a multi-walled nanotube less stable . In nanotube bundles hydrogen can also be adsorbed in the middle of different tubes

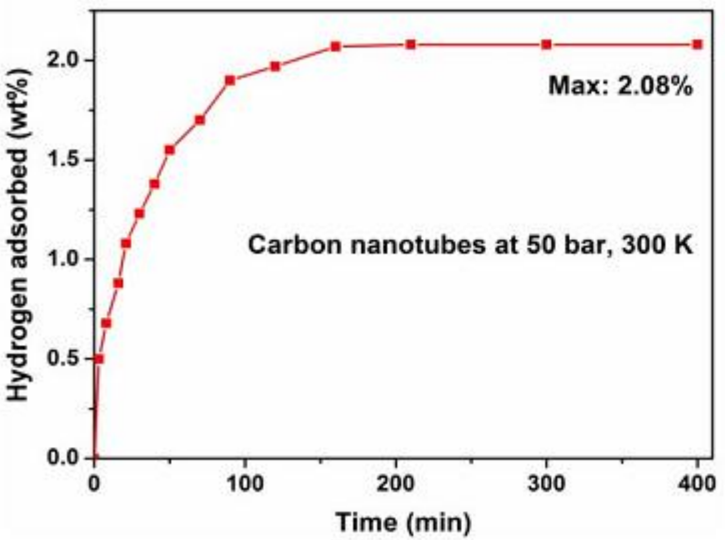
Recent results on hydrogen uptake of single-walled nanotubes are promising. At 0.67 bar and 600 K about 7 wt% of hydrogen have been adsorbed and desorped with a good cycling stability . Another result at ambient temperature and pressure shows that 3.3 wt% can be adsorbed and desorped reproducibly and 4.2 wt% with a slight heating.

Even though the price of the nanotubes is still high they have a good potential in storing hydrogen. When the manufacturing techniques are improved and some engineering problems solved, they may be highly competitive against other hydrogen storage technologies.

There are also some other forms of carbon that adsorb hydrogen. These are graphite nanofibers, fullerenes, and activated carbon.

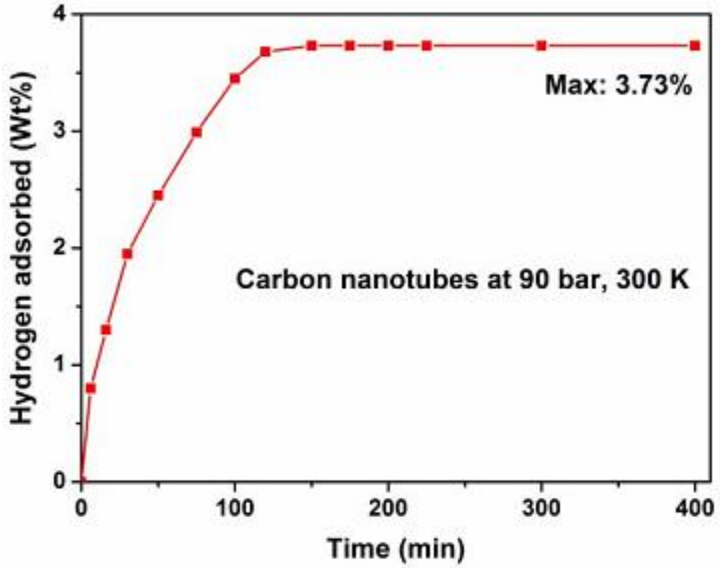


7. Absorption kinetics of carbon nanotubes at 300K and 20 bar pressure.

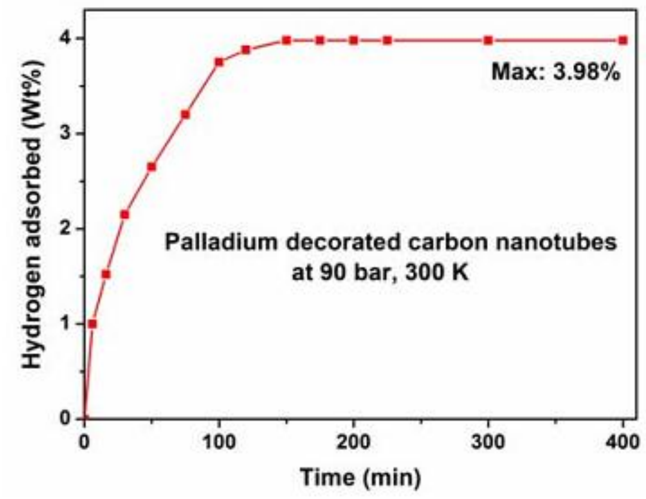


Absorption kinetics of carbon nanotubes at 300K and 50 bar pressure.

Compare with palladium decorated carbon nanotubes

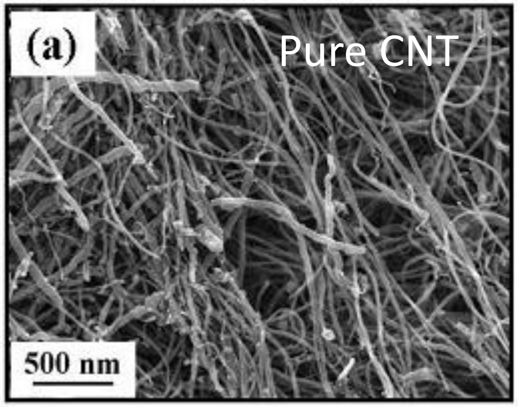


Absorption kinetics of carbon nanotubes at 300K and 90 bar pressure.

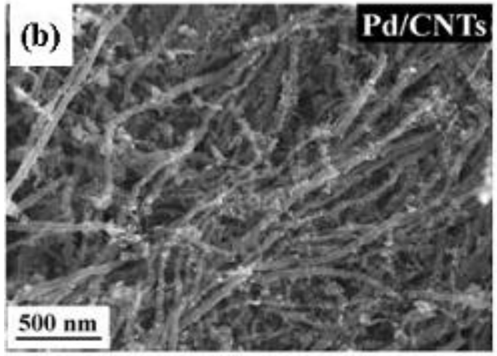


. Absorption kinetics of palladium decorated carbon nanotubes at 300K and 90 bar pressure.

The increase in hydrogen storage capacity in palladium decorated carbon nanotubes is due to 2 mechanisms;



1. Adsorption of the hydrogen molecules on the surface and interior regions of CNTs.
2. Dissociation of H_2molecules on the palladium particles and atomic H spills over to the spaces between adjacent carbon layers of CNTs



Cycle stability

Besides the high storage capacity and reversibility of the hydrogen storage, the storage medium has to be stable under repeated hydrogenation/dehydrogenation cycles.

This stability is largely determined by the microstructure and chemical changes during the hydrogen absorption and de-sorption process.

The combination of temperature, pressure, hydrogen absorption/desorption (expansion and contraction) can result in a change in microstructure and chemical composition of the storage material which in combination with the sensitivity to oxidation and contamination makes the cycle stability one of the more difficult targets to achieve.

For metal – hydride based batteries, metals (or combinations of) like Ce, La,Nd, Pr and metal oxides like Cr_2O3, Al_2O3 and $CeO_2$are often used to improve the cycle stability . For this reason these types of materials are also considered for improving the stability of the hydrogen storage materials .

A good cycling stability is reported for over-stoichimetric $La(Ni,M)_{5+x}$ (with M = Mn, Cu) . In addition one also has to keep in mind that the depth of hydrogen charge and discharge are of considerable influence on the cycle stability of the storage material.

Chemical storage

The technology is based on a very simple redox reaction of magnetite

$$Fe_3O_4 + 4H_2 \leftrightarrow 3Fe + 4H_2O$$

Fe_3O_4 must first be reduced with hydrogen at suburban H_2production plants or at residential gas stations.

Step 1: chemical H_2storage.
$Fe_3O4+4H_2 \rightarrow 3Fe+4H_2O$
Then, the reduced iron oxide (mainly Fe) is packed in cassettes. The cassettes will be transported to the gas stations and be mounted on PEFC vehicles. Addition of water into the cassettes would produce pure hydrogen and regenerate $F_e3O_4$according to equation below.

The hydrogen could be supplied directly to the PEFC on the vehicles without any purification treatment for CO.

Step 2: H_2recovery.
$3Fe+4H2O \rightarrow Fe3O4+4H2$

The cassettes with Fe_3O_4 after water decomposition are to be exchanged for the new ones packed with Fe at residential gas stations or service stations. The used Fe_3O_4should
be recycled many times. According to the equation the theoretical amount of hydrogen being chemically stored is 4.8 wt.% of Fe

Chemical hydrogen storage: hydrogen generation from ammonia borane

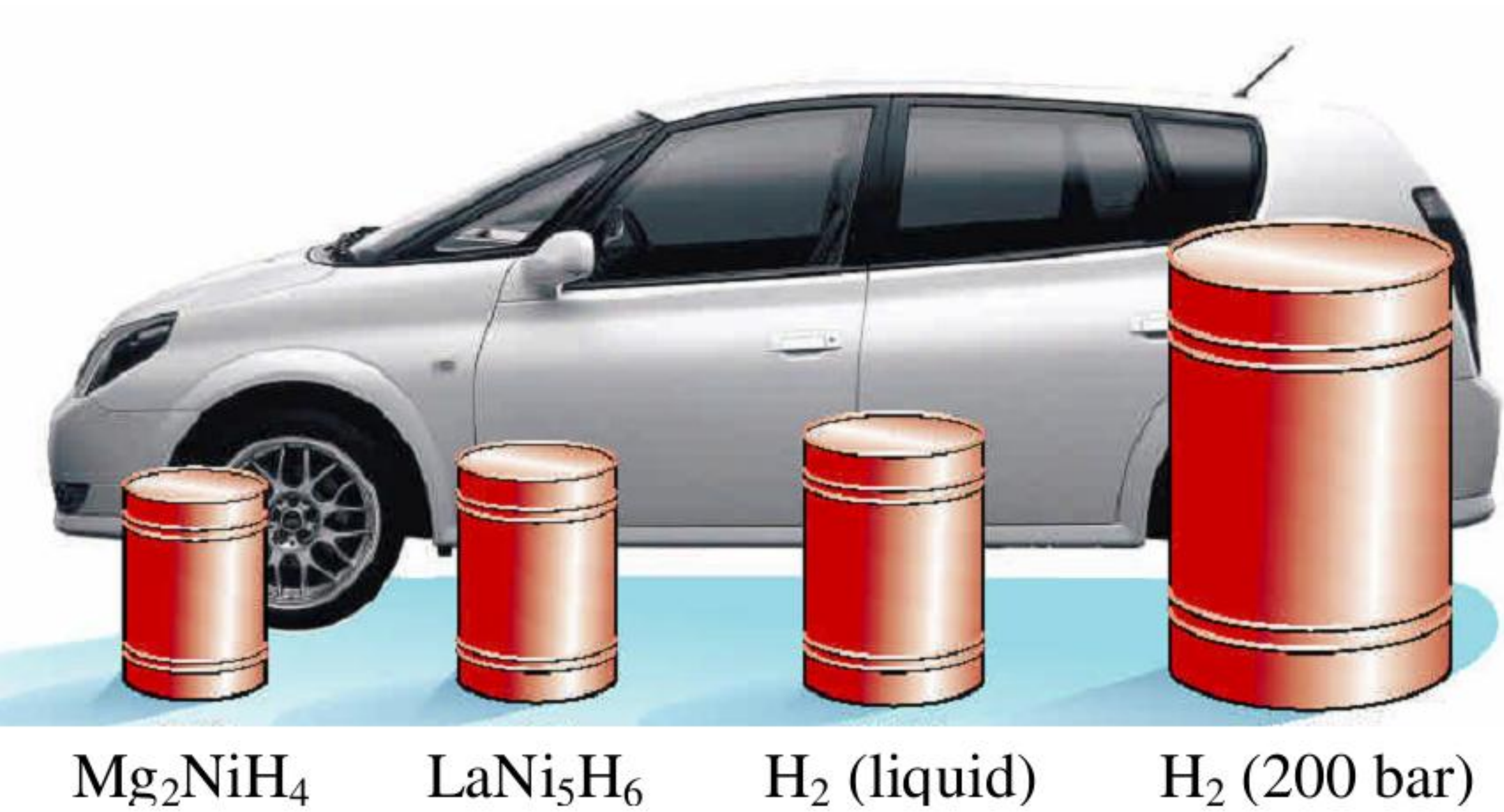
Generation of hydrogen from suitable carriers is a safe alternative to hazardous physical hydrogen storage. In this regard, boron hydrides with high gravimetric content of hydrogen are considered to be promising materials as carriers of hydrogen for portable applications

Ammonia borane ($H_3N{\cdot}BH_3$, AB) with 19.6 wt% of hydrogen has been attracting immense interest as a hydrogen storage medium in recent years

It possesses a volumetric density of 146 g H_2/lit and a gravimetric density of 196 g H_2/kg. These values are well above the US Department of Energy targets (2015) of a volumetric density greater than 82 g H_2/lit and a gravimetric density greater than 90 g H_2/kg

Ammonia borane is a stable white solid and a safe material to handle under ambient conditions, which makes it very attractive for practical applications. Ammonia borane was first synthesized by Shore and Parry in 1958 using $NaBH_4$and NH_4Cl in ether solvent

Release of hydrogen from AB can be accomplished either by thermolysis (neat or metal catalyzed) in the solid state and non-aqueous medium (ethereal solvents) or metal catalyzed reactions in solvents (water and methanol)


Mg_2NiH_4
$LaNi_5H_6$
H_2 (liquid)
H_2 (200 bar)

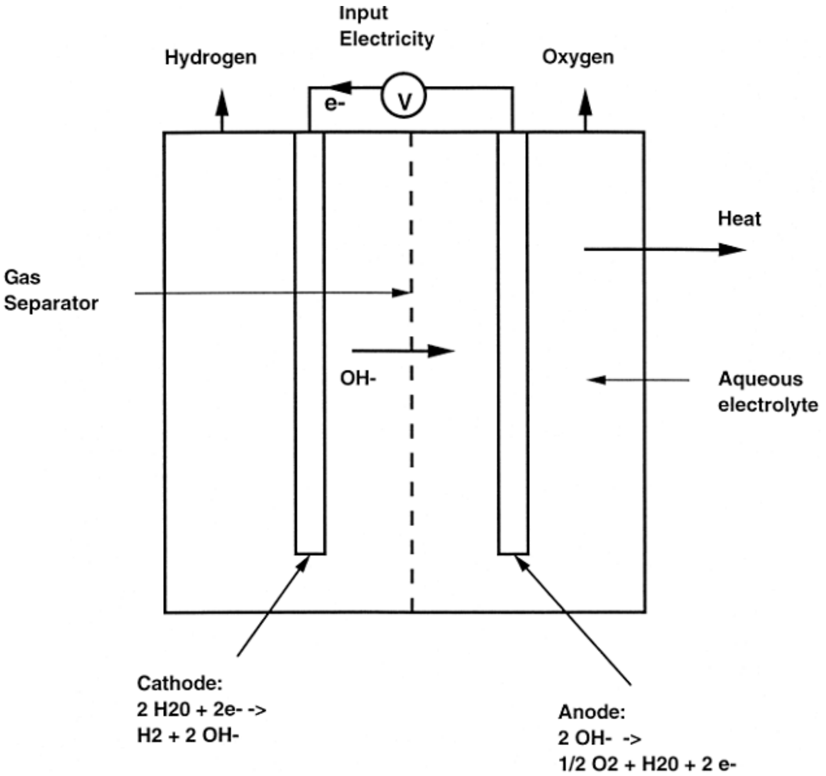
In early 2010, Honda Motor Company in Torrance, California opened a new more compact and efficient solar-hydrogen refueling station. Pictured below , the new station is designed to demonstrate what could be envisioned at the household level, where solar PV panels would be used to produce the electricity needed for hydrogen production through electrolysis. The system uses a 48-panel, 6-kilowatt solar PV system.

Honda’s New Solar Hydrogen Fueling System (Source: Honda Motor Company, 2010)

Electrolysis of Water Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity and an electrolyzer device. The overall

$$e^{-} + H_2O \text{ -> } ½ \, O_2 + H_2$$

The two most common types of electrolyzers are alkaline (use a potassium hydroxide electrolyte) and PEM (use a solid polymer membrane electrolyte). A schematic of an alkaline electrolysis system is provided in Figure. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen. The oxygen can then be used for productive purposes such as enriching the oxygen content of greenhouses for food production.




Norsk Hydro Electrolyzers 2,000 kW each

The requirements for effective on-board hydrogen storage are

1) Appropriate thermodynamics (favourable enthalpies of hydrogen absorption and desorption)
2) Fast kinetics (quick uptake and release)
3) High storage capacity (specific capacity to be determined by usage)
4) Effective heat transfer
5) High gravimetric and volumetric densities
6) Long cycle lifetime for hydrogen absorption/desorption
7) High mechanical strength and durability
8) Safety under normal use and acceptable risk under abnormal conditions
9) Cheap components and materials

From literature it is clear that to meet the requirements for hydrogen storage, the current status of the technology is insufficient.

For example to give an idea about the system requirements, to drive with an average car 100 km one needs 3 litre of gasoline (2.21 kg) (energy density gasoline 12.7 kWh/kg) for an average car. This is equivalent with 0.84 kg of hydrogen (energy density 33.3 kWh/kg)

To store this amount of hydrogen in for example LaNi 5(weight percentage of 1.4 wt.%), one needs 300 kg of metal-hydride material. Besides the weight problem also the heat development during hydrogenation is important. For an enthalpy of formation of $\Delta H = -35 kJ/mol\ H_2$, the heat release during a 3 minute refilling timeis 405 kW.

some important questions that need to be considered for practical applications are:

1) Does hydrogen physisorb or chemisorb?

2) Does it bind molecularly or dissociatively?

3) Where does the hydrogen reside?

4) What is the nature of its hydrogen diffusion mechanism?

5) What are the activation barriers for hydrogen desorption?

6) What adverse effect does hydrogen have on the structural and mechanical stability of the host material?

7) What is the nature of bonding of hydrogen with host atoms — ionic, covalent, or metallic?

8) What roles do surface morphology and defects play in hydrogen absorption and de-sorption?
9) In what ways is it beneficial to store hydrogen in novel materials, such as nanostructures and porous materials?
10) How do catalysts help in reducing the operating temperature and pressure for hy-drogen uptake and release?

High pressure hydrogen storage

For gaseous hydrogen storage under high pressure there are some techniques like steel tanks, composite tanks, glass spheres etc. The most matureand promising technique are the carbon-fibre-wrapped hydrogen composite storage tanks. These tanks are available, safety-tested, simple of construction and can contain pressures up to700 bar (6.7 wt.%). There are already several pilot applications in the world today using this technique, but high pressure storage has some disadvantages. **The large physical volume required (does not meet the volumetric target), high costs and safety issues are still under investigation and discussion. Furthermore, as the storage capacity of a composite tank is limited by the molecular interaction of the hydrogen, an increase in pressure is not proportional to an increase in storage capacity at higher pressure**
Another restriction is the considerable energyloss during pressurization of the hydrogen gas which is typically in the order of 12 – 16 % for compression to 800 bar (depending on the type of compression)

It might be the simplest way to store hydrogen in a cylinder of pressure up to 20 MPa,but the energy density is too low to satisfy the fuel demand of driving practice.

About four times higher pressure is needed to meet the driving purpose, however, such industrial cylinders have not been commercially available.

Industry sets up a goal to manufacture cylinders capable of withstanding pressure up to 70 MPa with a weight 110 kg to reach a gravimetric density 6%; and volumetric density 30 kg/m3

The hydrogen density as such is remarkably lower than the cryo adsorption method, and the high cost of compression and the cylinder might hinder the method to be accepted commercially.

Physisorption

The storage of hydrogen can rely on physisorption because the adsorbed gas can be released reversibly. There are different mechanisms of adsorption depending on the geometry of the adsorbent and the temperature of adsorption. Multilayer mechanism functions if the adsorption happens on an open surface and volume filling would happen in a pore narrower than 2 nm. Capillary condensation could happen in a pore larger than 2 but smaller than 50 nm. Adsorption in a pore larger than 50 nm is the same as that on open surfaces. However, all the mechanisms here mentioned assume the possibility of condensation of the adsorbed adsorbates. Such possibility does not exist at above-critical temperatures; therefore, a different mechanism of adsorption must assume. There is only one mechanism for the adsorption of supercritical gases on any kind of adsorbents, that is the monolayer surface coverage.

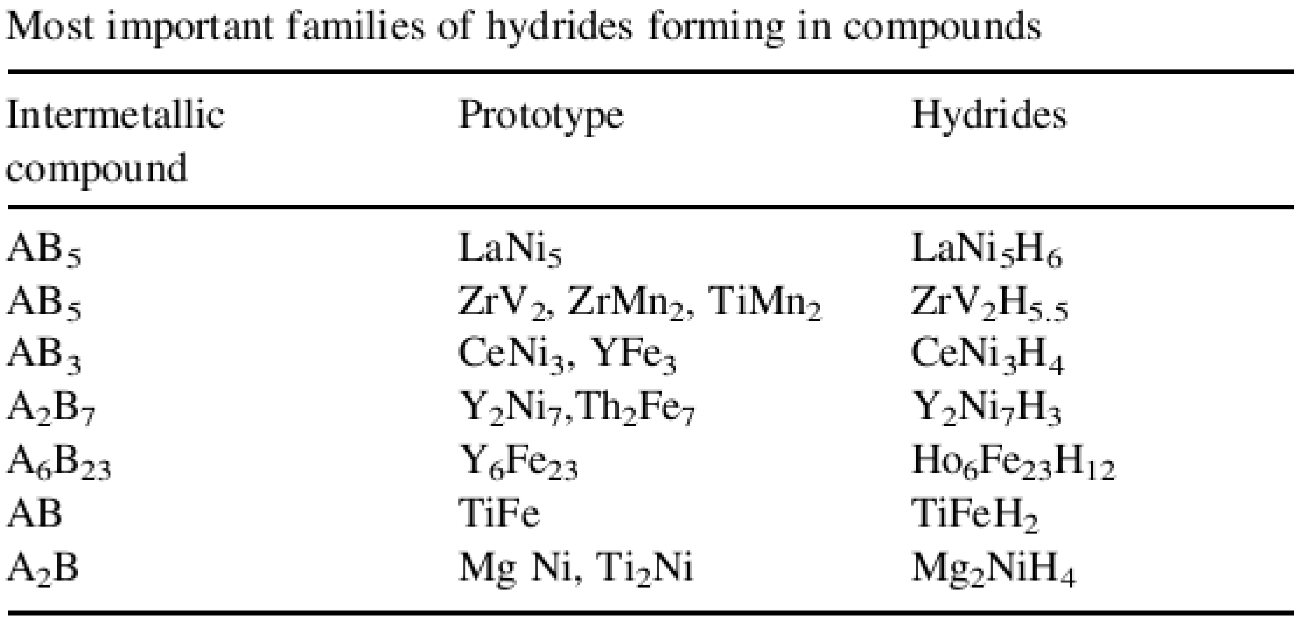
The single mechanism corresponds to the single type of isotherms of supercritical adsorption. This argument can be proved on considering the well-known BET theory of adsorptio. According to BET, the first molecular layer of adsorbate is fixed on the solid surface due to the interaction between gas and solid.
When the surface was completely covered with a layer of adsorbate, more gas molecules would be adsorbed above the first layer due to the interaction between the same species of adsorbate molecules forming the second layer, and so on for the subsequent layers. The interaction force received by the first layer molecules is, thus, different from that received by the second and subsequent layers. This difference must be reflected in the heat of adsorption of different layers. The experiment with nitrogen and carbon black[3]showed that the heat of adsorption of the first layer is 11–12 kJ/mol (0.11–0.12 eV) and it drops to the latent heat of condensation, 5.56 kJ/mol (0.058 eV) in the subsequent layers.

Obviously, the subsequent layers from the second cannot exist at above-critical temperatures, otherwise a classical law of physics, i.e. gas cannot be liquefied at above-critical temperatures no matter how high pressure applied, would be false.

The monolayer adsorbate is itself fixed by a weak interaction; therefore, significant physisorption is only observed at relatively low temperatures.

Metallic hydrides

Some metals and alloys absorb hydrogen and form hydrides. There are two classes of hydrides: metallic hydrides and complex hydrides. The main difference between them is the transition of metals to ionic or covalent compounds for the complex hydrides upon absorbing hydrogen. Some of the metallic hydrides of interest for the storage purpose are listed in table. The prototype metallic hydrides are composed of two elements. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. The B element is often a transition metal and forms only unstable hydrides. Nickel is often used as B element since it is an excellent catalyst for the hydrogen dissociation.



Most important families of hydrides forming in compounds

Intermetallic compound	Prototype	Hydrides
AB_5	$LaNi_5$	$LaNi_5H_6$
AB_5	ZrV_2, $ZrMn_2$, $TiMn_2$	$ZrV_2H_{5.5}$
AB_3	$CeNi_3$, YFe_3	$CeNi_3H_4$
A_2B_7	Y_2Ni_7, Th_2Fe_7	$Y_2Ni_7H_3$
A_6B_{23}	Y_6Fe_{23}	$Ho_6Fe_{23}H_{12}$
AB	TiFe	$TiFeH_2$
A_2B	Mg Ni, Ti_2Ni	Mg_2NiH_4

Some metal hydrides absorb and desorb hydrogen at ambient temperature and near the atmospheric pressure, and the volumetric density of the hydrogen atoms present in the host lattice is extremely high. A volumetric density of 115 kg/m 3 was reached in LaNi5H6.

However, all the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 wt%, for example, the gravimetric density of hydrogen in $LaNi_5H_6$is only 1.4%. Recent attention turns to the hydrides formed by light metals, and Mg becomes the focus.

The formation of metal hydrides is an exothermic reaction. Significant heat is released during absorbing hydrogen and the same amount of heat is required in order for hydrogen released from the hydrides. More stable the hydride is, more heat is needed to desorb hydrogen. An amount of energy approximately 25% higher than the heating value of hydrogen is needed for the release of hydrogen from MgH_2.

Although many efforts have been contributed to the Mg-based hydrides in recent years, it is still a challenge to find out an appropriate hydride of light metals.

Complex hydrides

Group I, II, and III elements, e.g. Li, Mg, B, Al, build a large variety of metal–hydrogen complexes. The number of hydrogen atoms per metal atom is 2 in many cases.

This kind of complexes shows the highest volumetric density, 150 kg/m 3 ,in $Mg_2FeH6$and $Al(BH_4)_3$,and the highest gravimetric density at room temperature known today in $LiBH_4$(18 wt%).

$NaAlH_4$ can reversibly absorb/desorb hydrogen at moderate temperatures; therefore, received more attention . $LiBH_4$ and $NaBH_4$ are also on the list of candidates . Some researchers thought complex hydrides as the promising solution of the hydrogen storage problem may be because this group of material has not been well studied with respect to the behavior as a hydrogen carrier.

The low dynamics of the hydrogen releasing process is a major problem. Unlike the metallic hydrides, hydrogen is released via cascade decompositions from the complex hydrides, and the step reactions call for different conditions. Therefore, there is a large difference between the theoretical and the practically attainable hydrogen capacities. Besides, significant changes in the particle morphology and elemental distribution were induced by hydrogen desorption

Liquefaction

This method faces two challenges: the efficiency of the liquefaction process and the boil-off of the liquid. The theoretical work necessary to liquefy hydrogen gas of room temperature is 3.23 kW h/kg, but the technical work is about 15.2 kW h/kg, which is almost half of the lower heating value of hydrogen. Gasification of liquid hydrogen inside the cryogenic (21.2 K) vessel is an inevitable loss even with a perfect insulation technique. The exothermic reaction of the conversion from ortho- to para-hydrogen provides a heat source of the gasification. The heat of conversion is 519 kJ/kg at 77 K, and 523 kJ/kg at temperatures lower than 77 K, which is greater than the latent heat of vaporization (451.9 kJ/kg) of normal hydrogen at the normal boiling point. The critical temperature of hydrogen is very low (33.2 K), above which liquid state cannot exist. Therefore, liquid hydrogen can only be stored in an open system otherwise the pressure in a closed system can be as high as 1000 MPa at room temperature. So, the boil-off of liquid means the emission of H2 into the atmosphere. The relatively large amount of energy necessary for liquefaction and the continuous boil-off of liquid limit this storage system to utilizations where the cost of hydrogen is not an important issue and the hydrogen is consumed in a rather short time, e.g. air and space applications.

An other aspect is the purity of the used hydrogen gas. Hydrogen can be produced by several techniques:
electrolysis of water (nuclear, renewable, conventional electricity), reforming processes (natural gas, coal, oil, diesel, and biomass)and some new/future techniques (photoelectrical, photobiological, thermal dissociation).

The hydrogen produced by these techniques requires purification, which impacts the economical feasibility. Therefore in practical applications the hydrogen is not expected to be of very high purity (>5N) and thus the storage materials need to be insensitive to these impurities.

The effect of gas impurities (H_2O, CxHy, H_2S, etc.) on the hydrogen storage capacity and the catalyst is often not considered as most research is performed under laboratory-conditions.

This implies small scale experiments under idealized conditions, no contaminations, and identical hydrogenation experiments, small amounts of materials, etc. Therefore it is interesting to investigate the mechanical stability, chemical stability, thermal conductivity and cycle life, because real life applications will operate under non-idealized conditions. Also the tolerance to impurities and contaminations, the adsorption/desorption kinetics under these conditions are properties that need to be considered

Hydrogen storage is a key issue in the success and realiza-tion of hydrogen technology and economy.
According to US DOE, the hydrogen-storage capacity target for commercializa-tion is 6.5wt% at the decomposition temperature between 60 and 120◦ C with high cycle life.

Although pure water contains 11.1wt% of hydrogen, its decomposition requires much thermal, electric, or chemical energy

pressurizedH2gas and cryogenic liquidH2pose safety and per-meation problems along with high cost, they do not meet future on-board applications goals set for hydrogen economy. Solid state hydrogen fuel storage either absorption in the interstices of metals and metallic alloys or adsorption on high surface area materials such as activated carbons gain the attention for pos-sible future hydrogen applications.