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An Analysis on Recent Developments in Single-Chamber Solid Oxide Fuel-Cells Technology: From Its Beginning

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Abstract – In single-chamber solid oxide fuel cells (SC-SOFCs), both anode and cathode are situated in a common gas chamber and are exposed to a mixture of fuel and oxidant. The working principle is based on the difference in catalytic activity of the electrodes for the respective anodic and catholic reactions. The resulting difference in oxygen partial pressure between the electrodes leads to the generation of an open circuit voltage. Progress in SC-SOFC technology has enabled the generation of power outputs comparable to those of conventional SOFCs. This paper provides a detailed review of the development of SC-SOFC technology.

The performance of a single-chamber solid oxide fuel cell (SOFC) was studied between 350 and 9008C in flowing mixtures of methane, ethane, propane, or liquefied petroleum gas and air with a fuel/air volume ratio of one, where their oxidation proceeded safely without explosion.

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INTRODUCTION

Solid oxide fuel cells (SOFCs) are considered as a next generation power generating technology because of their fuel flexibility and high overall efficiency due to the possible use in a cogeneration system. However, the elevated operating temperatures impose several challenges on reliability and long-term stability of these fuel cells. Specifically, material degradation, failure of the gas-tight sealing and mechanical stresses due to different thermal expansion coefficients between cell components lead to low cell performance and stability. The elevated temperatures additionally limit the use of SOFCs in small-scale portable power applications. Therefore, reduction of the operating temperature is one of the main challenges in SOFC research.

In conventional dual-chamber SOFCs, fuel and oxidant have to be supplied separately to the respective electrode and any mixing of the two reactant gases has to be avoided. The necessity of separate gas supply imposes complex gas management and gas manifolding, thus complicating not only stack assembly, but also downsizing of SOFC systems. Moreover, gas-tight, high-temperature and mechanically resistant sealing is inevitable in order to separate the cell into leakproof anode and cathode compartments. Sealing is generally achieved using glass or ceramic materials. The advantage of glass ceiling is its rigidity and high gas tightness. However, degradation over time as well as thermal stresses during cycling often cause cracks. Sealing by mechanical compression with mica increases thermo mechanical strength but results in higher leakage rates. In addition to the gas-tight sealing, the electrolyte has to be fully dense to avoid any gas cross-over between anode and cathode compartments.

The necessity of gas separation and sealing has a severe impact on the mechanical and thermal shock resistance of SOFCs and their long-term stability. Additionally, bulky cell designs limit miniaturization and stack build-up, and severe constraints exist on fabrication technique and material choice, thereby contributing to elevated fabrication costs. In order to avoid those challenges, SOFCs with only one gas chamber, the so-called, single-chamber solid oxide fuel cells (SC-SOFCs), are being developed. SC-SOFCs are operated in mixtures of fuel and oxidant, thus completely eliminating any needs for gas sealing.

To complement previous reviews on SC-SOFCs, the present review proposes to give a detailed summary on SC-SOFC technology from its early beginnings to the latest achievements. The following sections emphasize the history of this fuel cell technology, the operating principles, followed by the development of different SC-SOFC cell designs, and finally modeling of their performance.

While solid oxide fuel cells (SOFCs) exhibit a number of attractive features for power generation, including high energy conversion efficiency, fuel flexibility and relatively inexpensive electrode materials, the high temperatures required for operation (800–1000 °C) introduce a number of challenges. In particular, for planar SOFCs, thermal expansion mismatches between components can lead to failure of the seals that separate anode and cathode chambers. One strategy for addressing this challenge is to utilize so-called ‘single chamber fuel cells’ (SCFCs) in which the fuel and oxidant are allowed to mix and anode and cathode reactions take place within the same physical chamber.

The functionality of SCFCs derives from the selectivity of the electrode catalysts, with the anode preferentially oxidizing the fuel and the cathode preferentially reducing oxygen. The resulting oxygen partial pressure gradient generated across the cell in turn generates an electrical potential gradient. Useful power outputs are typically obtained under fuel rich conditions relative to complete oxidation. Although the power density and efficiency are typically lower than those of conventional dual-chamber SOFCs (as a consequence of incomplete fuel utilization and parasitic, non-electrochemical fuel oxidation), the latest advances in materials science and system design have greatly improved SCFC power densities, in part, by lowering the fuel cell operating temperature so as to minimize purely chemical oxidation of the fuel.

Despite the lower efficiency, SCFCs have advantages over dual chamber SOFCs that are particularly relevant for portable power generation. Because complications due to sealing are eliminated, the SCFC greatly simplifies the system design and enhances the thermal and mechanical shock resistance, thereby enabling rapid start up and shut down. The relatively low temperatures (400–600 °C) at which the most advanced SCFCs function also help to ease complications with on–off cycling. The reduced temperatures of operation provide additional benefits including expanding the choices of materials for fabrication of peripheral components and inhibiting carbon deposition via hydrocarbon cracking at the anode catalyst. Quite significantly, micro-SCFC systems can be designed to be thermally self-sustaining (such that no external heat source is required for fuel cell operation), a particularly important feature for portable applications.

There is worldwide interest in the development and commercialization of fuel cells for vehicles and portable electric devices. It is a presently accepted notion that polymer electrolyte fuel cells (PEFCs) are the only devices capable of operating at low temperatures. We believe, however, that PEFCs are not perfect from a practical point of view because they require hydrogen as the fuel, which is impractical in terms of storage and handling. An external reformer, therefore, must be used to convert more viable alcohols and hydrocarbons into hydrogen, thereby defeating their portability. There have been recent successes with solid oxide fuel cells (SOFCs) which perform well between 500 and 7008C directly using alcohols and hydrocarbons as the fuels.1-3 A further reduction in the operating temperature of internal-reforming SOFCs and an enhancement of their thermal- and mechanical-shock resistance would make this technology a promising alternative to PEFCs.

A novel type of fuel cell, which is distinguished from conventional fuel cells in design and principle, has been proposed by many researchers.4-8 This fuel cell consists of only one gas chamber, where both the anode and the cathode are exposed to the same mixture of fuel and air. We will use a single-chamber fuel cell (SCFC) as a notation for this type of fuel cell. Because there is no need to separate the supply of fuel and air, it is more thermally and mechanically shock resistant than conventional fuel cells. We have recently succeeded in applying this cell design to an SOFC constructed from an yttria-stabilized zirconia (YSZ) electrolyte with a Ni-based anode and a strontium-doped lanthanum manganite (LSM) cathode.9 This SCFC exhibits high power density in a flowing mixture of methane and air, but it must operate at the high temperature of 9508C in order to achieve sufficient ionic conduction in the solid electrolyte.

SINGLE-CHAMBER SOLID OXIDE FUEL CELLS

SC-SOFCs can be defined as fuel cells with only one gas compartment (thus single-chamber) operating in a non-equilibrium gas mixture of fuel and oxygen. The term “single-chamber” has been introduced in 1999 by Hibino et al., one of the pioneers of SC-SOFC technology, and is generally used. But “one-chamber”, “single-compartment”, “mixed-gas”, “mixed-fuels”, “mixed-reactant” and “separator free” fuel cells as well as “SOFCs with reaction-selective electrodes” can also be found in the literature.

In conventional dual-chamber SOFCs, gas-tight sealing together with a dense electrolyte separates the cell into two compartments. The oxidant is then fed to the cathode and the fuel to the anode through separate gas supplies without any intermixing of the two reaction gases (Figure 1a). The difference in oxygen partial pressure between the two separate electrode compartments leads to the establishment of an open circuit voltage (OCV).

In SC-SOFCs, the cell is located in a single gas chamber and a mixture of fuel and oxidant flows over the cell (Figure 1b). The working principle of SC-SOFCs is therefore based on the selectivity of the electrodes for the respective reactions; that is, the anode must be selective and electrochemically active for oxidizing the fuel and be inert to the reduction of the oxidant, whereas the cathode needs to exhibit selective reduction of oxygen and inertness to the fuel. Thus, both the electrocatalytic activity and the selectivity of the electrodes lead to the generation of the OCV and electricity in SC-SOFCs.

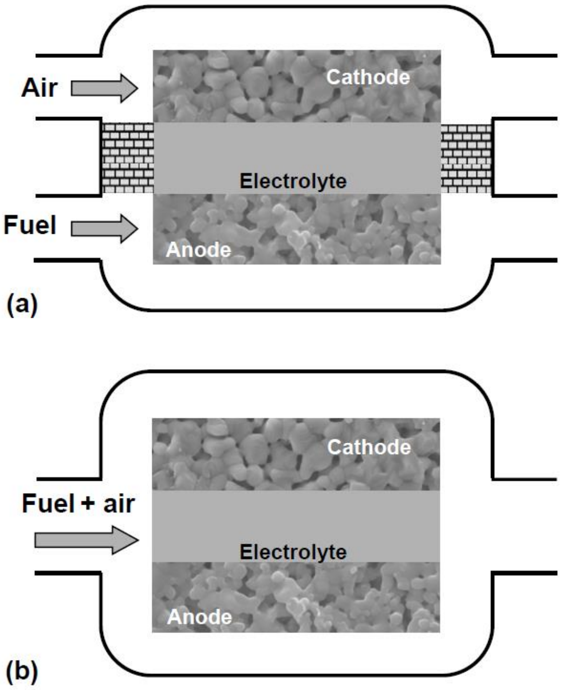
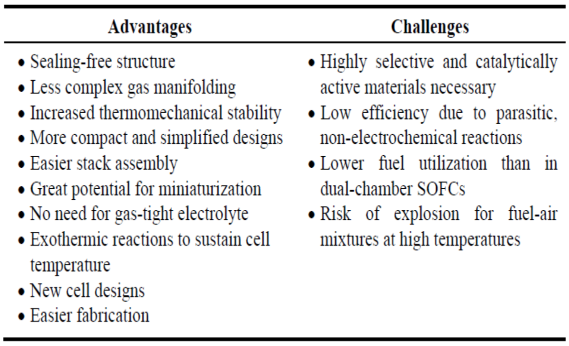


Figure 1. Schematics of (a) dual-chamber and (b) single-chamber SOFC.

In addition to SOFCs, the single-chamber operating mode has so far also been demonstrated for alkaline fuel cells, direct-methanol fuel cells (mixed-reactant direct-methanol fuel cells, MR-DMFCs), and microbial fuel cells. MR-DMFCs combine the advantage of reduced explosion risks through operation on diluted methanol-air mixtures at low temperatures (e.g. 90 °C) and of overcoming the problems of methanol cross-over and coupled low performance in conventional DMFCs.

Table 1 summarizes advantages and challenges of SC-SOFCs. A major drawback of SC-SOFCs is the insufficient selectivity of current electrode materials, resulting in low fuel utilization and cell efficiency. Therefore, one of the main challenges of SC-SOFC technology consists in finding highly selective materials for the next generation of SC-SOFCs with improved efficiencies for practical implementation. Another drawback of SC-SOFCs is the risk of explosion related to working with fuel-air gas mixtures at elevated temperatures.



Advantages	Challenges
• Sealing-free structure • Less complex gas manifolding • Increased thermomechanical stability • More compact and simplified designs • Easier stack assembly • Great potential for miniaturization • No need for gas-tight electrolyte • Exothermic reactions to sustain cell temperature • New cell designs • Easier fabrication	• Highly selective and catalytically active materials necessary • Low efficiency due to parasitic, non-electrochemical reactions • Lower fuel utilization than in dual-chamber SOFCs • Risk of explosion for fuel-air mixtures at high temperatures

Table 1. Advantages and challenges of SC-SOFCs.

Despite those challenges, however, SOFCs operated in the single-chamber mode exhibit several advantages over conventional SOFCs, making them an interesting alternative to overcome problems associated with dual-chamber operation. Due to the use of a gas mixture, one key advantage of SC-SOFCs consists in the elimination of the gas-tight sealing. Additionally, since the cell is located in one gas compartment, less complex gas manifolding and flow field structures are necessary for reactant supply. The resulting simplified, compact, sealing-free cell structure is expected to show enhanced thermal and mechanical resistance. Also, very thin electrolyte layers with defects, small cracks and pores are acceptable. SC-SOFC fabrication is therefore simpler, and reduced fabrication costs can be expected. Due to the use of a gas mixture, novel cell configurations such as fully porous and single-face SC-SOFCs with coplanar electrodes become possible that could not work under conventional, dual-chamber operating conditions.

BEGINNING OF SC-SOFCS

Early works on single-chamber fuel cells - The concept of single-chamber and mixed-gas operation has its beginnings in the 1950s and 1960s. Back then, the possibility was investigated of using oxyhydrogen gas from radiolytically split water in nuclear reactors to generate electricity by electrochemical recombination of the gas mixture in a fuel cell. Such a H_2-O_2 radioisotope power supply was proposed as a nuclear-electric system for applications in space. Already at this stage, the necessity for selective electrodes was pointed out by researchers from Siemens-Varta. Cathodes of active carbon with well dispersed silver were found to be selective for reducing the oxygen from the gas mixture, but not promoting the electrochemical oxidation of hydrogen. Similarly, the reaction selective anode made of platinum and/or palladium should only enable the reaction of hydrogen. A liquid solution of KOH was proposed as electrolyte. In an oxyhydrogen gas mixture with 9% O2 and 91% H2, such an alkaline fuel cell generated an OCV of approximately 1 V and a maximum current density of 4 mA·cm^{-2} at room temperature. A connection of three single cells in series being operated at 60 °C and a mixture of oxygen and hydrogen with a ratio of O2 to H2 of 1:2 led to a power output of 85 W.

In 1961, Grimes et al. proposed a simplified and compact fuel cell design based on an alkaline fuel cell working with a mixture of liquid fuel and oxidant. The cell was composed of a KOH electrolyte solution to which methanol as fuel and hydrogen peroxide as oxidant could easily be added and mixed. Silver was chosen as cathode with elevated selectivity for hydrogen peroxide and sufficient inertness towards the fuel. At the platinum anode, however, both oxidant and fuel were reacting, creating a chemical short circuit of the system and an unstable OCV. By adjusting the concentrations of methanol and hydrogen peroxide, a stable OCV of 0.81 V could finally be achieved. A combination of 40 single cells in series connection led to an overall output of 15 V at 40 A.

Also in 1961, Eyraud et al. developed an all-solid-state electrochemical device operated in a fuel-oxidant gas mixture as an attempt to increase specific power of fuel cells. Reaction selective electrodes with Pt or Pd for the anode and Cu or Ni for the cathode were combined with a micro-porous, gas-permeable solid alumina or polymer electrolyte. The elaboration of an electrolyte with reduced thickness was found essential to decrease the ohmic cell resistance. In an atmosphere of humidified air, a Ni-Al2O3-Pd cell delivered an OCV of –0.35 V. When hydrogen was added, the OCV was 0.6 V.

In 1965, van Gool further investigated the principles of using gas mixtures in fuel cells. He pointed out that such fuel cells work through heterogeneous catalysis of the fuel and that the catalysts must show high selectivity for the respective reactions. Guidelines for the selection of electrode materials were presented. Based on surface-migration of ions he also proposed fully porous designs and a fuel cell with coplanar, interdigitated electrodes. The first report of operating such a mixed-reactant surface migration cell with coplanar electrodes dates from 1981 where Louis et al. patented a cell design with rectangular, closely-spaced anodes and cathodes on the same side of the electrolyte. Series and parallel connection of various single cells on the same substrate was proposed to enhance power output.

Development of SC-SOFCs –

In 1992, a two-chamber solid electrolyte fuel cell was adapted to supply each electrode chamber with fuel-air mixtures. Cells were fabricated from Pt electrodes on an YSZ (yttria-stabilized zirconia) electrolyte and were operated at elevated temperatures in contrast to Dyer’s room temperature device. Fuel cell operation was initialized either by an electrical pulse or different gas flow rates between the electrodes. For different electrode materials (e.g. Au and Pt), fuel cell operation was based on different electrochemical exchange rates of the two electrodes. Cell operation was possible using different fuels and at temperatures of up to 450 °C. At 350 °C for a methane-air mixture, an OCV of 0.95 V and a current of 0.065 mA at 0.64 V were measured. In another cell design, different gas flow rates were generated between the electrodes, enabling fuel cell operation without an initializing electrical pulse and up to 600 °C.

Hibino and co-workers are the pioneers in implementing the single-chamber operating mode for high temperature SOFCs, making the use of hydrocarbon fuels possible and decreasing the risk of explosion as compared to H2-O2 mixtures. In 1993, Hibino et al. operated the first SC-SOFC in a methane-air mixture at 950 °C. In addition to the experimental demonstration of generating a significant current, outlet gas analysis and electrode potential measurements were used to elucidate the working mechanisms. The difference in catalytic activity of the electrodes for the partial oxidation of methane was found to lead to the generation of an OCV.

SC-SOFCS WITH INTEGRATED CURRENT-COLLECTORS

Conventional fuel cells rely on the strict separation of the oxidant and the fuel in order to prevent parasitic side reactions. Highly active but non-selective electrodes are used. However, with reaction selective anode and cathode materials it is possible to operate a fuel cell in a mixture of fuel and air. In the past, high costs have hampered the commercialisation of fuel cell systems. For SOFCs the costs are partly due to processes and technologies required for sealing the cells at high temperatures. Single chamber solid oxide fuel cells (SC-SOFCs) with

reaction selective electrodes offer the possibility to simplify SOFC designs because only one gas compartment is necessary. Both anode and cathode are exposed to the same mixture of fuel and oxidant. In such a system the driving force for the ionic current in the electrolyte is not due to the difference of oxygen partial pressures in the two sealed gas compartments. It is the selectivity of the two different electrodes for either the partial oxidation of methane (anode) or the reduction of oxygen (cathode) that gives rise to the observed OCV.

This approach was proposed by van Gool (1965) and is in principle applicable to all fuel cell types. So far, however, this concept has only been tested for SOFCs and direct methanol fuel cells. The first functioning “Single Chamber” device based on boehmite-electrolyte was fabricated by Dyer in 1990. It operated at room temperature on a mixture of hydrogen and oxygen gas and generated a voltage of up to 1 V and a maximum power density of 5 mW/cm2.

A theoretical explanation for the operating principle of a SC-SOFC was given by Riess et al.. One of the first SC-SOFCs was based on Yttrium Stabilised Zirconia (YSZ) and operated on mixtures of methane and air at 950°C. The anode was made of Ni-YSZ and the cathode of Au. The cell generated an OCV of 0.35V and a maximum electric power of 2.4 mW/cm2.

FULLY POROUS SC-SOFCS

In single chamber SOFCs both electrodes are exposed to a gas mixture of fuel and air and leaks in the electrolyte are of no concern. However, the anode and cathode must be physically separated from each other in order to avoid a short circuit in the cell. If the electrolyte of the cell is permitted to be porous, the fabrication costs could be drastically reduced. The electrolyte layer could be processed by screen printing and sintering at relatively low temperature because full density would not have to be achieved. Suzuki et al. compared the performance of anode-supported SC-SOFCs with dense and with porous electrolytes and found that the porous electrolyte had a smaller resistance to the ionic current than the dense one. The reason for this had been postulated by van Gool 40 years ago and was due to the enhanced ionic conductivity at the surface of the electrolyte. The results of Suzuki et al. showed that the cell with porous electrolyte had an OCV that was 0.1 V lower than for the cell with dense electrolyte, which could be attributed to the fact that some hydrogen reached the cathode through the pores in the electrolyte, thereby reducing the oxygen partial pressure at the cathode. The power output of porous cell at 744°C was 660 mW/cm2 in flowing mixtures of CH4-air (900 ml/min). In previous work we have shown that electrolyte supported SC-SOFCs based on $Ni\text{-}Ce_{0.8}Gd_{0.2}O_{1.9}$ $/Ce_{0.9}Gd_{0.1}O_{1.95}/$ $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ performed well at a furnace temperature of 700°C (350 mW/cm^2. The SC-SOFCs described here are based on the same materials as previously used. They were fully porous anode-supported

cells with a thin electrolyte layer (30 µm in thickness) fabricated by screen printing. The main difference to Suzuki's work is that here the cells were operated in a flow-through configuration. It has been shown that the flow configuration during the measurement of SCSOFCs has a drastic effect on the OCV and the power output. Stefan et al. showed that the configuration where the anode is exposed to the gas mixture first and reaches the cathode afterwards, should be avoided. This is why in the described experiments, the cathode was always the electrode that was exposed to the gas at first. The aim of this work was to make a proof of concept for fully porous SC-SOFCs with flow-through configuration.

CONCLUSION

Single Chamber Solid Oxide Fuel Cell technology offers a potential solution to current problems including faster startup times, reduced temperature operation, self-sustaining operation, and reduced carbon coking. The results to date are encouraging, although the cell efficiency and fuel utilization of the best SCFC reported to date is significantly lower than for conventional SOFCs. As reported by several researchers, significant opportunity exists to increase power densities by reducing the polarization losses in the electrolyte. This can be accomplished by making the electrolyte thinner, by choosing alternate materials, and by using better fabrication procedures. However, with these low fuel efficiencies values, competition with current SOFCs using traditional technologies seems difficult.

Single-chamber fuel cells have significant potential, particularly for applications in which the simplicity of a single gas channel and absence of seals is of paramount importance. We have demonstrated that very useful power densities may be achieved, and this may be done at relatively low operating temperatures, making thermally self-sustaining operation possible.

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