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Ceramics and glasses for energy technologies

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Abstract: Energy technology is one the high priority areas of research and development, primarily due to rapid depletion of the existing resources of energy and their deleterious effect on the environment. Several of the emerging energy technologies, having higher conversion efficiency and higher energy/ power density are based on some of the unique properties of a few ceramic and glassy materials both in the areas of energy conversion and storage. Examples are Solid Oxide Fuel Cell (SOFC) based on oxygen ion conducting solid electrolyte and electronically conducting anodic and cathodic current collectors, lithium ion battery in which lithium intercalated cobalt oxide is used as the cathode material, sodium sulphur battery for which sodium ion conducting beta alumina is the electrolyte material, energy harvesting based on piezoelectric ceramics and clean coal technology, which make use of the porosity and high temperature resistance of silicon carbide ceramics. Their basic principles and application potentialities are briefly discussed here with emphasis on the materials aspect in each case.

Keywords: Energy, environment, ceramics, glasses, solid oxide fuel cell, lithium ion battery, sodium-sulphur battery, energy harvesting, clean coal technology.

1. Introduction

Human civilization has travelled a long distance since the pre-historic days. It has reached the current stage primarily because there has been availability of different sources of energy at different stages of its journey. Initially it was wood from the greeneries on the surface of the earth. At a later stage, it became the fossil fuels in the form of solid coal, liquid crude oil or the gaseous fuel e.g. natural gas; all from the underground. Even today these fossil fuels continue to be the major sources of energy for the sustainable growth of human civilization. It is evident from Fig. 1 that the world energy consumption has continuously increased over the years, which is around 5 times in a period of 50 years (1965-2015).

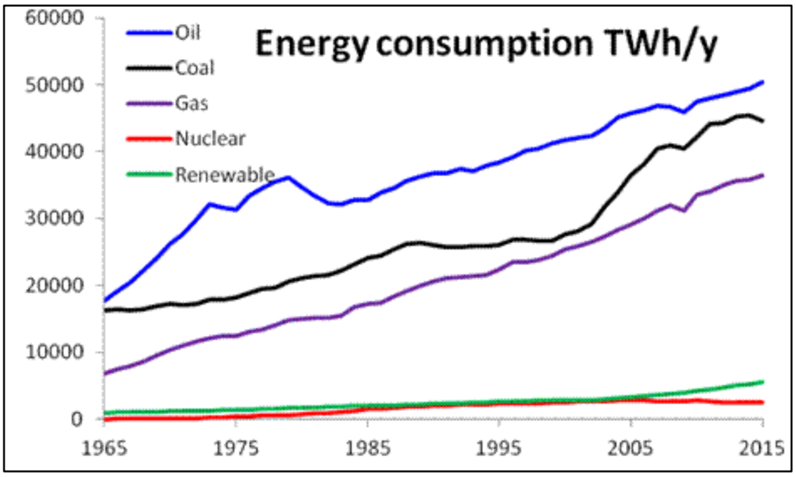


Fig. 1: World energy consumption over a period of 50 years [1]

The role of energy is so important that 'per capita energy consumption' has been recognised as one of the parameters to measure the extent of socio-economic development of a country. Fig. 2 provides the plot of this parameter for a large number of countries including India. Both in terms of social progress and per capita energy consumption, our country is placed quite low, particularly when compared with the so called developed countries. The ever-increasing demand of energy for the desired socio-economic development has given rise to a different type of challenges to the scientist and technologists.

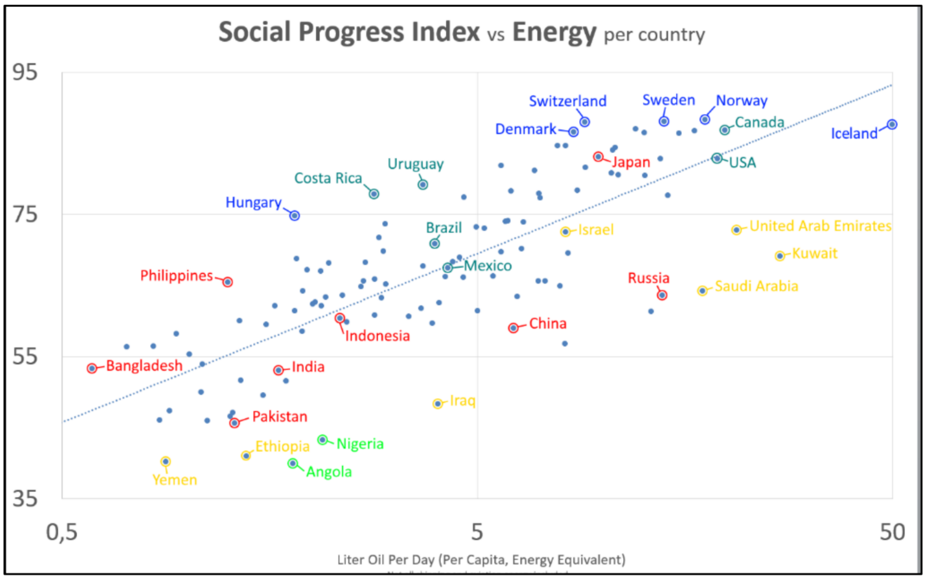


Fig. 2: Social progress index against per capita energy consumption for different countries [2].

The source of fossil fuel is not unlimited and is depleting at a dangerously high rate [3]. Therefore, alternative sources of energy must be identified and the necessary technologies have to be developed for harnessing them in an economic manner. This particular activity has been going on for the last several decades and has led to the development of a number of alternatives known as the "Renewable Energy" sources. As the name suggests these energy sources are either non-ending or continuously renewed through natural processes. For example, solar, wind and wave energies appear to be non-ending as long as human civilization exists on this planet. In addition there are other strategies to reduce the consumption of fossil fuels by increasing the energy conversion efficiencies of the existing technologies based on fossil fuels. This leads to less fuel consumption for the generation of same amount of energy and thereby saving the fuel for extended period of use. Another area where energy technologies are becoming more and more important is the environmentalconcern. All fossil fuels basically contain hydro-carbons and therefore produce significant amounts of greenhouse gas, CO_2 in particular, when burnt for the generation of usable form of energy. For this reason, uses of fossil fuels are more and more discouraged. Instead hydrogen gas, which produces non-polluting water vapour as the product of combustion, is slowly coming up as the preferred fuel of the future. This requires development of alternative technologies for cost effective generation of usable form of energy such as electricity. Automobile sector, which uses liquid fossil fuel (petrol / diesel), is one of the most polluting sectors and therefore extensive research and development are in progress for the development of electric vehicles either based on rechargeable battery or fuel cells using hydrogen as the fuel or supercapacitors, which is a device for storing large enough quantity of electrical energy.

All these developing technologies use different kinds of functional materials including ceramics and glasses, which will be discussed in details in the following sections.

By definition, ceramics are inorganic, non-metallic materials with relatively high melting points and therefore are useful for high temperature applications. From the chemistry point of view, they are composed of more than one element and may be oxides, carbides, nitrides, borides, silicides etc. Examples are Al_2O_3, SiO_2, ZrO_2, MgO, TiO_2,SiC, Si_3N_4, ZrB_2, $MoSi_2$etc. Chemical bonds are either totally ionic, or combination of ionic and covalent. Mixed cationic compounds e.g. $3Al_2O_3.2SiO_2$ (mullite), $BaO.TiO_2$ (barium titanate), $NiO.Fe_2O_3$ (Ni-ferrite), YBa2Cu3O7-δ (yttrium barium cuprate) etc. are also quite common. These wide range of compounds possess many exotic properties in terms of electrical, magnetic, mechanical, chemical and optical effects leading to many different unconventional applications. Several of them are non-stoichiometric in nature and give rise to interesting electrical and catalytic properties. These so called 'Advanced Ceramics' may be categorised as Electro-ceramics, Structural Ceramics, Electronic substrate and Packages, Ceramic Dielectric, Piezoelectric Ceramics, Magnetic Ceramics Conducting Ceramics Automotive Ceramics, Aerospace Ceramics, Wear Resistant Ceramics, Cutting Tools, Optical Ceramics, Bio-ceramics and so on. Many of them are essential components of the devices, which are important in the area of renewable energy [4].

Examples of a few technologies in which ceramics and glasses play important roles include

1) Different Types of Fuel Cell.
2) Rechargeable Batteries with high energy density.
3) Energy Harvesting
4) Clean Coal Technology.

2. The Fuel Cell

Fuel Cell is an electrochemical device which generates electrical power continuously as a gaseous fuel is electrochemically burnt (oxidised) in a continuous manner. Research and Development on fuel cells are going on over a century. There are a large number of Hand Books, Review articles and Reports published during this period. A few of them are mentioned here [5-11].

As in any electrochemical deviceit is constituted of an electrolyte, anode and cathode. The electrolyte may be either a liquid or solid having purely ionic conductivity, the anode and the cathode on the other hand are gaseous in character. However, there are solid current collectors with electronic conductivity on both anodic and cathodic sides. Important characteristics of a fuel cell are:

i) It generates electricity.
ii) Unlike a battery, which is also an electrochemical device, it requires a continuous flow of reactants.
iii) A fuel cell uses gaseous hydrogen or hydrocarbon as the fuel. The use of hydrocarbon, however, requires a reformer, which converts hydrocarbon to hydrogen.

Both for battery and fuel cell the electromotive force of the device is related to the thermodynamic free energy change for the overall chemical reaction between the anodic and cathodic materials used.

The overall electrochemical reaction occurring in a fuel cell using hydrogen and oxygen as the reactants may be described as:

$$H_2 \text{ (fuel)} + O_2\text{/ Air (oxidant)} \longrightarrow W + Q + H_2O \text{ (product)} \quad (1)$$

where W is the rate of electrical work done by the system and Q is the rate of heat transferred into the system from the surroundings at constant pressure and temperature.

Based on the thermodynamic principle, the E_{ocv}, the open circuit voltage of the cell may be expressed as

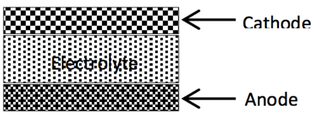
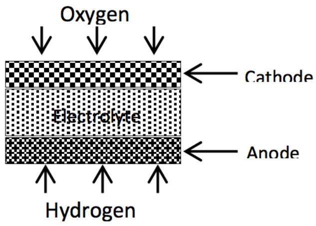
$$E_{ocv} = (RT/nF) \ln P_{O2}(oxidant)/P_{O2}(Fuel) \qquad (2)$$

This is known as the Nernst Equation in which R is gas constant, T is temperature, F is the Faraday constant, which is equal to 96,490 coulombs, 'n' is the number of electrons transferred during the reaction and P_{O2} refers to oxygen partial pressure. Based on the fact that the value of $n = 4$ for the above reaction (Eq. 1), the theoretical EMF of a fuel cell is controlled by the ratio of oxygen partial pressures of the fuel and the oxidant and its theoretical value under NTP condition is ~1.18 V and the theoretical conversion efficiency may be as high as 95% [12].

2.1 Fuel Cell and battery

The similarities and the differences between a battery and a fuel cell are listed in Table 1 below.

Table 1: Similarities and differences between Battery and Fuel Cell

Battery	Fuel Cell
	
Generate power electrochemically	Generate power electrochemically
Electrodes are the working materials	Gases are the working materials, Cathode and anode are current collectors
Electrodes get consumed	Electrodes do not get consumed
Limited period operation as long as the cathode and anode are available	Continue to operate as long as fuel gas and oxidant are supplied
Storage device	Conversion device

2.2. Heat Engine vs Fuel Cell

Coal is known to be the major fuel for generation of electricity particularly through thermal power plants (Fig. 1). Heat engine, which follows the Carnot's cycle, is the principle used in these plants. The efficiency of converting the chemical energy of the fuel to electricity is only of the order of 30-35%. Rest of the energy is wasted at different steps as the conversion is not direct but there are at least three steps namely: (i) chemical to thermal, (ii) thermal to mechanical, and (iii) mechanical to electrical as shown in Fig. 3 (below).

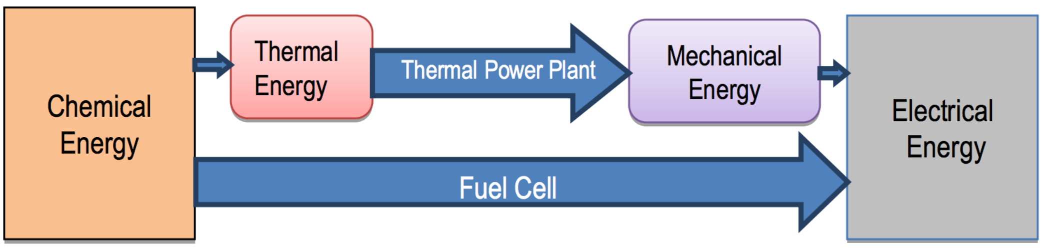


Fig. 3: Energy conversion steps in Thermal Power Plants and fuel cells.

Fuel cell, in comparison, is a single step process of converting chemical energy to electrical energy and therefore gives rise to very high plant efficiency of 60-65%. In addition to higher conversion efficiency, other advantages of the fuel cell are: (i) zero emission; both particulate and CO_2, (ii) no noise pollution, (iii) much less footprint, and (iv) an enabling technology acting as a technology platform which can promote several other related technologies.

2.3 Types of Fuel Cell and their Conversion Efficiency

There are at least six different types of fuel cell depending on the specific electrolyte and their operating temperature, which may vary from room temperature to 800ºC [5]. The electrolytes may be either KOH (Alkaline Fuel Cell) or phosphoric acid solution (Phosphoric Acid Fuel Cell). However, one of the most useful one is Polymer Exchange Membrane Fuel Cell (PEMFC), in which a specific polymer (NAFION) having high proton conductivity is used as the electrolyte. This operates at a temperature of 80-100ºC and isthe most attractive fuel cell for use in transportation (automobiles) sector. Other types of fuel cell are Molten Carbonate Fuel Cell (MCFC) operating at ~700ºC in which CO_3^{2-} ion is the conducting species and finally the Solid Oxide Fuel Cell (SOFC), which uses a high temperature oxide namely Yttria Stabilized Zirconia (YSZ) with significant oxygen ion conductivity as the electrolyte [13-15]. This is an all ceramic fuel cell with highest possible conversion efficiency among all the different fuel cellsas well as other forms of power generating systems(Fig. 4). It operates at around 800ºC and is suitable for stationary applications as distributed power plants. Originally it used to be operated at around 1000ºC due to relatively low ionic conductivity of the electrolyte [16,17]. Currently it has been brought down to ~800ºC through several innovative processing techniques particularly to reduce the electrolyte thickness. Of course, attempts are still being made to reduce the operating temperaturefurther [18].

It may be noted that Fuel cells have the highest energy conversion efficiency (40-65%) depending on the type and capacity, when SOFC is combined with a gas turbine, not only the plant capacity is enhanced but the efficiency may be increased to more than 70%. Incidentally, a gas turbine can be combined only with SOFC, because it operates at a high temperature and therefore the exhaust gas temperature is also high, suitable for operating a micro gas turbine. This possibility does not exist with any other type of fuel cell. Another very interesting characteristic of SOFC is that it can be operated with a very wide range of capacities, a few kilowatts to a few hundred kilowatts. Accordingly, SOFC plants are quite suitable as distributed power sources and can be deployed at the points of use. No transmission line would be required. Thermal power plants are economical only above hundred MW.

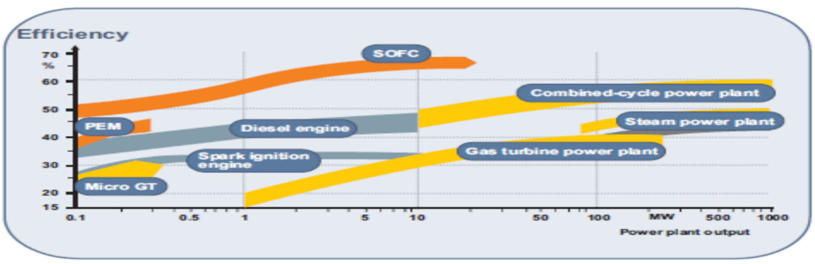


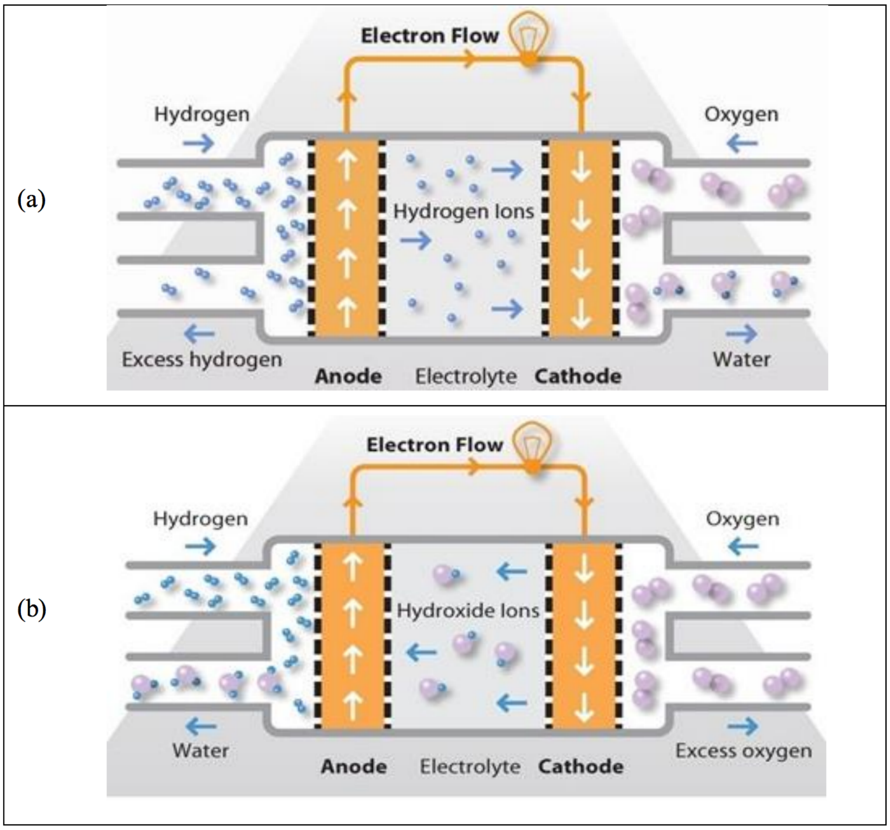
Fig.4: Efficiencies vs plant capacity for different types of power generating systems including fuel cells of two types (PEMFC and SOFC) [19].

2.4 Working Principle of Different Types of Fuel Cell

The working principles of four important types of fuel cell are presented in Fig. 5 [20]. It may be noted that in all these cases hydrogen gas is the fuel and oxygen is the oxidant. As mentioned earlier, alkali fuel cell uses a liquid electrolyte (KOH solution) with OH^-ion mobility operating in the temperature range 70-100ºC, PEM fuel cell uses solid polymer electrolyte with H^+ (proton) ion conduction with an operating temperature of 80-120ºC, molten carbonate fuel cell (MCFC) operates at a temperature 650-700ºC using a molten carbonate (eutectic mixture of lithium and potassium carbonates) electrolyte with CO_3^{2-} ion mobility and finally Solid Oxide Fuel Cell, which is an all ceramic fuel cell and on which our further discussion will follow, uses a high temperature resistant ceramic electrolyte namely Yttria Stabilized Zirconia (YSZ electrolyte with O^{2-} ion conduction.

2.5 Solid Oxide Fuel Cell

Our focus in this article is on Solid Oxide fuel Cell, all the components of which are either ceramics or glass. Extensive R&D has taken place over the last 50 years on this fuel cell and several hundred research and review papers have been published. A few representative ones are listed here [16,17,21-31]. The most common materials used in this fuel cell are:



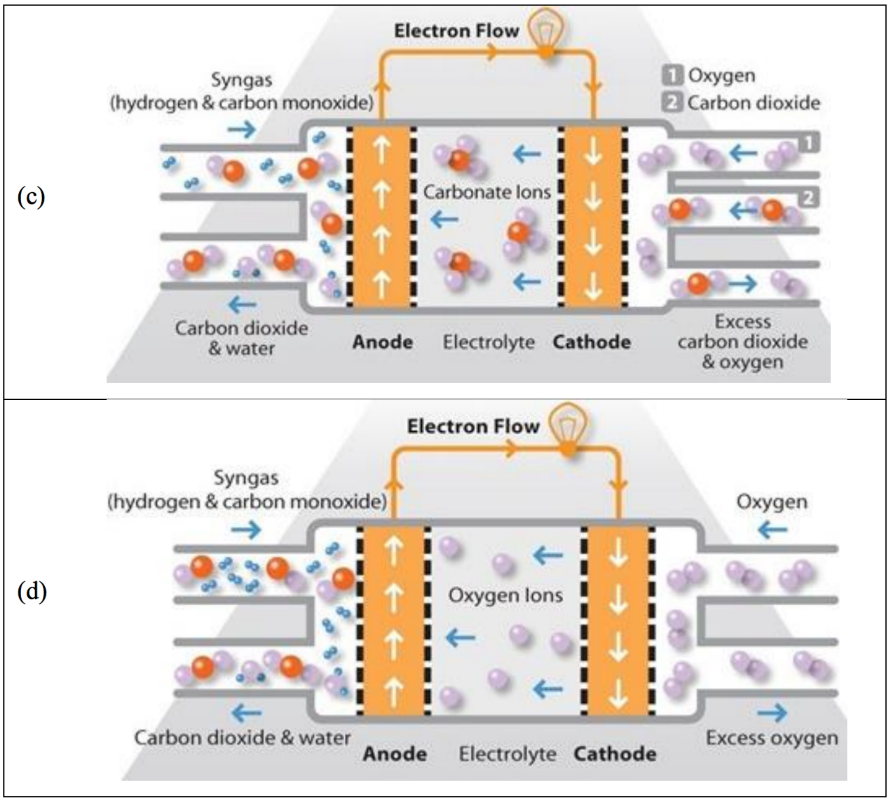


Fig.5: Pictorial representation of the working principle of four important types of fuel cell: Alkaline fuel cell (a), Polymer electrolyte membrane fuel cell (b), Molten carbonate fuel cell (c), and Solid oxide fuel cell (d) [20].

i) Electrolyte: 9mole% Y_2O_3 stabilised ZrO_2 (9YSZ)

ii) Cathodic current collector: $La_x Sr_{1-x}MnO_3$ (LSM)

iii) Anodic current collector: Ni-8YSZ Cermet

The present author and his group have carried out extensive research on the powder synthesis, sintering, microstructure development and related properties of the above materials [32-40]. A few years back Badwal and Foger made a comprehensive review of the emerging technologies and related materials in the area of energy conversion and storage [41]. Various other researchers together with this author's group have studied different alternative materials as well. This will be discussed later.

2.5 Design of SOFC

2.5.1 Material Selection

The basic concept of constructing a Solid Oxide Fuel Cell is to separate the fuel and oxidant compartments with a dense (non-porous) ceramic electrolyte, the most common is yttria stabilized zirconia (YSZ), which is known to be an excellent oxygen ion conductor. On the cathode side oxygen molecules when come in contact with the electrolyte gets ionized producing oxygen ion and migrates towards the anode side through the electrolyte. Similarly on the anode side when hydrogen gas comes in contact with the electrolyte gets ionized into hydrogen ion and reacts with oxygen ion migrating from the other side resulting into the formation of water vapour. Under any circumstances oxygen and hydrogen gases should not come in direct contact with each other to avoid possible explosion. The electrons to be supplied in the cathode side or to be extracted from the anode side for ionization of the respective gases are performed by two electronically conducting ceramics which are also designated as current collectors. The cathodic current collector which is in contact with oxygen needs to be an oxide so that it does not get further oxidised during use. The anodic material which is in contact with a highly reducing gas like hydrogen cannot be a simple oxide, which may get reduced by hydrogen. The material also needs to be electronically conducting. The best choice for the purpose is a cermet (composite material) of metallic nickel and YSZ, which is stable even in the presence of hydrogen. Since the complete system (combination of all the three materials) has to perform at high temperature, it is essential that their thermal expansion coefficients are comparable to each other. This is certainly not an easy situation to achieve.Summary of the property requirements of all the components are presented in Table 2, which includes three additional components e.g. interconnect, glass seal and interlayer, the purposes of which are discussed later.

2.5.2 Construction

There are two basic designs of SOFC as presented in Fig. 6: (i) Tubular and (ii) Flat plate or planardesign. In the former design, a tube like configuration having a multilayer wall structure consisting of the electrolyte and the two electrodes is fabricated. The inner wall is made of the cathode material and is having a larger thickness to support the rest of the layers which are only a few microns in thickness. In addition, there is a thin strip of interconnect material, which is electronically conducting and do not chemically react with any of the other three materials. The purpose of this interconnect is to connect cathode of one cell (tube) to the anode of the next cell, which is stacked over the first tube (cell). In an actual plant, a large number of such tubes (up to 2 meters long) are stacked both side wise and vertically so that each cell is connected both in series and parallel to get higher voltage as well as draw large current from the stack. Such a stacking is necessary because each cell can generate less than 1 Volt (~ 0.7 V). This particular design was originally developed by Westinghouse, USA and later it was transferred to Siemens, Germany. They fabricated a large number of prototype units with a maximum capacity of 250 kW and demonstrated at different parts of the world using hydrogen as well as natural gas as the fuel. Unfortunately, it could not achieve the required cost effectiveness and therefore the particular design is discontinued. One of the great advantages of this design is that the oxidant and fuel compartments are easily separated; one flows through the inner core of the tube and the other flows through the outside.

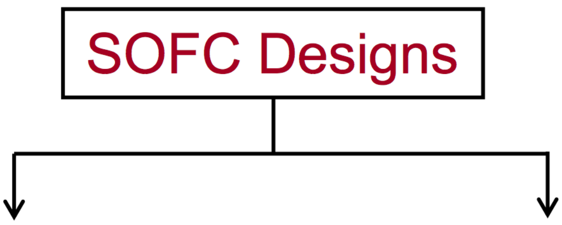
Major developmental work has now shifted to planer design in which all the components are in the form of flat plates or sheets except the inter-connect, which is relatively thick and is grooved on both sides allowing the flow of fuel and oxidant (either oxygen or air). It may be noted that the grooves on either side are at right angle to each other for better connectivity to the external pipeline without the possibility of mixing with each other.

Table 2: Summary of the property requirements for different components of SOFC

Sl. No.	Functional Layer	Property Requirements
1.	Electrolyte	i) Purely ionic conductor. Sufficient conductivity at the operating temperature. ii) Full densification without any pore iii) As thin as possible to reduce internal resistance iv) Chemical stability in contact with both oxidizing and reducing atmospheres. v) Thermal expansion coefficient comparable with other components.

2.	Cathode	i) Purely electronic conductivity ii) Porous structure iii) Chemical stability in contact with the electrolyte and in highly oxidizing atmosphere. iv) Thermal expansion coefficient must be comparable with other components.
3.	Anode	i) Mostly electronic conductor with small amounts of ionic conductivity. ii) Porous structure. iii) Chemical stability in contact with the electrolyte and in highly reducing atmosphere. iv) Thermal expansion coefficient must be comparable with other components.
4.	Interconnect	i) Purely electronic conductivity ii) Fully Dense iii) Grooved on both sides in perpendicular directions. iv) Thermal expansion coefficient must be comparable with other components
5.	Glass Seal	i) Electrically insulating. ii) A glassy material with relatively high softening point. iii) Should get partially crystalized during cooling iv) Capable of thermal cycling v) Thermal expansion coefficient must be comparable with other components
6.	Interlayer	i) Electronically conducting ii) Should have nano-porous structure. iii) Chemically stable in contact with electrolyte and the electrodes.

The planar design may be constructed in different ways. Two of them are shown here. In the first case the thickness of the electrolyte is more than either the cathode or the anode. This is known as the 'electrolyte supported'. In the second case, which is currently more popular than the others, the thickness of the anode is greater than the other two. There are different techniques for fabrication of these layers. Thicker layers are fabricated by calendaring (rolling) or multilayer tape casting followed by sintering. Thinner layers are normally deposited by screen printing or plasma spray or sputter coating.



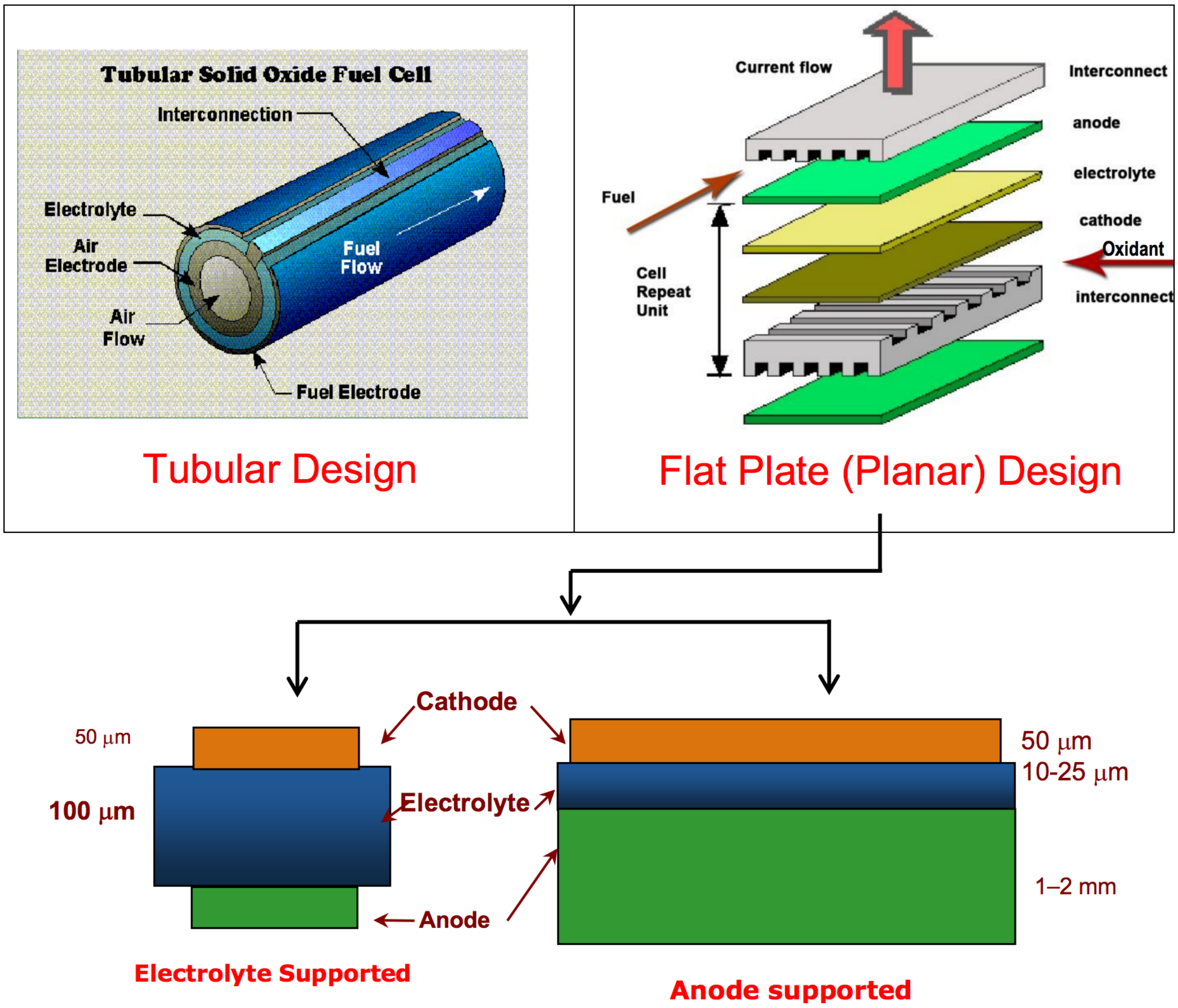


Figure 6: Different designs of SOFC [Adapted from Refs. 42&43]

2.6 Details of single cells of planar configuration

An exaggerated view of the cross section of a single unit (cell) of planer SOFC is presented in Fig. 7. The most important component is obviously the YSZ electrolyte layer (yellow in color). This is an oxygen ion conducting material; the direction of their movement is shown by the arrows (from cathode to anode). This layer is normally quite thin; of the order of 10-20µ and is fully dense (pore free). Oxygen movement takes place through lattice migration. No molecular diffusion of the gases are allowed, which may lead to explosion. On the anode side the reactions involved with both type of fuels namely hydrogen and carbon monoxide have been shown as this is the only type of fuel cell in which both these gases can be used as the fuel. Both cathode and anode layers are porous in nature so that the gaseous oxygen and hydrogen cancome in contact with the electrolyte layer. In fact it is the triple point contacts (electrolyte, porous cathode or anode and the gaseous oxidant or fuel gas) where electron transfers take place; either oxygen atom is ionized to oxygen ion (at the cathode) or oxygen ion releases its electrons to be captured by the anode. These electrons flow through the external circuit giving rise to electrical current. Thinner is the electrolyte layer, lower is the internal resistance of the cell facilitating drawing of higher current in the external circuit. In addition to the three layers mentioned above, one more layer of grooved interconnect (Fig. 6) is also essential for making a series connection of the individual cells.

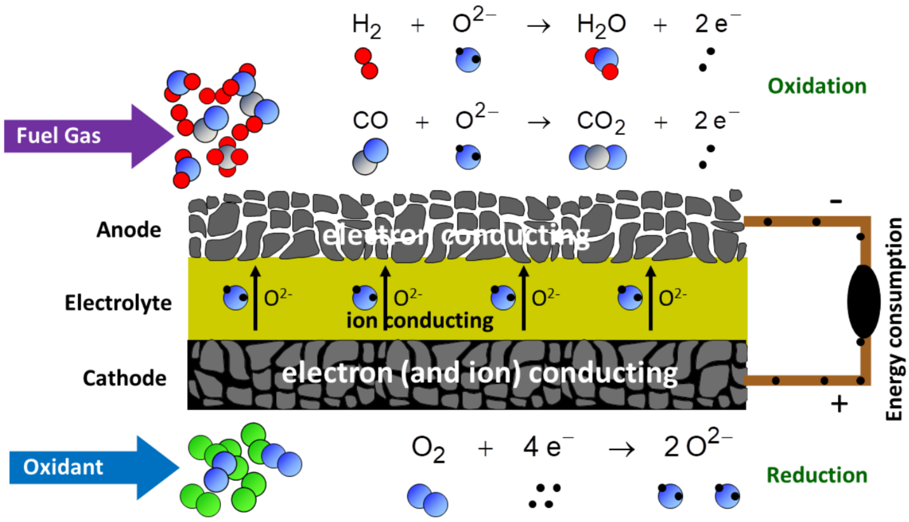


Fig. 7: Cross-section of a single unit of planar SOFC

The planar design also requires a fifth material which has not been shown in Figs. 6 & 7. That is a sealing glass, a thin layer of which is placed at all the four boundaries of the interconnect (both sides) to avoid the leakage of the gases, the fuel and the oxidant so that they do not come in direct contact with each other. Some researchers have also used nano-structured very thin layers, known as inter-layers between the electrolyte and the cathode or the anode in order to enhance the current density of the cells by way of increasing the number of triple points.

Photographs of a few single cells (looking like thin plates of multi-layer ceramics) with an area of 2" x 2" are presented in Fig. 8. In actual power stacks consisting of single cells of larger size of 4" x 4" are preferred. Several of these unit cells (50-100Nos.) are stacked one over the other with intermediate interconnect layer to develop power units of 5-10 kW. A typical microstructure of the cross-section of a single unit cell is presented in Fig. 9. Inclusion of an interlayer with a thickness of around 10μm is also seen in the picture.

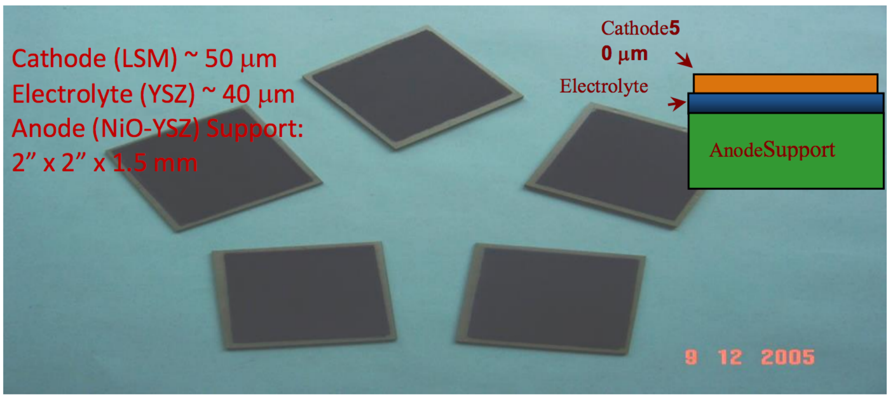


Fig.8: Typical anode supported planar SOFC single cells consisting of sintered three layer structure as shown in the top right hand corner. Typical thickness is 1.5-2.0 mm. These plates are often referred to as Membrane Electrode Assembly (MEA). Here the electrolyte is called the membrane because it preferentially allows only O^{2-} ions to pass through. (*Courtesy*: Fuel Cell and battery division, CSIR-CGCRI, Kolkata)

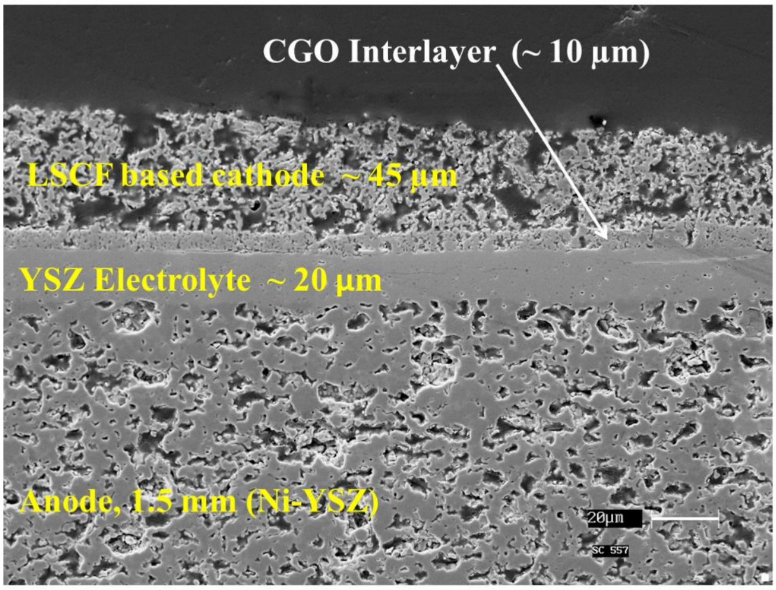


Fig.9: Microstructure of the cross-section of an SOFC Unit cell. Dense structure of the electrolyte and the porous structure of the electrodes are evident. This is an anode supported cell for which anode thickness is of the order of 1.5mm; thickness of the electrolyte is ~20µm; cathode is around 45µm. The cathodic interlayer is ~10µm with finer pores. CGO stands for Gadolinium doped cerium oxide (ceria) (*Courtesy*: Fuel Cell and battery division, CSIR-CGCRI, Kolkata)

2.7 Different alternative materials being tried for SOFC

In addition to the most common materials, e.g. YSZ (electrolyte) LSM (cathode) and NI-YSZ (anode), researchers have experimented with a large variety of alternative materials, a few of which are listed in Table 3.

Table 3: Alternative ceramics and glasses used for fabrication of SOFC [Compiled from the data presented in references 44 – 53]

	Electrolyte	Cathode	Anode	Interconnect	Composites of Glass Seals (mole%)
Most popular	9m/o YSZ	La (Sr)MnO_3 (LSM)	Ni-YSZ Cermet	Ferritic Steel	35BaO, 15CaO, 5Al_2O_3, 37SiO_2, 8B_2O_3
Alternative Materials	Gd – CeO_2 (GDC) Sc stabilized ZrO2 (ScSz) Sr – Mg doped La-Gallate(LSGM) La2Mo2O9	La-Co ferrite (LCF) (La,Co)FeO_4 (LCF) (LaSr)$CoFe_2O_4$ (LSCF) (BaSr)$CoFeO_4$ (BSCF) (La, Sr)Co03	Ni-Gd_2O_3 doped CeO_2 (CGO/ GDC) Gd_3O_3,Sm_2O_3 or Y_2O_3 doped CeO_2	Stainless Steel During the initial stages of development $LaCrO_3$ (LaCa)CrO_3 was used	35BaO, 5 La_2O_3 10Al_2O_3, 33SiO_2, 17B_2O_3 45BaO, 5Al_2O_3, 50SiO_2 25SrO, 20La_2O_3, 7 Al_2O_3, 40 B_2O_3, 8 SiO_2

3. Direct Carbon Fuel Cell

During the last few years, particular attention has been focused on this type Fuel cell in which solid carbon is used as the fuel which has several important advantages. Firstly, the energy released from the electrochemical oxidation of carbon to CO_2 by oxygen (23.95kWh/l) far exceeds that of most other non-solid fuels (e.g. hydrogen, methane etc.). Secondly, from thermodynamic consideration, the entropy change for carbon oxidation is zero and therefore from the theoretical energy conversion efficiency (η) is unity. This can be explained in the following way:

In terms of "2nd law" of thermodynamics the energy conversion efficiency (η) is defined as the ratio between of free energy (ΔG, the maximum energy that can be converted to electrical energy) and enthalpy (ΔH, the total chemical energy stored in the fuel).

$$\eta = \Delta G/\Delta H = (\Delta H - T\Delta S)/\Delta H$$

Now, for the reaction, $C+O_2 \rightarrow CO_2$, at 600 °C, $\Delta S \sim 0$ and $\Delta G = -395.4$ kJ/mol

ΔS being "zero" for carbon oxidation, $\eta = 1$. So, theoretically it becomes 100% efficient whereas, for oxidation of H_2 this value is only 76% and that of CO is only 66%. Again, if we can ensure compete combustion, CO production can be avoided. Moreover, as the fuel and exhaust gases are in different phases, there is less mixing between them. So, fuel utilization factor is also close to1 [54]. A schematic configuration of such a fuel cell is presented in Fig. 10 [55].

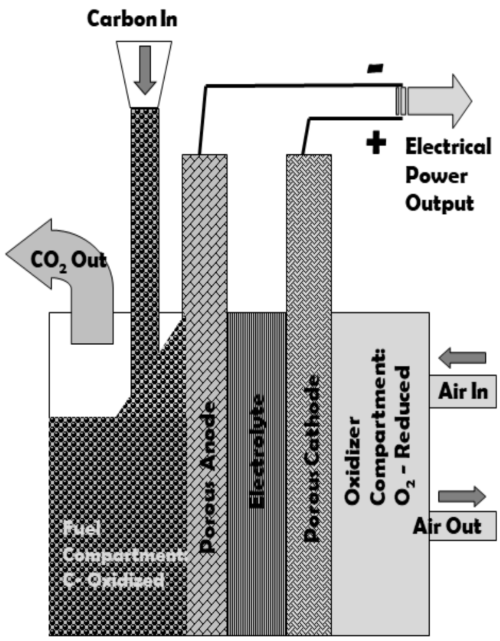


Fig.10: Schematic design of a Direct Carbon Fuel Cell (DCFC) [55]

In this case one uses a composite electrolyte, which is a mixture of YSZ and an eutectic mixture of alkali carbonates; either Na- and K- carbonate or Li-and Na-carbonate giving rise to a mixed ion electrolyte YSZ provides O^{2-} ion conductivity and the carbonate mixture provides $CO3^-$ conductivity. Both are required for the oxidation of solid carbon.

4. Energy storage devices

The most well-known storage device or in other words rechargeable battery is the lead-acid battery, which is used extensively in automobiles, inverters and for many other purposes. In addition, there is Ni-Cd, Ni-Metal hydride and of course the lithium ion battery, the heart of mobile phones laptops, cameras, watches etc. Comparison of their storing capacities is presented in Fig. 11 [56]. It is interesting to note that from the points of view of both weight and volume lithium ion battery has the largest specific capacity. Its open circuit voltage is also the highest. Let us discuss this system in alittle more details.

4.1 Lithium Ion Battery

4.1.1 Working Principle and Functional Materials:

i) Both anode and cathode are Lithium intercalated materials with sufficient Electronic Conductivity.

ii) Anode: Lithium intercalated graphite (LiC_6)

iii) Cathode: Lithium intercalated $LiCoO_2$ (Li_xCoO_2)

iv) Electrolyte (Liquid): Alkyl Carbonate + $LiPF_6$ [Solution of $LiPF_6$ in a mixture of Ethylene Carbonate and Di methyl Carbonate (EC-DMC) filled in a porous membrane called separator]

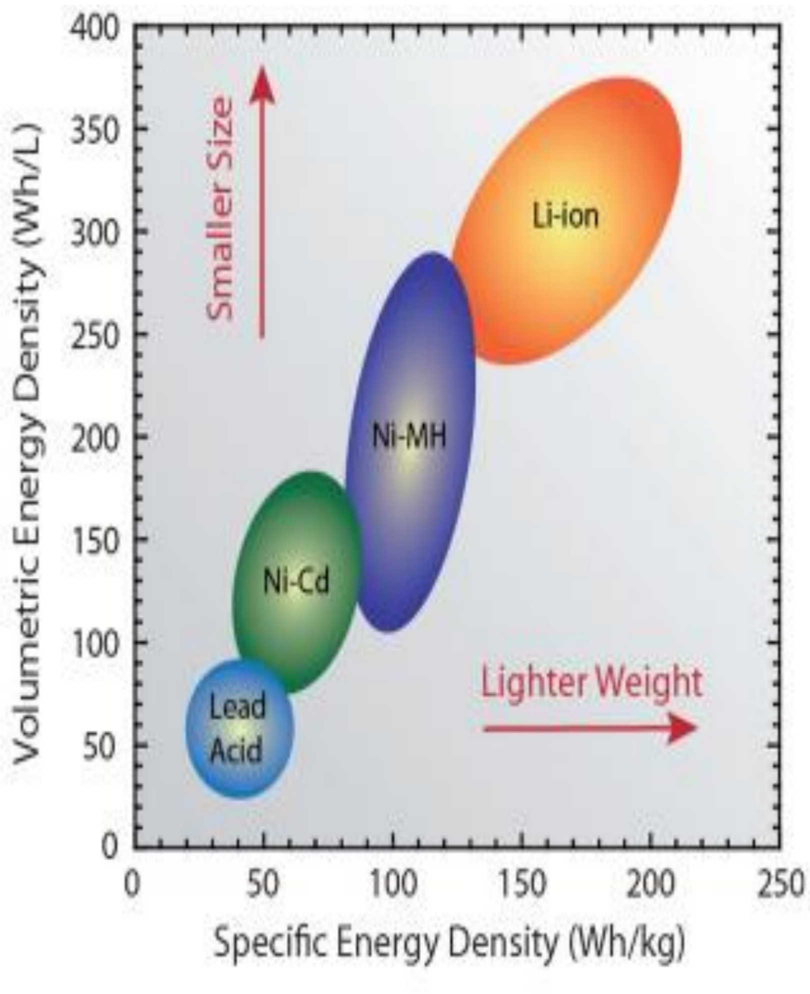


Fig. 11: Energy storing capacities of different rechargeable batteries [56].

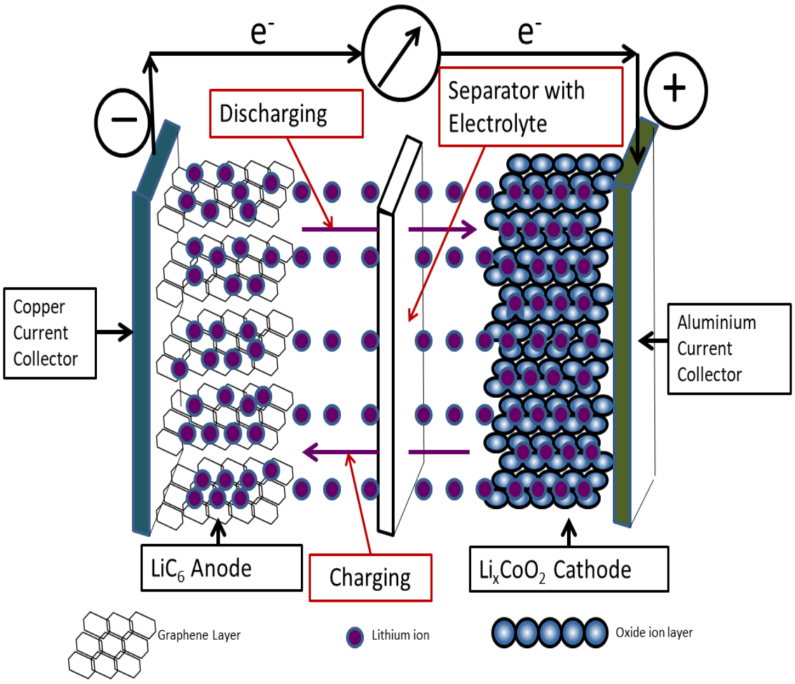


Fig. 12: Expanded View of Lithium Ion Battery Assembly

Atomistic movement of the lithium ion during charging and discharging cycles are explained in Fig.12. The chemical reactions are as follows:

(i) Discharging Process (Spontaneous)

Anodic reaction: $Li_xC_6 \rightarrow$ Graphite + $Li^+ + e^-$

Cathodic reaction: $CoO_2 + xLi + xe^- \rightarrow Li_xCoO_2$ $(Co^{4+} \rightarrow Co^{3+})$

(ii) Charging Process (Non-Spontaneous)

Anodic reaction: Graphite + $xLi^+ + xe^- \rightarrow Li_xC_6$

Cathodic reaction: $Li_xCoO_2 \rightarrow CoO_2 + xLi + xe^-$ $(Co^{3+} \rightarrow Co^{4+})$

(iii) *Overall Chemical Reaction:* $yC + LiMO_2 \rightleftharpoons Li_x C_y + Li_{(1-x)} MO_2$

where x is of the order of 0.5; $y = 6$ and $E_{ocv} = 3.7$ V

Even though Li_xCoO_2 is currently themost common cathode materials used today, it has a few disadvantages as follows: (i) Transformation of rhombohedral to monoclinic structure after repeated charge-discharge cycles. Accordingly, only 50% of theoretical capacity is realized, (ii) There are only a few sources of cobalt in the world and consequently the cost is exorbitant, and (iii) The oxide is not fully compatible with the organic electrolyte.

Researchers therefore are on the lookout for alternative materials not based on cobalt oxide. The potential of some of them are presented in Fig.13, which also includes some alternative anode materials replacing the well-known LiC_6. One may notice that several of the tetra-valent metals can replace graphite as the anode material.

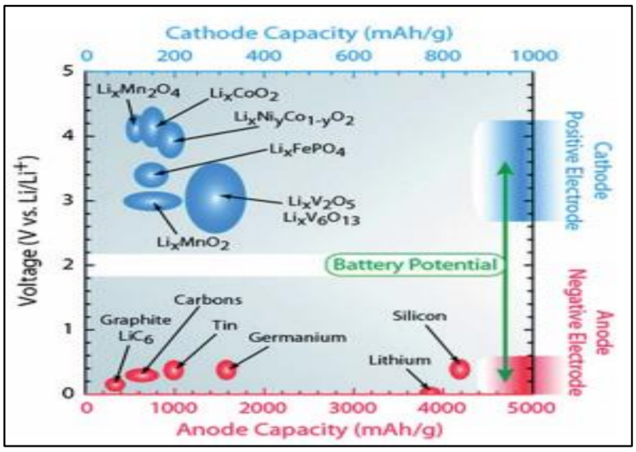


Fig. 13: Electrochemical data of a few alternative cathode and anode materials [57].

Among the alternative cathode materials, $Li_xMn_2O_4$ and Li_xFePO_4 are quite promising from practical point of view. In addition to the low power devices mentioned earlier, serious attempts are being made to use large size lithium ion batteries for the development of electric vehicles replacing low energy density lead-acid batteries. There cost is an important issue and therefore $LiFePO_4$ is being thought of as a potential cathode material for which prototypes are already available. Importance of nano-scale architecture for cathode materials has been demonstrated by several workers. The subject has recently been reviewed by Chen et al. [58]

4.2 Sodium-Sulphur Battery

In addition to lithium ion battery, sodium-sulphur battery is also a rechargeable-cum-storage battery, which is under development as a stationery power source. The electrolyte in this case is a high ceramics known as β"-alumina with chemical composition $Na_2O.11Al_2O_3$ with Na^+ ion conductivity. The electrolyte is used in the form of a one end closed tube as shown in Fig. 14(a). Molten sodium metal is used as the anode and Na_2S_x as the cathode. Operating temperature is around 150ºC. Photograph of a typical β"-alumina one end closed tube is shown in Fig. 14(b).

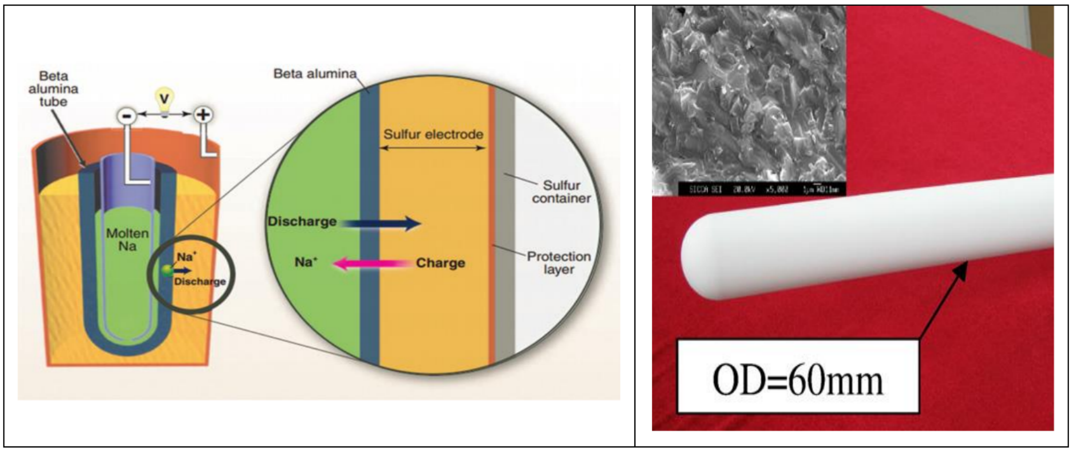


Figure 14: (a) Typical construction of a sodium-suphur battery [59], (b) Photograph of one β'' Alumina [60]

Following are the reactions involved in these cells:

i) Anodic Reaction: $2Na = 2N^{+} + 2e^{-}$

ii) Cathodic Reaction: $xS + 2e^{-} = S_x^{2-}$

iii) Overall Reaction: $2Na + xS = Na_2S_x$

Prototypes of up to 50kW capacity have already been fabricated [60].

5. Energy Harvesting

The world is in the lookout for every possible way to generate and store additional energy from all kinds of unconventional sources even if the overall level of generation may not be very high. However, the advantage of harnessing such power may be useful at the local level particularly for running different electronic devices, which do not require very high level of power. Harnessing such small level of power in a distributed manner is normally known as "Energy Harvesting". The most important technique of energy harvesting is the use of piezoelectric transducer, which is capable of generating electricity from mechanical pressure or vibration.There are many areas where piezoelectric energy harvesting has been tried out.Examples are: vibration of bridges, vibration in the wings of an aircraft, vibration in helicopter rotor, pressure on the pavements and walkways, vibration in the gymnasium instruments, vibration in the railways, automobiles etc.

Piezoelectric effect has been known for a long time, however its exploitation in energy harvesting is relatively of recent origin. There are several piezoelectric materials, natural and synthetic known to us (Table 4). It may be noted that some of the natural and most of the synthetic materials may be regarded as "Ceramics".

Table 4: List of a few natural and Synthetic Piezoelectric Materials [61]

Natural	Synthetic
Quartz	Lead Zirconate Titanate (PZT)
Rochelle salt	Zinc Oxide (ZnO)
Topaz	Barium Titanate ($BaTiO_3$)
Sucrose	Gallium Orthophosphate ($GaPO_4$)
Silk	Potassium Niobate ($KNbO_3$)
Enamel	Lead Titanate ($PbTiO_3$)
	Lithium Tantalate ($LiTaO_3$)
	Langasite ($La_3Ga_5SiO_{14}$)
	Sodium Tungstate (Na_2WO_3)

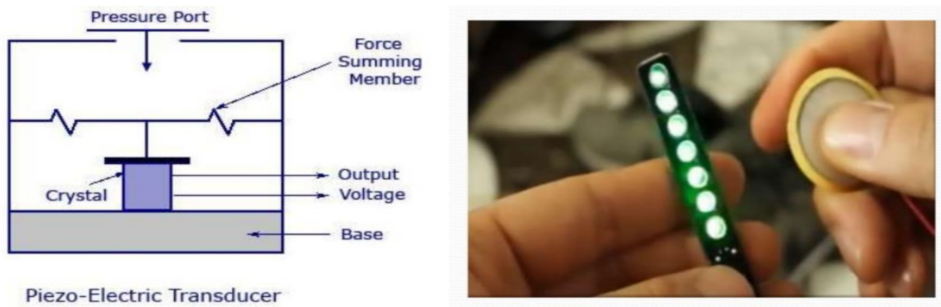


Fig. 15: Demonstration of energy harvesting with the help of piezo-transducer [61]

In above Fig. 15 demonstrates how piezo transducers can generate power through a simple arrangement (left) in order to illuminate a few LED bulbs (right). In this case the piezo-transducer is in the form of a disc is hand-held.

In order to enhance power generation, flexible piezoelectric strips made from electro-spun PZT ceramic fibres embedded in a polymer are used as shown in Fig. 16.

Fig. 16: Flexible Piezocomposites for energy harvesting [62]

6. Clean Coal Technology

While renewable energy technologies are in the developmental stage particularly to make them economically attractive, parallel efforts are being made how to make established technologies like the thermal power plants (based on coal) more efficient and environment friendly. In this context introduction of Integrated Gasification Combined Cycle (IGCC) technology utilizing different types of high temperature ceramics, is one such possibility. In this technology, coal, instead of simply burning in a boiler to generate steam, is first treated in a gasifier to generate syngas, from which particulates are separated with the help of the ceramic (porous silicon carbide) filter and part of hydrogen is separated with ion selective solid membrane and the purified gas is finally burnt to produce steam. Different uses of ceramics in IGCC may be summarized as follows:

- Oxygen enrichment of feed air to the gasifier through oxygen transport membrane (YSZ)
- Cleaning of syngas at a high temperature (~1000°C) and high pressure (~30bar) by porous silicon carbide tubular filters.
- Use of ion transport membrane for separation of hydrogen.
- Refractory lining in the gasifier.

By this process overall conversion efficiency increases and also the pollution remains under control. The technology is still under developmental stage.

In addition to above, abrasion resistance ceramics (sintered aluminium oxide in particular) is extensively exploited for lining of the internal surface of the large diameter steel pipes to carry the pulverized coal from the pulverizing plant to the boiler and also to transport burnt coal ash from the boiler to the dumping grounds. Other areas which use abrasion resistant ceramic tiles include different kinds of hoppers used in metallurgical and mineral processing plants. Besides sintered ceramics, some of these hoppers also use tiles prepared by melting natural rocks like basalt. Such tiles may be termed as “glass ceramics” which is basically crystalline compounds dispersed in a glassy matrix.

7. Summary and Conclusions

It may easily be concluded from the above discussion that a variety of ceramics, glasses or glass-ceramics having important functional propertiesareplaying important roles in renewable energy technologies, in the areas of energy conversion and storage. They are also important for enhancing the conversion efficiency and suppress the environmental pollution of the existing thermal power plants based on coal. Piezo-electric ceramics are also plying important roles in harnessing energy from different types of vibrations experienced by us in our daily life and industrial activities.

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