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Journal of Advances in Science and Technology

Vol. VII, Issue No. XIII, May-2014, ISSN 2230-9659

AN INTERNATIONALLY INDEXED PEER REVIEWED & REFEREED JOURNAL

Journal of Advances in Science and Technology
Vol. VII, Issue No. XIII, May-2014, ISSN 2230-9659

A Comparative Evaluation on Solid Oxide Fuel Cell (SOFC): Theoretical Review

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Abstract – Solid oxide fuel cell (SOFC) is a promising alternative energy source, with its advantages of high operating efficiency, fuel flexibility, low emissions and relatively low cost. However, there are several challenges concerning the SOFC research. Little is known about the complex interfacial electrochemistry and thermochemistry, and it is also difficult to diagnose problems and optimize cell performance. Therefore, physics-based models are needed to better understand the underlying mechanisms of SOFCs.

The generation of energy by clean, efficient and environmental-friendly means is now one of the major challenges for engineers and scientists. Fuel cells convert chemical energy of a fuel gas directly into electrical work, and are efficient and environmentally clean, since no combustion is required. Moreover, fuel cells have the potential for development to a sufficient size for applications for commercial electricity generation. This paper outlines the acute global population growth and the growing need and use of energy and its consequent environmental impacts. The existing or emerging fuel cells' technologies are comprehensively discussed in this paper. In particular, attention is given to the design and operation of Solid Oxide Fuel Cells (SOFCs), noting the restrictions based on materials' requirements and fuel specifications. Moreover, advantages of SOFCs with respect to the other fuel cell technologies are identified.

Solid oxide fuel cells (SOFCs) have the promise to improve energy efficiency and to provide society with a clean energy producing technology. The high temperature of operation (500-1000 ^{0}C) enables the solid oxide fuel cell to operate with existing fossil fuels and to be efficiently coupled with turbines to give very high efficiency conversion of fuels to electricity. Solid oxide fuel cells are complex electrochemical devices that contain three basic components, a porous anode, an electrolyte membrane, and a porous cathode.

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INTRODUCTION

A fuel cell is an energy conversion device that converts the chemical energy of a fuel directly to electrical energy and heat, without the need for direct combustion as an intermediate step. It gives much higher conversion efficiencies than conventional thermo-mechanical methods. Similar to batteries, the operating principles of fuel cells are electrochemical combination of reactants to generate electricity. In fuel cell a combination of a gaseous fuel (e.g. hydrogen or hydrocarbon fuels) and an oxidant gas (e.g. oxygen in the air) go through electrodes and half-cell reaction occurs on anode and cathode respectively, with the active charge carrier species going through an ion conducting electrolyte. In this way, electrons are released into external circuit to produce electricity. However, unlike a battery, a fuel cell does not require recharging. A fuel cell operates as long as both fuel and oxidant are supplied to the electrodes and is environment friendly, with negligible influence exerted on the natural environment.

Fuel cells are generally classified by the chemical characteristics of the electrolyte used as the ionic conductor in the cell. By far the greatest research interest throughout the world has focused on Proton Exchange Membrane fuel cells (PEMFCs) and Solid Oxide fuel cells (SOFCs).

Present materials' science has made the fuel cells a reality in some specialized applications. By far the greatest research interest throughout the world has focused on Proton Exchange Membrane (PEM) and Solid Oxide (SO) cell stacks. PEMs are well advanced type of fuel cell that are suitable for cars and mass transportation.

SOFC technology is the most demanding from a materials standpoint and is developed for its potential market competitiveness arising from:

- SOFCs are the most efficient (fuel input to electricity output) fuel cell electricity generators currently being developed world-wide.

- SOFCs are flexible in the choice of fuel such as carbon-based fuels, eg, natural gas.
- SOFC technology is most suited to applications in the distributed generation (ie, stationary power) market because its high conversion efficiency provides the greatest benefit when fuel costs are higher, due to long fuel delivery systems to customer premises.
- SOFCs have a modular and solid state construction and do not present any moving parts, thereby are quiet enough to be installed indoors.
- The high operating temperature of SOFCs produces high quality heat byproduct which can be used for co-generation, or for use in combined cycle applications.
- SOFCs do not contain noble metals that could be problematic in resource availability and price issue in high volume manufacture.
- SOFCs do not have problems with electrolyte management (liquid electrolytes, for example, which are corrosive and difficult to handle).
- SOFCs have extremely low emissions by eliminating the danger of carbon monoxide in exhaust gases, as any CO produced is converted to CO2 at the high operating temperature.
- SOFCs have a potential long life expectancy of more than 40000–80000 h.

Solid oxide fuel cells (SOFCs) offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies; since their efficiencies are not limited by the Carnot cycle of a heat engine. These fuel cells provide many advantages over traditional energy conversion systems including high efficiency, reliability, modularity, fuel adaptability, and very low levels of NOx and SOx emissions.

Quiet, vibration-free operation of SOFCs also eliminates noise usually associated with conventional power generation systems. Up until about six years ago, SOFCs were being developed for operation primarily in the temperature range of 900 to 1000oC; in addition to the capability of internally reforming hydrocarbon fuels (e.g., natural gas), such high temperature SOFCs provide high quality exhaust heat for cogeneration, and when pressurized, can be integrated with a gas turbine to further increase the overall efficiency of the power system.

However, reduction of the SOFC operating temperature by 200oC or more allows use of a broader set of materials, is less-demanding on the seals and the balance-of-plant components, simplifies thermal management, aids in faster start up and cool down, and results in less degradation of cell and stack components. Because of these advantages, activity in the development of SOFCs capable of operating in the temperature range of 650 to 800oC has increased dramatically in the last few years. However, at lower temperatures, electrolyte conductivity and electrode kinetics decrease significantly; to overcome these drawbacks, alternative cell materials and designs are being extensively investigated.

An SOFC essentially consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte. The operating principle of such a cell is illustrated in Fig. 1. Oxygen supplied at the cathode (air electrode) reacts with incoming electrons from the external circuit to form oxide ions, which migrate to the anode (fuel electrode) through the oxide ion conducting electrolyte. At the anode, oxide ions combine with H2 (and/or CO) in the fuel to form H2O (and/or CO2), liberating electrons. Electrons (electricity) flow from the anode through the external circuit to the cathode. The materials for the cell components are selected based on suitable electrical conducting properties required of these components to perform their intended cell functions; adequate chemical and structural stability at high temperatures encountered during cell operation as well as during cell fabrication; minimal reactivity and interdiffusion among different components; and matching thermal expansion among different components.

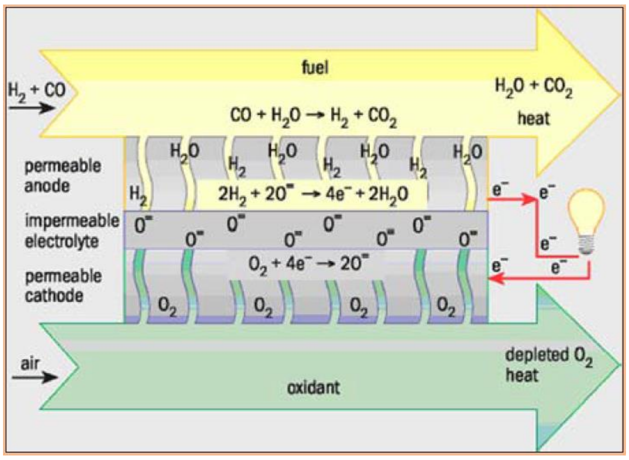

Fig. 1. Operating principle of a solid oxide fuel cell.

SOLID OXIDE FUEL CELLS

SOFC is a high temperature fuel cell technology. They are extremely useful in large, high-power applications such as full-scale industrial stations and large-scale electricity-generating stations. SOFC system usually utilizes a solid ceramic as the electrolyte and operates at extremely high temperatures (600°C~1000°C). This high operating temperature allows internal reforming, promotes rapid electro-catalytic reactions with non-precious metals, and produces high quality byproduct heat for co-generation. Efficiencies for this type of fuel cell can reach up to 70%.

SOFC technology is very demanding from a materials standpoint and has potential advantages and competitiveness in the following aspects. 1) It is the most efficient fuel cell in terms of generating electricity. Moreover, the high operating temperature of SOFCs produces high quality heat byproduct which can be used for co-generation or combined cycle applications. This can further increase the overall energy efficiency. 2) It is flexible in the choice of fuels such as hydrocarbon fuels, e.g., natural gas. 3) SOFCs do not need expensive noble metals that could be issues in resource availability and cost. 4) Any carbon monoxide produced is converted to carbon dioxide at the high operating temperature; therefore SOFCs have very low emissions in exhaust gases.

SOFCs are composed of all-solid-state materials. And the solid state character of all SOFC components puts no fundamental restriction on the cell configuration. Cells are being constructed in many different configurations, such as planar button cell, flat-plates cells, tubular cells or rolled tubes.

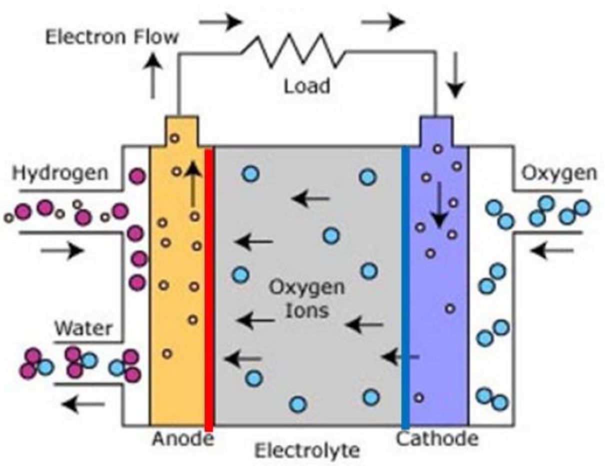

Figure 2 Demonstration of the SOFC, when hydrogen carried by nitrogen and 3% water mixture is used as fuel at the anode side and oxygen carried by air is fed from the cathode side1. (Not drawn to scale).

A SOFC consists of two electrodes sandwiched around a hard ceramic electrolyte such as the remarkable ceramic material called zirconia (Figure 2). Fuel gas such as hydrogen is fed into the anode of the fuel cell and oxygen, usually carried by air, enters the cell via the cathode. The anode disperses the hydrogen gas equally over its whole surface and conducts the electrons that are freed from hydrogen molecule, to be used as power in the external circuit. The cathode distributes the oxygen fed to it onto its surface and conducts the electrons back from the external circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water. The electrolyte determines the operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the electrons. It also allows the flow of charged ions from one electrode to the other to maintain the overall charge balance.

Each component of the SOFC serves several functions and must therefore meet certain requirements such as proper stability (chemical, phase, morphological, and dimensional), proper conductivity, chemical compatibility with other components, similar thermal expansion to avoid cracking during the cell operation, dense electrolyte to prevent gas mixing, porous anode and cathode to allow gas transport to the reaction sites, high strength and toughness properties, easiness to be fabricated, amenable to particular fabrication conditions, compatibility at higher temperatures at which the ceramic structures are fabricated, relatively low cost, etc.

COMPONENTS OF SOLID OXIDE FUEL CELLS

Electrolytes - The large number of oxygen ion electrolytes that have been investigated can be grouped into a small number of structure types: fluorite-based systems (doped bismuth oxide, zirconia, ceria, pyrochlore); 15 perovskite and related intergrowth structures (lanthanum gallate, brownmillerites, BiMeVOX); La-MOX and apatites. All have some limitations and so the search for better systems continues. Many oxide conductors show order-disorder phase transitions and only show high conductivity above the transition where the oxygen ion sublattice “melts”, at least to some degree. In these cases, suitable doping can suppress the phase transition and lead to higher conductivities at lower temperature.

All such compounds and others such as doped ceria and zirconia, which although they do not show macroscopic phase transitions, show evidence for vacancy-dopant short-range order apparent in non-Arrhenius behavior of the conductivity with temperature. Defect cluster growth and ultimately phase segregation are also observed on long-term annealing.

Cathodes - Two schematic models for the reactions that occur at cathodes for a single phase cathode material to illustrate the various coupled reaction and transport processes that occur and the different types of interfaces that are present. The behavior of an electrode with low oxygen ion conductivity such as $La_{0.9}Sr_{0.1}MnO_3$ is qualitatively described.

The cathode reaction is represented by diffusion of oxygen gas into the pore space, dissociation, and diffusion to the triple phase boundary between gas phase, the electrode and the electrolyte and then ion transfer into the electrolyte.

A schematic of a mixed conducting cathode structure here, oxygen molecules diffusing into the porous structure are reduced to form ions at the surface of a mixed conducting cathode material and also at the triple phase boundaries between the current collector, cathode material and gas phase, and between the cathode material, electrolyte, and gas phase. The oxygen ions that are formed on reduction diffuse either through the cathode material or along the surface to the electrolyte, where they are transferred to the electrolyte either across the solid-solid interface between the cathode and the electrolyte or in the vicinity of the triple phase boundary. The mixed conductor would be expected to show lower resistance because of the larger area available for reaction and ion transfer across the interface. Gasphase diffusion into the porous structure must also be considered and is known to become important at high current densities.

Anodes - The literature on anode materials for solid oxide fuel cells is very extensive and can be only briefly summarized here. For more details, a number of excellent review studies are available.

Usually, hydrogen is considered to be the primary fuel for fuel cells but in the case of SOFCs, because of their high operating temperature, hydrocarbon fuels can be used directly. Because for the foreseeable future most hydrogen will come from reforming natural gas, liquid hydrocarbons or coal gasification, direct utilization has a significant efficiency advantage, though it does introduce further requirements on the anode material. Hydrocarbons such as methane can be fed directly to the cell (dry) or cofed with water (internal reforming). The latter requires higher operating temperatures because of the endothermic nature of steam reforming. In practice, some form of external reforming or partial oxidation is used to provide a mixture of hydrocarbons, hydrogen, and carbon monoxide to the cell.

Fuels and fuel processing Fuels –

Most solid oxide fuel cells still use hydrogen as fuel, and fuel cells which can use other fuels typically work best with hydrogen. Today however, running SOFCs on direct hydrocarbons is of great interest, Natural gas. due to its widespread availability and distribution infrastructure, is an ideal choice for stationary SOFC applications. Propane and butane are preferred for portable applications due to their high energy density. Furthermore, they are readily available, inexpensive, and the lowest molecular weight hydrocarbons that can be easily used as liquids, Methanol and ethanol have also been considered for portable fuel-cell applications. Though there are reports on the operation of SOFCs with ethane, propane, butane, and octane, these are limited to a laboratory environment. A list of fuels that can be used in SOFCs is given in.

The choice of the appropriate fuel also strongly depends on the operating temperature of the cell. Natural gas and higher hydrocarbons can be efficiently internally reformed in SOFCs operating above 600 °C. For operating temperatures as low as 500 °C oxygenates such as methanol or ethanol are considered the most suitable fuels due to the low temperature required for reforming these fuels. Running SOFCs 011 these alternate fuels calls for a good understanding of the tliermo chemistry in the anode, because the hydrocarbons easily undergo cracking and partial oxidation.

Fuel processing -

Today, existing installations of SOFC plants do not feed hydrocarbon fuels. mainly due to electrode stability issues. Instead, hydrocarbons are prereformed prior to feeding to the fuel cell stack. Furthermore, SOFC anodes are not tolerant to sulfur content in natural gas. Therefore all existing installations require some amount of fuel processing at least, The high temperature, at which a SOFC is operated, prevents poisoning of the anode by adsorption of CO. Therefore. SOFCs can principally use hydrocarbons as fuel. The electrochemical activity of various chemical species is still a debatable topic. However there is no doubt on the high electrochemical activity of H2 and CO. Therefore, any fuel used in SOFC shall finally be converted into H_2 and/or CO for enabling charge transfer. The fuel processing can be achieved either intemaly or extemaly, An external reformer results in additional costs of the overall system and hence internal reforming is an attractive option. Internal reforming can be carried out either in a separate fuel reformer integrated within the stack (indirect internal reforming), or directly on the fuel cell anode (direct internal reforming), Indirect internal reforming increases the system efficiency by recuperating the waste heat from the stack into the fuel supply.

The direct internal reforming of hydrocarbons can eliminate the need of a fuel reformer and the extra cooling air which would otherwise be required in an SOFC running 011 hydrogen. Thus the direct internal reforming may result in an increased overall efficiency. However, direct internal reforming of hydrocarbons without upstream reforming is challenging due to the possibility of anode fouling that is the formation of carbonaceous over layers (coke).

Issues related to coking have been recently studied by many groups,

SOFC BENEFITS AND LIMITATIONS

SOFCs have many advantages: they can be modular, they can be distributed to eliminate the need for transmission lines, they operate quietly and are vibration free. SOFCs could provide higher system efficiency, higher power density, and simpler designs than fuel cells based on liquid electrolytes. At low enough costs, they could compete with combined cycle gas turbines for distributed applications. The high cell operating temperature enables high reactant activity and therefore facilitates fast electrode kinetics (large exchange currents) and reduced activation polarization. This is especially advantageous as precious platinum electrocatalysts are not required and the electrodes cannot be poisoned by carbon monoxide. As a result, carbon monoxide is a potential fuel in SOFCs. Moreover, the operating temperatures are sufficiently elevated, thereby performance issues are not related to kinetics (activation overpotentials) but to ohmic losses due to charge transport across components and component interfaces. The benefits of SOFCs also include:

- Energy security: reduce oil consumption, cut oil imports, and increase the amount of the country's available electricity supply.
- Reliability: achieves operating times in excess of 90% and power available 99.99% of the time.
- Low operating and maintenance cost: the efficiency of the SOFC system will drastically reduce the energy bill (mass production) and have lower maintenance costs than their alternatives.
- Constant power production: generates power continuously unlike backup generators, diesel engines or Uninterrupted Power Supply (UPS).
- Choice of fuel: allows fuel selection, hydrogen may be extracted from natural gas, propane, butane, methanol and diesel fuel.

Up until now, SOFCs have been most fuel-efficient operating at 1000^{0}C. Unfortunately, this high temperature decreases the cell lifetime and increases the cost of materials, since expensive high temperature alloys are used to house the cell, and expensive ceramics are used for the interconnections, increasing the cost of the fuel cell substantially. Lower operating temperature has been recognised worldwide as the key point for low-cost SOFCs. The reduction in the temperature will therefore allow the use of cheaper interconnecting and structural components, such as stainless steel. A lower temperature will also ensure a greater overall system efficiency and a reduction in the thermal stresses in the active ceramic structures, leading to a longer expected lifetime of the system and make possible the use of cheaper interconnect materials such as ferritic steels, without LaCrO3 protective coatings, as already mentioned.

For some years, scientists and researchers throughout the world have been on a quest to drop the operating temperature of SOFCs without sacrificing their performance. The 600–1000□C operating temperature of the SOFC requires a significant startup time. The cell performance is very sensitive to operating temperature. A 10% drop in temperature results in 12% drop in cell performance, due to the increase in internal resistance to the flow of oxygen ions. The high temperature also demands that the system include significant thermal shielding to protect personnel and to retain heat.

APPLICATIONS OF SOFCS

Combined with low noise and ability to utilize readily-available fuel such as methane and natural gas, SOFC generators are best suited for the provision of power in utility applications, due to the significant time required to reach operating temperatures, and can have broad applications ranging from large-scale power plants to smaller home-scale power plants and portable/emergency power generators. SOFCs could be used in many applications. Each proposed use raises its own issues and challenges. Their most needed uses are:

- High power reliability: computer facilities, call centres, communication facilities, data processing centres high technology manufacturing facilities.
- Emission minimisation or elimination: urban areas, industrial facilities, airports, zones with strict emissions standards.
- Limited access to utility grid: rural or remote areas, maximum grid capacity.
- Biological waste gases are available: waste treatment plants, SOFC can convert waste gases (methanol from biomass) to electricity and heat with minimal environment intrusion.

FUTURE OF SOFCS

Focusing their efforts on SOFCs, which have been on the verge of commercial viability for years, researchers around the world are making a concerted effort in the development of suitable materials and the fabrication of ceramic structures which are presently the key technical challenges facing SOFCs. Programs are underway in Japan and in the US that use a relatively simple ceramic process to develop a thin film electrolyte that decreases the cell resistance, and both double the power output and significantly reduce the cost of SOFCs. There is also a current effort in integrating the SOFCs and developing a novel stacking geometry. The demonstration of low-temperature SOFC operation directly on methane, signals an important new opportunity for making simple, cost-effective power plants. The global SOFC making company continues to realize very significant improvements in basic fuel cell design. A measure of their success is the realisation of a 48.6% improvement in single cell power densities which represents the highest published power densities for commercial-sized SOFCs in the world. Changes in cell composition and design have resulted in these improved power densities. Higher power densities contribute to lower weight, size and cost of fuel cell systems. SOFCs could someday be suitable for small-scale residential market applications if ultimate cost goals of $1000/kW are reached.

CONCLUSION

The challenge in successfully commercializing SOFCs offering high power densities and long term durability requires reduction of costs associated with the cells and the balance-of-plant.

Energy exploitation of fossil fuels is reaching its limits. Future alternatives must therefore be developed for long-term and environmental-friendly energy supply needed by a constantly growing world population. SOFCs provide highly efficient, pollution free power generation. Their performance has been confirmed by successful operation power generation systems throughout the world. Electrical-generation efficiencies of 70% are possible nowadays, along with a heat recovery possibility. SOFCs appear to be an important technology for the future as they operate at high efficiencies and can run on a variety of fuels, from solar hydrogen to methanol, from biomass to gassified coal.

In sum, the SOFC is a complicated area where multicomponent gas transport, gas phase reaction, heterogeneous catalytic reaction and charge transfer in electrochemistry are all involved and coupled together. In order for the SOFC to be better understood and engineered, much more research works need to be carried out, to investigate the mechanism of transport, reaction and catalytic electrochemistry.

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