

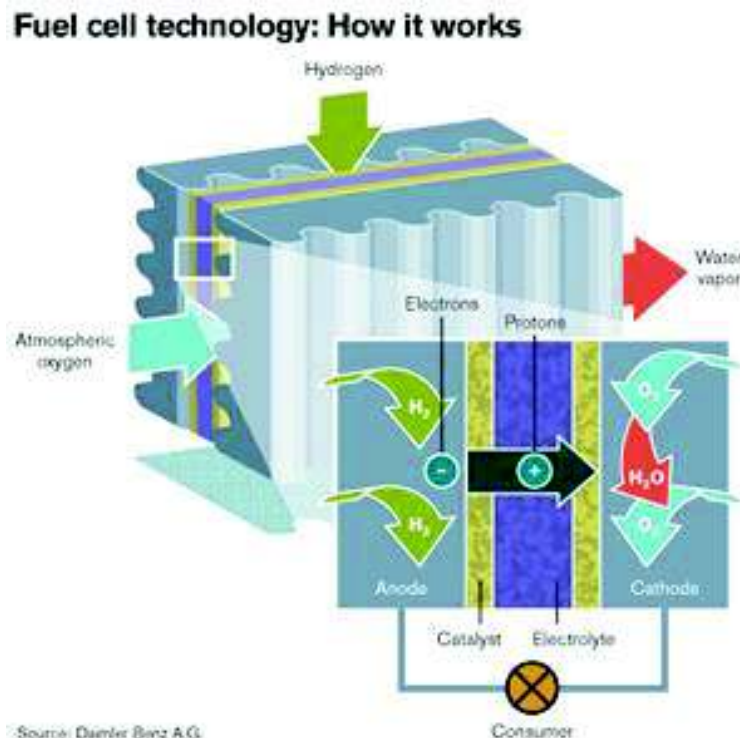
INTRO..

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



PRINCIPLES OF FUEL CELL

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.

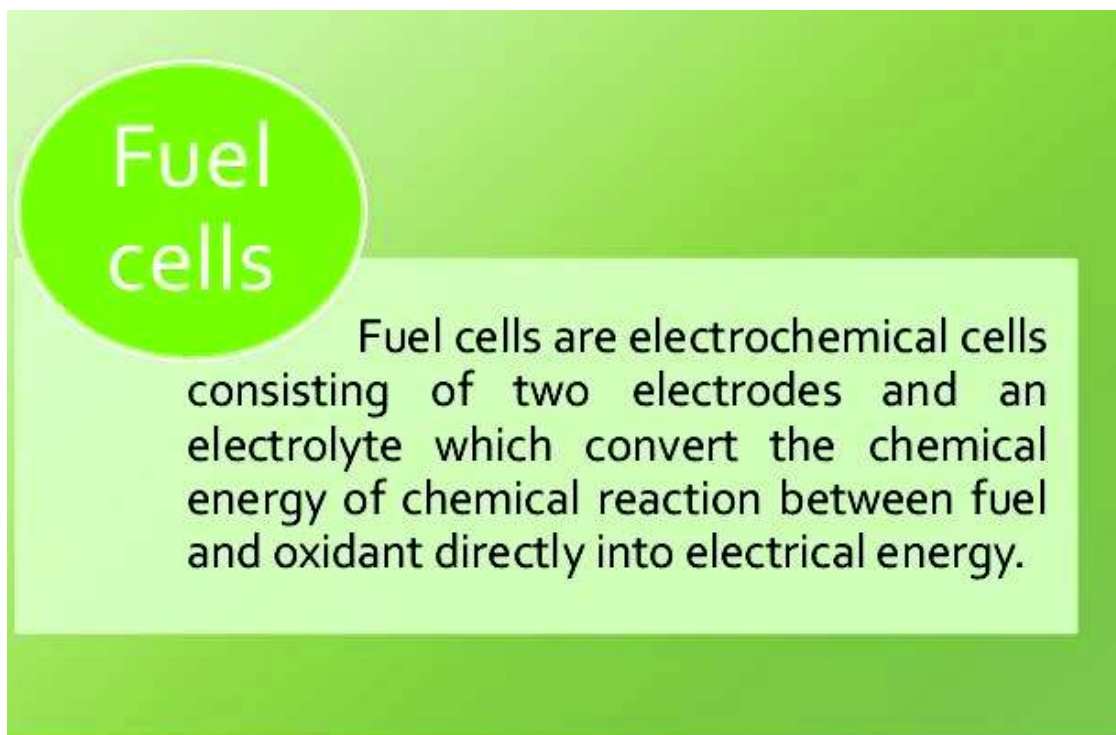
The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the

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 employ. 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.



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

Classification of Fuel Cells

- 1. Alkaline Fuel cell (AFC)**
- 2. Phosphoric Acid Fuel cell (PAFC)**
- 3. Molten Carbonate Fuel Cell (MCFC)**
- 4. Solid Oxide Fuel Cell (SOFC)**
- 5. Ion Exchange Membrane Fuel Cell (IEMFC)**
- 6. Bio molecule Fuel Cell (BFC)**

ALKALINE FUEL CELLS (AFC)

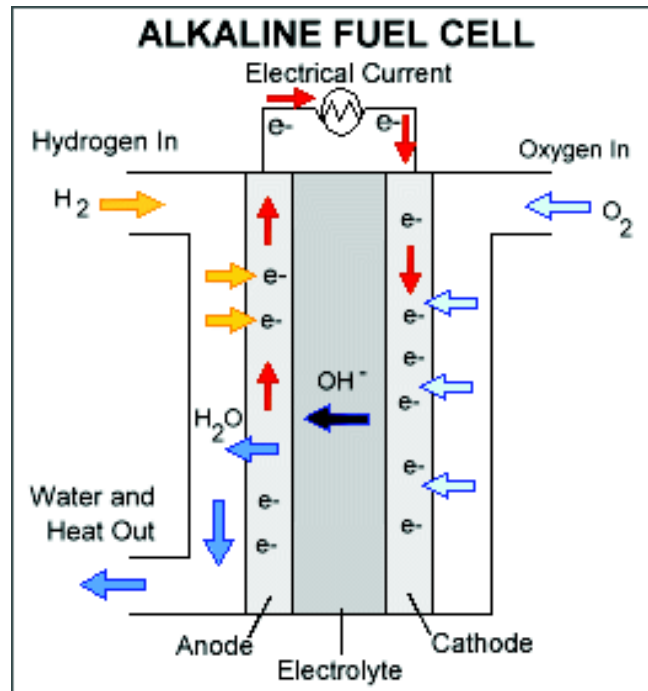
The alkaline fuel cell uses an alkaline electrolyte such as 40% aqueous potassium hydroxide. In alkaline fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.

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 100°C and 250°C (212°F and 482°F). However, more-recent AFC designs operate at lower temperatures of roughly 23°C to 70°C (74°F to 158°F).

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 potassium 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: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

Cathode Reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$



PHOSPHORIC ACID FUEL CELL (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

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"

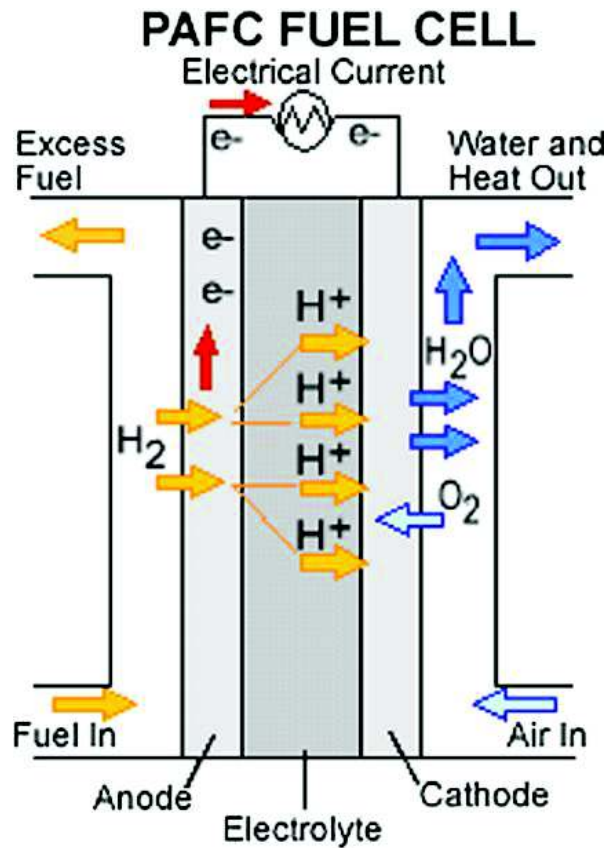
**Of modern fuel cells. It is one of the most mature cell types and the first to be
used commercially, with over 200 units currently in use.**

**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.**



MOLTEN CARBONATE FUEL CELLS (MCFC)

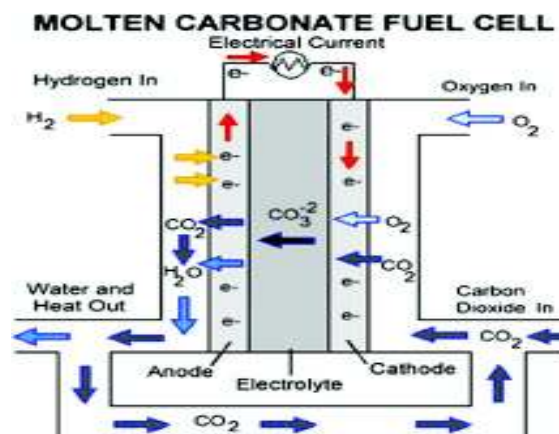
The molten carbonate fuel cell uses a molten carbonate salt as the electrolyte. It has the potential to be fuelled with coal-derived fuel gases, methane or natural gas. These fuel cells can work at up to 60% efficiency

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 aluminium oxide (LiAlO₂) matrix. Since they operate at extremely high temperatures of 650°C and above, no precious 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.

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.



Anode Reaction: $\text{CO}_3^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$

Cathode Reaction: $\text{CO}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$

Overall Cell Reaction: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

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.

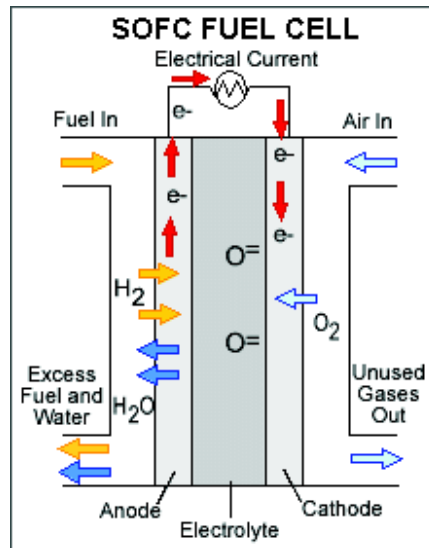
Efficiencies of around 60 per cent and are expected to be used for generating electricity and heat in industry and potentially for providing auxiliary power in vehicles.

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.

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 800°C that have fewer durability problems and cost less.



ION EXCHANGE MEMBRANE FUEL CELL (IEMFC)

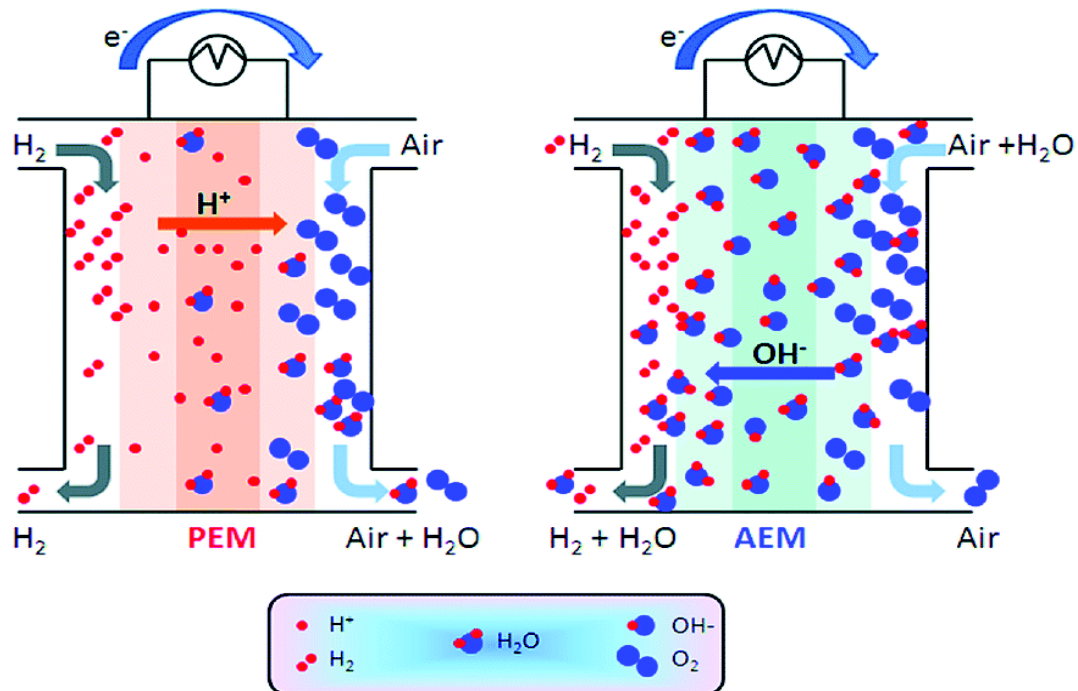
An ion exchange membrane fuel cell includes a module enclosing a membrane electrode diffusion assembly which has an active area defined by a surface area, and which produces an average current density of at least about 350 mA per square centimeter of surface area when supplied with a dilute fuel at a nominal voltage of about 0.5 volts.

What does ion exchange membrane fuel cell contains:

An ion exchange membrane fuel cell, comprises multiple modules each enclosing a membrane electrode diffusion assembly, and wherein at least membrane fuel cell, by hand, while the remaining modules continue to operate, and wherein each of the modules produce heat energy during operation, and wherein each of the modules have an anode heat sink which removes a preponderance of the heat energy generated by the respective modules

APPLICATIONS

The major application of this fuel cells focuses on transportation primarily because of their potential impact on the environment, e.g. the control of emission of the green house gases (GHG). Other applications include distributed/stationary and portable power generation. Most major motor companies work solely on this fuel cells due to their high power density and excellent dynamic characteristics as compared with other types of fuel cells.[44] Due to their light weight, IEMFCs are most suited for transportation applications. IEMFCs for buses, which use compressed hydrogen for fuel, can operate at up to 40% efficiency. Generally IEMFCs are implemented on buses over smaller cars because of the available volume to house the system and store the fuel. Technical issues for transportation involve incorporation of PEMs into current vehicle technology and updating energy systems. Full fuel cell vehicles are not advantageous if hydrogen is sourced from fossil fuels; however, they become beneficial when implemented as hybrids. There is potential for IEMFCs to be used for stationary power generation, where they provide 5 kW at 30% efficiency



BIOMOLECULE FUEL CELL (BFC)

A biomolecule fuel cell is a bio-electrochemical system that drives an electric current by using bacteria and mimicking bacterial interactions found in nature. MFCs can be grouped into two general categories: mediated and unmediated. The first MFCs, demonstrated in the early 20th century, used a mediator: a chemical that transfers electrons from the bacteria in the cell to the anode. Unmediated MFCs emerged in the 1970s; in this type of MFC the bacteria typically have electrochemically active redox proteins such as cytochromes on their outer membrane that can transfer electrons directly to the anode. In the 21st century MFCs started to find a commercial use in wastewater treatment.

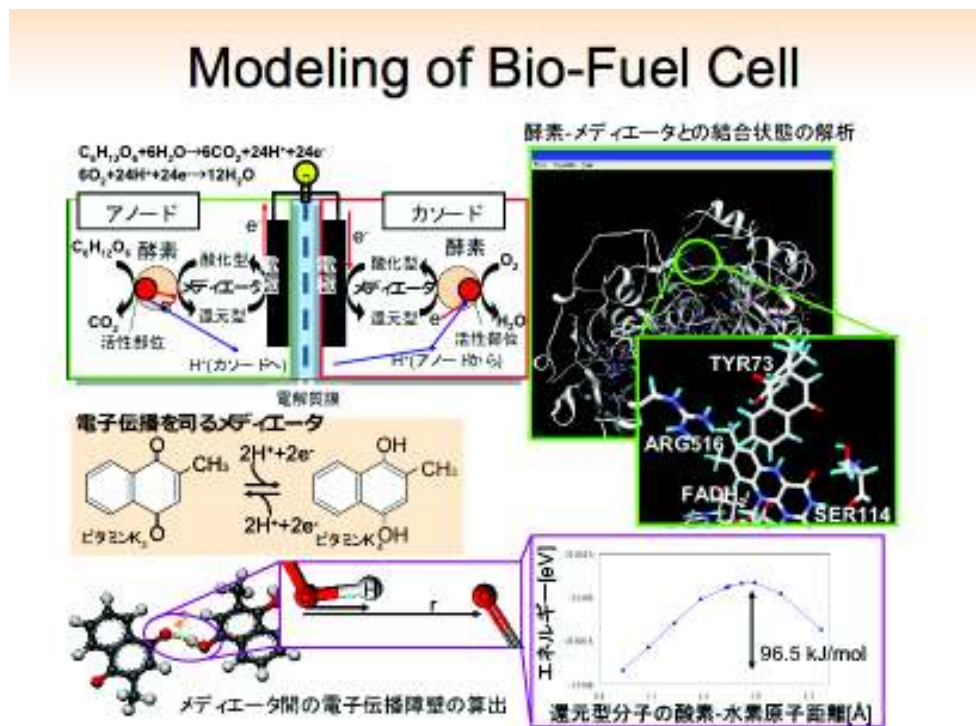
A microbial fuel cell (MFC) is a device that converts chemical energy to energy by the action of microorganisms. These electrochemical cells are constructed using either a bioanode and/or a biocathode. Most MFCs contain a membrane to separate the compartments of the anode (where oxidation takes place) and the cathode (where reduction takes place). The electrons produced during oxidation are transferred directly to an electrode or, to a redox mediator species. The electron flux is moved to the cathode. The charge balance of the system is compensated by ionic movement inside the cell, usually across an ionic membrane. Most MFCs use an organic electron donor that is oxidised to produce CO₂, protons and electrons. Other electron donors have been reported, such as sulphur compounds or hydrogen. The cathode reaction uses a variety of electron acceptors that includes the reduction of oxygen as the most studied process. However, other electron acceptors have been studied, including metal recovery by reduction, water to hydrogen, nitrate reduction and sulphate reduction.

Power Generation

MFCs are attractive for power generation applications that require only low power, but where replacing batteries may be impractical, such as wireless sensor networks.

Virtually any organic material could be used to feed the fuel cell, including coupling cells to wastewater treatment plants. MFCs are clean and the best method of energy production. Chemical process wastewater and synthetic wastewater have been used to produce bioelectricity in dual- and single-chamber mediator less MFCs (uncoated graphite electrodes).

Higher power production was observed with a biofilm-covered graphite anode. In theory, an MFC is capable of energy efficiency far beyond 50%. Rozendal obtained energy conversion to hydrogen 8 times that of conventional hydrogen production technologies.





Green Chemistry Reactions and Reagents:

GREEN CHEMISTRY

Green is a strong colour. Green is the colour of chlorophyll, and green is the colour of money. Being green has long been a battle cry of Environmental activists, and being green has become an important marketing tool for businesses. And for chemists, it is becoming increasingly important to be green by applying the principles of green chemistry to all facets of the chemical sciences: basic and applied research, production, and education.

Green chemistry, also known as sustainable chemistry, is an umbrella concept that has grown substantially since it fully emerged a decade ago. By definition, green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.

Last month, some 200 scientists and policymakers from more than 30 countries gathered on the campus of the University of Colorado, Boulder, to discuss the progress and prospects of green chemistry.

A BOULDER VISIO



Introduction

Over the past few years, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment. This new approach has received extensive attention and goes by many names including Green Chemistry, Environmentally Benign Chemistry, Clean Chemistry, Atom Economy and Benign by Design Chemistry. Under all of these different designations there is a movement toward pursuing chemistry with the knowledge that the consequences of chemistry do not stop with the properties of the target molecule or the efficacy of a particular reagent.

One obvious but important point- nothing is benign. All substances and all activity have some impact just by their being. What is being discussed when the term benign by design or environmentally benign chemistry is used is simply an ideal. Striving to make chemistry more benign wherever possible is merely a goal. Much like the goal of "zero defects" that was espoused by the manufacturing sector, benign chemistry is merely a statement of aiming for perfection.

While it has already been mentioned that nothing is truly environmentally benign, there are substances that are known to be more toxic to humans and more harmful to the environment than others. By using the extensive data available on human health effects and ecological impacts for a wide variety of individual chemicals and chemical classes, chemists can make informed choices as to which chemicals would be more favourable to use in a particular synthesis or process. Simply stated, Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstock, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment.

Green Chemistry is an approach to the synthesis, processing and use of chemicals that reduces risks to humans and the environment. Much innovative chemistry has been developed over the past several years that are effective, efficient and more environmentally benign. These approaches include new synthesis and processes as well as new tools for instructing aspiring chemists how to do chemistry in a more environmentally benign manner.

Solvent Free Reactions

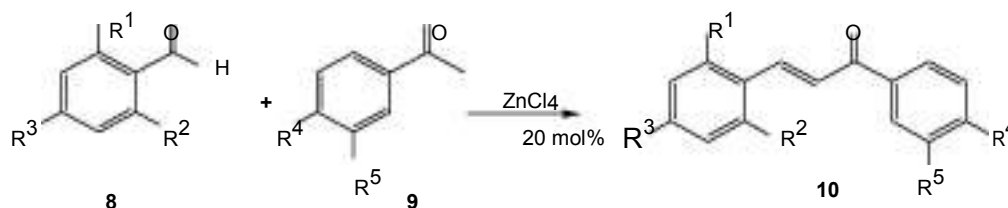
Environmental concerns in synthetic chemistry have led to a reconsideration of reaction methodologies. This has resulted in investigations into atom economy, the use of supercritical CO₂, ionic liquids, and other procedures to reduce the disposal problems associated with most chemical reactions. One obvious route to reduce waste entails generation of chemicals from reagents in the absence of solvents. Therefore the design of green processes with no use of hazardous and expensive solvents, e.g., “solvent-free” reactions, has gained special attention from synthetic organic chemists. As a result, many reactions are newly found to proceed cleanly and efficiently in the solid state or under solvent-free conditions.

Less chemical pollution, lower expenses, and easier procedures are the main reasons for the recent increase in the popularity of solvent-free reactions.

While an obvious approach to chemical synthesis, there are many problems associated with this approach, the chief of which is the role of diffusion/interactions between reactants. Further, it is never clear that the reactions in the solid state will generate the same products as those found in the presence of solvents. Generally, Michael additions are conducted in a suitable solvent in the presence of a strong base either at room temperature or at elevated temperatures. Due to the presence of the strong base, side reactions such as multiple condensations, polymerizations, rearrangements and retro-Michael additions are common. These undesirable side reactions decrease the yields of the target adduct and render their purification difficult. Better results can be obtained by employing weaker bases such as piperidine, quaternary ammonium hydroxide, tertiary amines etc. There have been some reports on Michael reactions catalyzed by potassium carbonate in organic solvents, and water in the presence of surfactants or phase-transfer catalysts. To a large extent, mild bases restrain the formation of side products, thus improving the yield of the desired Michael adducts. Recently, non-conventional procedures like conducting the reaction on the surface of a dry medium or under microwave irradiation were found to facilitate the Michael reaction. For the purposes of eco-friendly “Green Chemistry”, a reaction should ideally, be conducted under solvent-free conditions with minimal or no side-product formation and with utmost atom-economy. Even though microwave-assisted solvent-free Michael addition reactions on BiCl₃ or CdI₂, EuCl₃, CeCl₃·5H₂O, and alumina surfaces are known. Rao and Jothilingam have studied

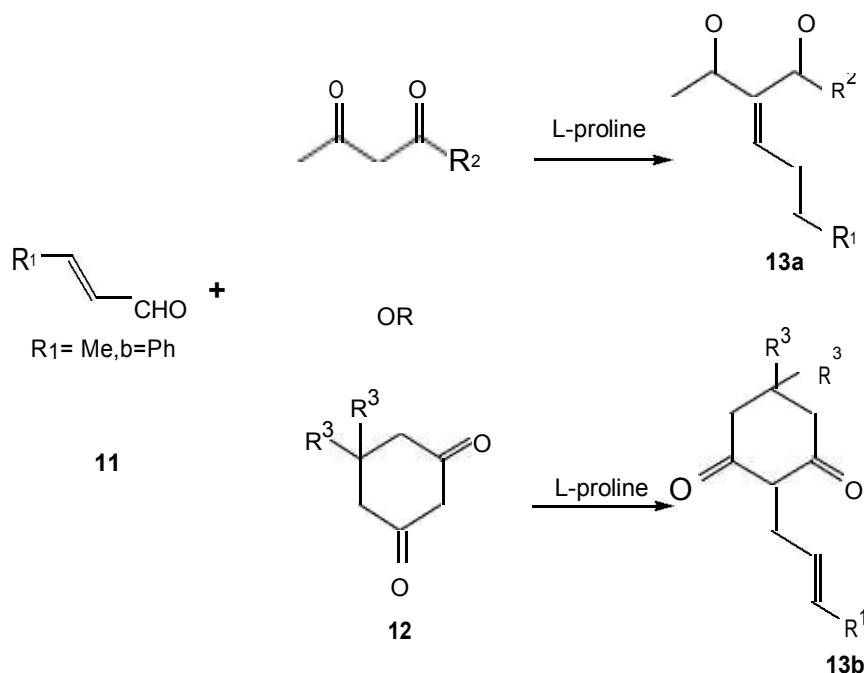
Michael addition of some active methylene compounds (**2a-f**) to four Michael acceptors (**1a-f**) viz (i) 1, 3-diphenyl-2-propene-1-one (chalcone), (ii) phenyl vinyl ketone, (iii) 1, 4-diphenyl-2-butene-1,4-dione (dibenzoyl ethylene), and (iv) methyl vinyl ketone on potassium carbonate surface under microwave irradiation

Loh et al.⁵¹ have developed an efficient and environmentally friendly protocol for Mukaiyama aldol reaction of ketene silyl acetyls (**5**) with different aldehydes (**6**) in the presence of a catalytic amount of DBU under solvent free conditions at room temperature (Scheme 2). 15 mol% of the catalyst (zirconium chloride) yielded the 1, 4-Michael adduct along with the aldol product (Scheme 3).



Scheme 3

A series of conjugated dienones and enones which were synthesized by a reaction of both conjugated and simple aldehydes, respectively, with 1,3-dicarbonyl compounds (**11**) and aldehydes (**12**) under solvent-free conditions at room temperature in the presence of 10 mol % of L-proline as catalyst. All the products were obtained selectively as E-isomers with the exception of allyl acetoacetate which gave a mixture of both E and Z isomers with an E-isomer in the predominant form.



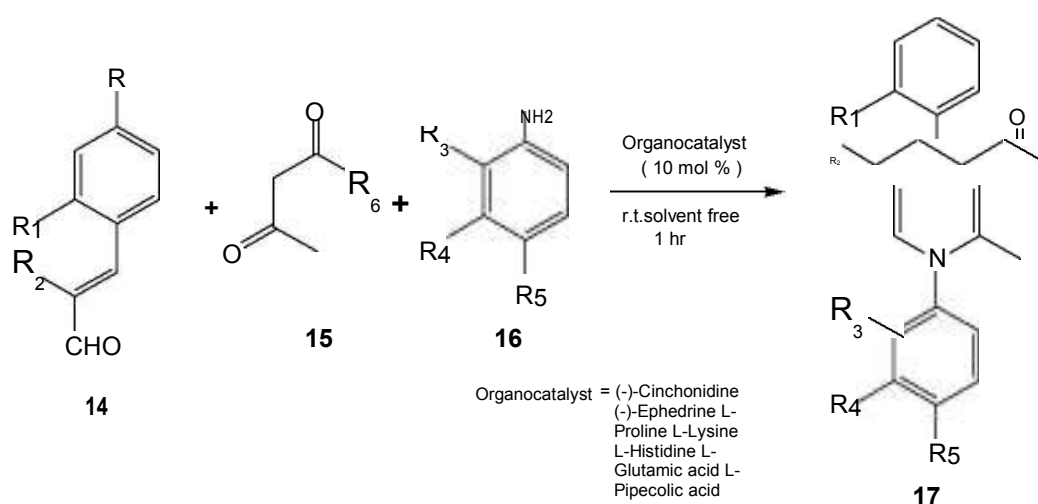
R₂=OMe, OEt, OCMe₃, Me, Ph, OCH₂-CH=CH₂

R₃= H, Me

The multi-component reactions (MCRs) involve three or more reactants which are combined together in a single reaction flask to generate a product incorporating most of the atoms contained in the starting material. Due to intrinsic atom economy,

selectivity underlying such reaction, simpler procedure, equipment, time and energy saving as well as environmental friendliness MCRs are gaining much importance in both academia and industry. 1, 4-Dihydropyridines (1, 4-DHPs) and their derivatives are important class of bioactive molecules in the field of drug and pharmaceuticals. These compounds are well known as calcium channel modulators and have emerged as one of the most important classes of drugs for the treatment of hypertension. 1,4-Dihydropyridine derivatives possess a variety of biological activities such as HIV protease inhibition MDR reversal, adiolprotection, vasodilator, antitumour, bronchodilator and hepatoprotective activity.

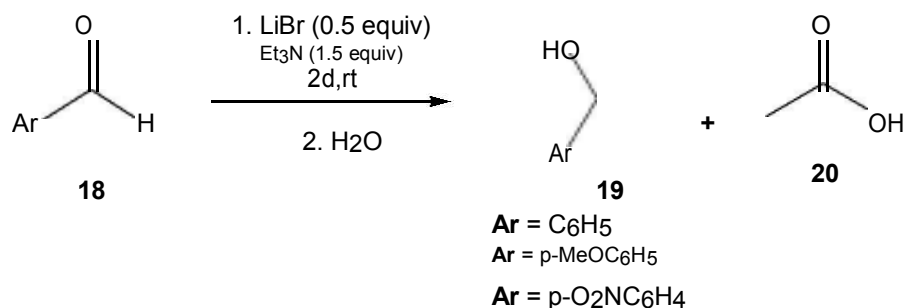
The catalytic property of small organic molecules like cinchona alkaloids and amino acids have been shown as quite promising and highly efficient organocatalysts for multi-component reactions.



Scheme 5

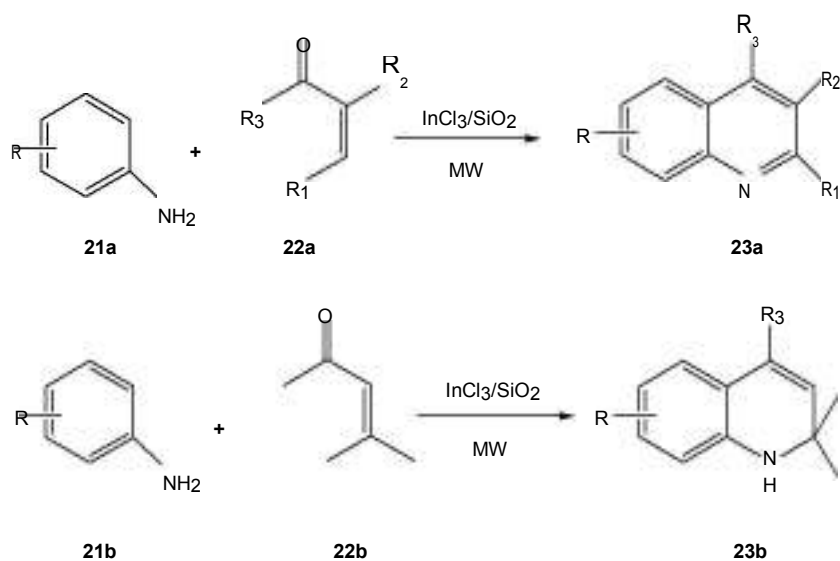
Recent developments in the classical Cannizzaro reaction involve the use of various Lewis acidic reagents, heterogeneous catalytic systems, and

supercritical solvents. Mojtahedi et al. reported that a selective conversion of aldehydes (**18**) with no α -hydrogen to their respective alcohols (**19**) and/or carboxylic functionalities (**20**) of choice is practically attainable under catalysis of lithium bromide (LiBr) in the presence of triethylamine (Et_3N) at room temperature in a solvent free environment (Scheme 6).



Scheme 6

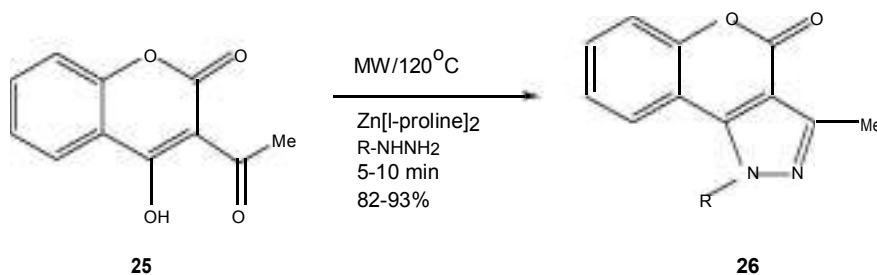
Ranu et al. reported a convenient and efficient procedure for the synthesis of quinolines and dihydroquinolines (**23a**, **23b**) by a simple one-pot reaction of anilines (**21a**, **21b**) with alkyl vinyl ketones (**22a**, **22b**) on the surface of silica gel impregnated with indium(III) chloride under microwave irradiation without any solvent (Scheme 7).



Scheme 7

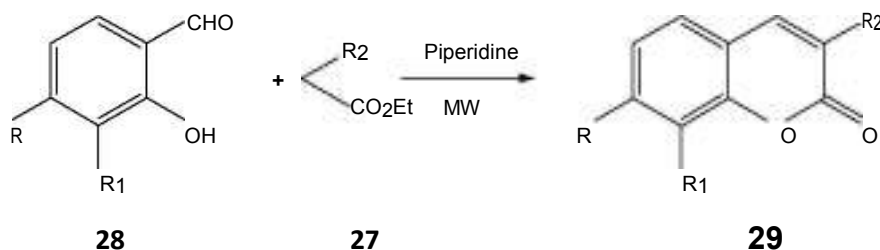
Manvar et al. described the hydrazones of 3-acetyl-4-hydroxycoumarin (**24**) undergo ring cyclization to give 3-methyl-1-substituted phenyl-1H-chromeno [4,3-c]pyrazol-4-ones (**25**) under the influence of microwave irradiation by using $\text{Zn}[\text{l-proline}]_2$, a novel Lewis acid catalyst. The overall yields of the products were found to

be 82–93%. Without use of the catalyst, no reaction progress was observed. The reusability of the catalyst was also checked and found up to seven cycles (Scheme 8).



Scheme 8

Villemin and Martin have synthesized 5-nitrofurfurylidine by the condensation of 5-nitrofurfuraldehyde with active methylene compounds under microwave irradiation using K₁₀ and ZnCl₂ as a catalyst. The useful synthesis coumarins via the microwave promoted Pechmann reaction has been extended to solventless systems wherein salicylaldehydes (**28**) undergo Knoevenagel condensation with a variety of ethyl acetate derivatives (**27**) under basic conditions (piperidine) to afford coumarins (**29**) (Scheme 9).



Scheme 9

Ballini et al. reported the Conjugate addition of both linear and cyclic α -nitro ketones (**30**) to conjugated enones (**31**) under heterogenous, solvent-free and mild acidic conditions by mixing at room temperature stoichiometric amounts of substrates with silica (silica/substrate = 350 mg mmol⁻¹) and leaving the mixture at room temperature for the suitable reaction time giving good yields of 2-nitro-1,5-diones(**32**) and it is worthy to note that no products arising from the cleavage of α -nitro cycloalkanones were observed under these reaction conditions

Microwave induced green synthesis

With increasing community concern over possible influences of chemicals and chemical practices on the environment microwave induced green synthesis has received considerable attention for direct, efficient, and environmentally unobtrusive synthesis. The first microwave-assisted organic syntheses was reported in 1986. By using this technique, considerably shorter reaction times than normal had been obtained for common organic transformations such as esterification, hydrolysis, etherification, addition, and rearrangement. Inadequate controls in the rudimentary equipment employed, however, generated hazards, including explosions. In the electromagnetic radiation spectrum, microwaves (0.3 GHz–300 GHz) lie between radio wave (R_f) and infrared (IR) frequencies with relatively large wavelength. Microwaves, a non-ionizing radiation incapable of breaking bonds, are a form of energy and not heat and are manifested as heat through their interaction with the medium or materials wherein they can be reflected (metals), transmitted (good insulators that will not heat) or absorbed (decreasing the available microwave energy and rapidly heating the sample). Microwave reactions involve selective absorption of electromagnetic waves by polar molecules, non-polar molecules being inert to microwaves. When molecules with a permanent dipole are submitted to an electric field, they become aligned and as the field oscillates their orientation changes, this rapid reorientation produces intense internal heating. The main difference between classical heating and microwave heating lies in core and homogenous heating associated with microwaves, whereas classical heating is all about heat transfer by preheated molecules. In microwave induced organic reactions, the reactions can be carried out in a solvent medium or on a solid support in which no solvent is used. For reactions in a solvent medium, the choice of the solvent is very important.

Microwave chemistry generally relies on the ability of the reaction mixture to efficiently absorb microwave energy, taking advantage of “microwave dielectric heating” phenomena such as dipolar polarization or ionic conduction mechanisms. In most cases this means that the solvent used for a particular transformation must be microwave absorbing. The ability of a specific solvent to convert microwave energy into heat at a given frequency and temperature is determined by the so-called loss tangent ($\tan \delta$), expressed as the quotient, $\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the dielectric loss, indicative of the efficiency with which electromagnetic radiation is converted into heat, and ϵ' is the dielectric constant, describing the ability of molecules to be polarized by the electric field. A reaction medium with a high $\tan \delta$ at the standard operating frequency of a microwave synthesis reactor (2.45 GHz) is required for good absorption and, consequently, efficient heating.

A natural insecticide with anti-juvenile hormone activity in some insects, on basic Montmorillonite K10. It is a cleaner chemical reaction and forms an important component of Green Chemistry. The reported synthesis, a clay-catalysed, microwave-assisted condensation of sea amol with 3-methyl-2-butenal, is a unique example of Green Chemistry reaction.

