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Measurement techniques in solid oxide fuel cells: infrared thermal imaging

Introduction

Fuel cells are promising technology of energy conversion that directly converts chemical energy of fuel to electrical energy for a range of stationary, transport and portable power applications (Giddey 2012: 6; Badwal 1997: 2; Webe 2004: 21; Minh 1993: 12; Hellman 2007: 9). There are many different types of fuel cells that operate from near room temperature up to 1000°C. They all use different construction materials and face the diverse challenges of technology and commercialization. Fuel cells offer many advantages over traditional power generation systems. Those include high efficiency (40–50% electric, 65–75% with heat recovery), high energy density, low chemical and pollutant emissions, ability to co-generate heat and electricity at load centres, high quality power supply (without electrical noise), minimum distribution infrastructure and losses, modularity and flexibility of fuel.

The low temperature fuel cells include direct or indirect alcohol (methanol, ethanol) fuel cells, hydrogen based polymer electrolyte membrane systems and alkaline fuel cells, operate in temperature typically below 100°C. These fuel cells have found applications in small portable power and transport applications and have power ranges from less than W to over 100kW. They offer rapid start and shut down, excellent load following characteristics specifically required for transport vehicles and unlimited thermal cycling capability. The phosphoric acid fuel cell which runs around 200–220°C is the most commercialized technology developed primarily for stationary distributed heat and power generation applications. The intermediate temperature fuel cell system is the Molten Carbonate Fuel Cell (MCFC) with working temperature of 650°C. The two high temperature fuel cells are the solid oxide (SOFC) and direct carbon (DCFC) fuel cells with operating temperature in the 700–1000°C range. Direct carbon fuel cells utilize solid carbon as the fuel instead of gaseous fuels (CO, H₂, CH₄) used in SOFCs and produce an output stream rich in CO₂ (Giddey 2012:6). The main advantage of SOFCs and DCFCs is their ability to co-generate high grade heat (>600°C) if required in end-use application. SOFCs operate with gaseous fuels such as H₂, CO or hydrocarbons. Reforming of methane is possible in-situ due to the high operating temperature to generate H₂ and CO. DCFCs utilize solid

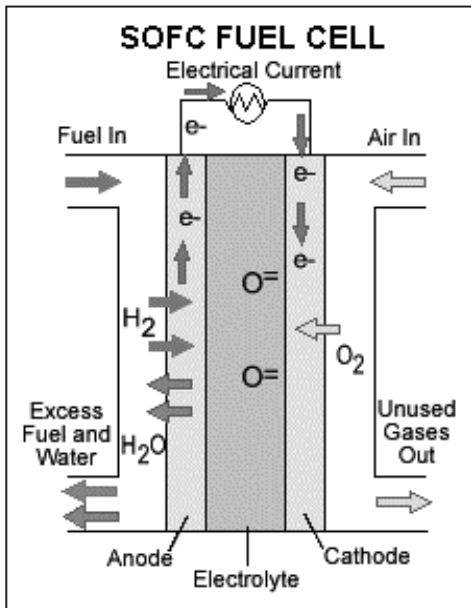


Fig. 1. Basic operating principle of a SOFC [Fuel cell type 5]

carbon as the fuel and offer the large advantage of extremely high electric efficiency (>65–70%) and production of pure stream of CO₂ without additional cost of capture and energy penalty (Giddey 2012:6).

A solid oxide fuel cell (SOFC) operates at a temperature range of 700 to 1000°C. An oxygen ion conducting ceramic such as yttria stabilised zirconia (YSZ) is used as an electrolyte. Oxygen from air is converted to oxygen ions at the cathode/electrolyte interface and then transported through the electrolyte to the anode, where they react with hydrogen and/or CO to create water and/or CO₂ (Fig. 1). High operating temperature of SOFCs generate high demands for construction materials. In addition to superb electrical and electrochemical properties, high chemical and thermal compatibility in the fuel cell operating environments deserves great attention. It is a matter of utmost importance that stability occurs for a long time of over 40000–50000h required for stationary applications (Badwal 2001: 3).

SOFCs are made up of a number of components (air and fuel electrodes, electrolyte, sealing materials when required, interconnects and fuel distribution system). These elements are mostly constructed from ceramic, metal or metal ceramic composites. Each material is required to operate in multiple property space and is obliged to meet several criteria.

An electrolyte of a solid oxide fuel cell must have a high conductivity of oxygen ion (i.e. >0.1S/cm) over a broad range of oxygen partial pressure. In terms of material to be a good electrolyte, it must meet multi-faceted property criteria. In addition to high ionic conductivity, it must be nearly fully dense with no open porosity (to avoid any cross diffusion of fuel and oxidant elements). The electrolyte is in contact with both air and fuel electrodes and sealing materials and must not only be chemically inert with respect to these materials but also have well-chosen thermal expansion co-efficient (TEC) and good mechanical properties. The electrolyte is exposed

to highly oxidising environments on the side of the air electrode and highly reducing environments on the fuel electrode side and must be chemically and structurally stable with an ionic transference number close to unity. It should also have high tensile strength and toughness not only to facilitate of handling but also to resist thermal and mechanical stresses during manufacturing and cell operation. Through clever designs and techniques, some of the requirements can be circumvented.

A cathode in a solid oxide fuel cell is required to have high electronic conductivity, preferably high oxygen ion conductivity, a coefficient of thermal expansion (TEC) that closely matches the electrolyte, chemical stability during manufacturing of the cell and while operating at work temperatures and oxygen partial pressures, good catalytic properties for oxygen molecule dissociation and reduction. SOFC cathode is responsible for a large part of the cell voltage losses, and most of that is due to high polarisation losses associated with the oxygen reduction reaction.

A primary function of SOFC anode is to facilitate the electrochemical oxidation of fuel and provide pathways for electrons released during oxidation reaction to reach the current collector. Characteristics of a material to be suitable as SOFC anode includes sufficient ionic and electronic conductivity, electrocatalytic activity towards the fuel, phase compatibility with electrolyte and current collectors, micro-structural stability at SOFC operating temperature and matching thermal expansion properties with other components. For SOFCs fuelled with hydrocarbon fuels, there are additional requirements, such as catalytic activity for hydrocarbon cracking, sulphur tolerance and resistance to coking. As electrochemical reaction takes place at anode- electrolyte interface a sufficient porosity (>30 vol%) is needed to allow transport of reactant/products (Islam 2013: 10).

There are numerous papers on solid oxide fuel cells, but they focus more on the materials, including synthesis, conduction mechanisms and applications. However, despite the fact that several different measurement methods have been used for determining the electronic, mechanical and structural properties of the materials, there has been no demonstration of these methods used for defining SOFC materials. Each of the methods have their advantages and disadvantages, which makes a straightforward comparison of results and evaluation of the properties of the materials difficult. Therefore, in this article we provide a list of the different measurement methods used in ceramic fuel cells.

In the first section, we give a brief introduction of the measurement method, after which general information about the specific measurement are elaborated. There are an overview of the methods and the results obtained by each method are given for dilatometry, impedance spectroscopy, current-voltage characteristics and mid-infrared thermal imaging. Finally, conclusions for the methods are drawn and recommendations about future measurements are given.

Dilatometric studies

Dilatometry (DIL) is a thermoanalytical technique for the measurement of expansion or contraction of a material subjected to a controlled temperature/time program. The determination of the thermal expansion behavior by dilatometry is a simple method in which a volume change, can easily be detected (Taylor 1998:19).

Most solid materials expand upon heating and shrink when cooled. Changing the length with temperature for a solid material can be expressed as:

$$\frac{(l_f - l_0)}{l_0} = \alpha(T_f - T_0) \quad \alpha = \frac{1}{l} \left(\frac{dl}{dT} \right)$$

where l_0 and l_f represent the original and final lengths with the temperature change from T_0 to T_f .

Mechanical dilatometry techniques are extensively used. With this technique, the sample is heated in a furnace and displacement of the ends of the sample are transmitted to a detector by means of push rods. The linear thermal expansion coefficient (TEC, or α) is a material property that is indicative of the extent to which a material expands upon heating. Various substances expand by different amounts. In low temperature, the thermal expansion of uniform linear objects is proportional to temperature change. However, thermal expansion coefficients is heavily influenced by the preparation method (e.g. co-precipitation, impregnation, sintering etc.) and the conditions supplied. Nevertheless, dilatometry is a good instrument for measuring the thermal expansion behavior as suitable for the application in SOFCs.

It is important that the thermal expansion coefficients of all SOFC components match well. Thermal expansion coefficients (TECs) of anode material like nickel-based cermet and electrolyte material often do not match with each other. For example, the TEC of nickel is considerably higher than that of some electrolytes, such as YSZ, which may result in the deterioration of the cell. Furthermore, nickel easily sinters at higher temperatures, which results in a decrease in the porosity of the anode. It was observed that the thermal expansion coefficient of Ni-YSZ cermet increases linearly with nickel content (Minh 1993: 12). Reduction of nickel content is beneficial as far as the match between the TECs of the two adjacent phases – the anode and the electrolyte – is concerned, and makes it possible to avoid the cracking of the cell during operation (Haberko 2010: 7).

Electrochemical impedance spectroscopy

In order to increase the efficiency of fuel cells it is very important to understand the transport properties of the anode, cathode and electrolyte. Therefore, measurements of conductivity of materials are very important. Currently, there are many test methods which allow to measure the conductivity of materials such as impedance or current-voltage characteristics measurements (Primdahl 2002: 16; Primdahl 2002: 17).

Electrochemical impedance spectroscopy (EIS) method involves applying an alternating sinusoidal current of known frequency and phase on the test material and measuring the current response (Barsoukov 2005: 4). In theory, the answer current should also be sinusoidal, whose amplitude and phase shift corresponds to the properties of the sample such as conductivity.

The results of studies using the EIS are usually presented as Nyquist plots, and ionic conductivity, or of the individual parts of cells can be calculated from the characteristic semicircles. In practice, the electrical equivalent circuit is used to determine the conductivity of individual components. However, the process of choosing

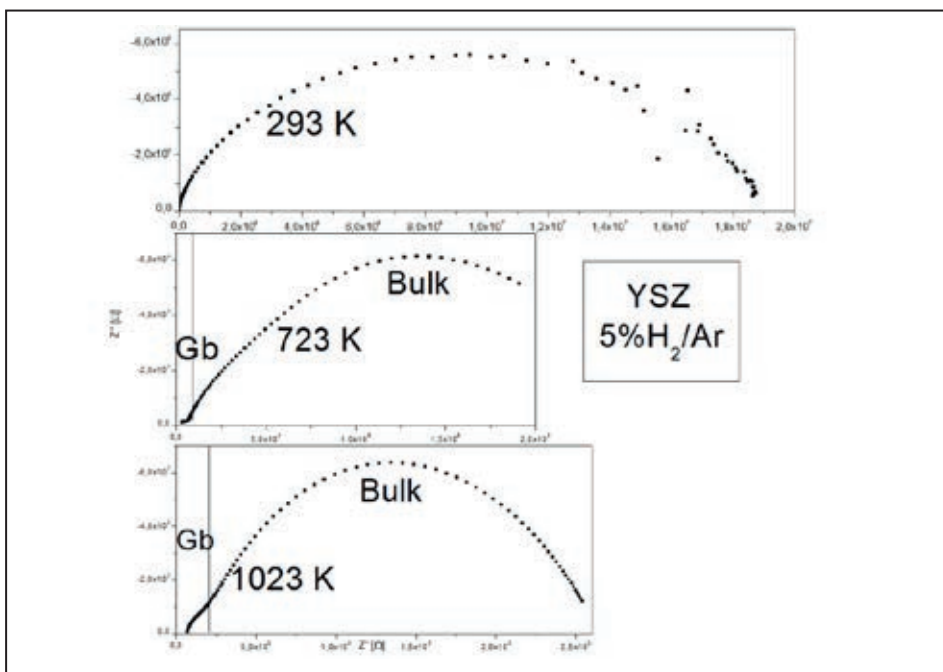


Fig. 2. Experimental Nyquist plots of the studied YSZ samples at different temperatures on the complex impedance plane

the equivalent circuit and fitting curves must be made with a great care to minimize errors of analysis. For example, if the mechanism of conductivity of the material varies with temperature, it must also correspond with a changing electrical equivalent circuit. More detailed information about the measurements of conductivity by EIS can be found in Ref. (Barsoukov 2005: 4). Błąd! Nie zdefiniowano zakładki.. Temperature affects the conductivity of investigated anode materials. In Figure 2. the measured data of YSZ anode are shown.

At low temperatures semicircle coming from the bulk conductivity is visible. However, with increasing temperature more semicircles are seen. Semicircle at higher frequencies assigned to bulk conductivity, and the semicircle appearing for the mid-frequency to grain boundary (Gb) conductivity. With increasing temperature ionic conductivity also increases. When the number of different conduction mechanisms increases and more semicircles appear, often overlapping, analysis of this type of data becomes even more difficult.

Current–voltage characteristics, fuel cell properties

In the constant current method, an external constant current is conducted through the sample. First, ions in the material move in the direction of the current until a steady state is achieved. In this state, only electrons and externally supplied ions corresponding to the gas atmospheres continue to move assuming that the sample does not deteriorate, e.g. nickel particles do not transform into nickel (di)

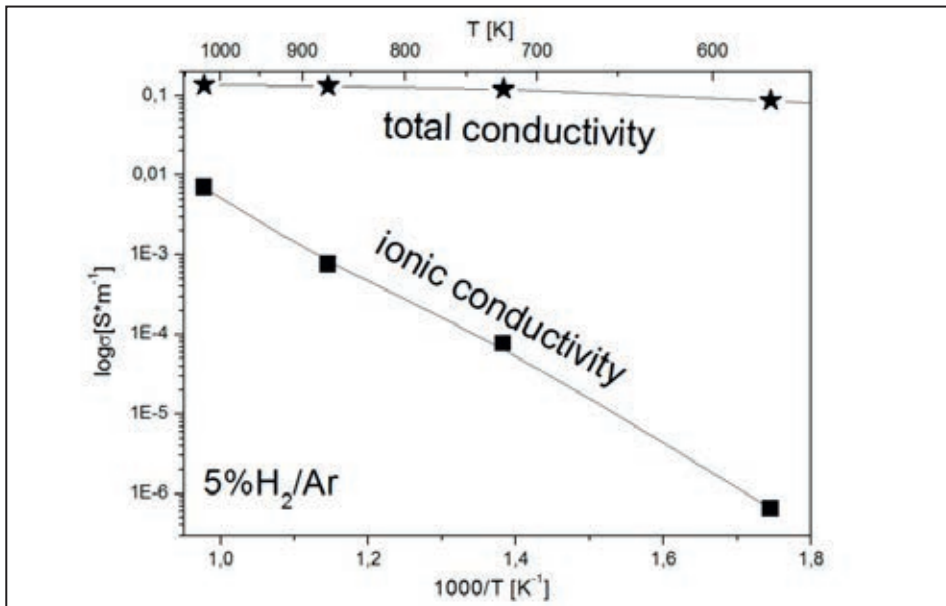


Fig. 3. Arrhenius plots of $\log(T\sigma)$ of total and ionic conductivities

oxide (Patakanga 2014: 13). In the end, ionic conductivity can be determined from the voltage and current values assuming that the electronic conduction, as well as other effects related to the polarization, can be determined or are negligible.

Typically, a two or four-point method is used to measure electrical conductivity. Polarization effects originating from the electrodes may be omitted in the 4-point method, but the position of the electrodes and the contact area between the electrodes and the sample should be specified. Otherwise, this can lead to artifacts.

The impact of using different electrodes is presented in Ref. (Haberkro 2010: 7) where the anode conductivity was measured by a 2-point method using two different sets of electrodes. The potential of the electrode was varied from 0 to 2 V. The electrodes are arranged according to the scheme: "Pt(paste)/anode/Pt(paste)" and "Pt(paste)/ZrO₂/anode/ZrO₂/Pt(paste)", where the ZrO₂ was electron blocking electrode.

As the conductivities with blocking electrodes were lower than without them, it seems that the major part of conductivity comes from electrons (Fig. 3). In fact, the electronic conductivity determined from the IeV curve was 4×10^3 times higher than the ionic. The straight line dependencies show that the studied materials exhibit ohmic behavior.

This shows that the role of the electrode conductivities is significant and should be taken into account when new materials for SOFC are designed.

Infrared thermal imaging

One of the major problems of the use of fuel cells is the selection of materials for their construction retaining its chemical, structural, electrical and thermo-mechanical properties for a long time running under extreme conditions of temperature

and pressure. In order to meet these requirements fuel combustion processes in different cell operating conditions as well as the chemical and structural changes leading to a reduction in the efficiency of the SOFC cell type should be examined and analyzed. A comprehensive understanding of these processes is possible using electrochemical research methods such as impedance spectroscopy and current-voltage measurements. However, these methods are not able to identify the local chemical processes taking place in situ at the surface of electrodes.

For proper control of fuel cells the temperature measuring device (thermocouple) can be located in the vicinity of cell. This allows to make a temperature map of a single cell or set of cells (fuel cell stack) (Kim 2006: 11). However, placing thermocouples close to the surface of cells, can lead to penetration, deterioration, and finally to its destruction. Adzic et al. (Adzic 1997: 1) have used a flat-type thermocouple to probe the temperature distribution at the cathode of a planar SOFC. The thermocouple was placed in close proximity (as close as $5\mu\text{m}$), but not in contact with the electrode surface. Localised hot spots measured were as much as 16°C above the mean surface temperature. An alternative to discreet temperature sensors is the use of infrared measurements. This technique has the advantage of not requiring sensor placement or connecting leads, high spatial resolutions and frame collection can be achieved. The technique is ideal for measuring the outer surface temperature of a fuel cell or stack. In order to investigate the temperature within a fuel cell, the construction needs to be modified to allow optical access to the surface of interest (Fig. 4).

Infrared thermal imaging has been performed on PEM cells (polymer electrolyte membrane) for measuring current density, the effects of saturated steam consumption or fuel type (Hakenjos 2004: 8; Wang 2006: 20). These studies showed

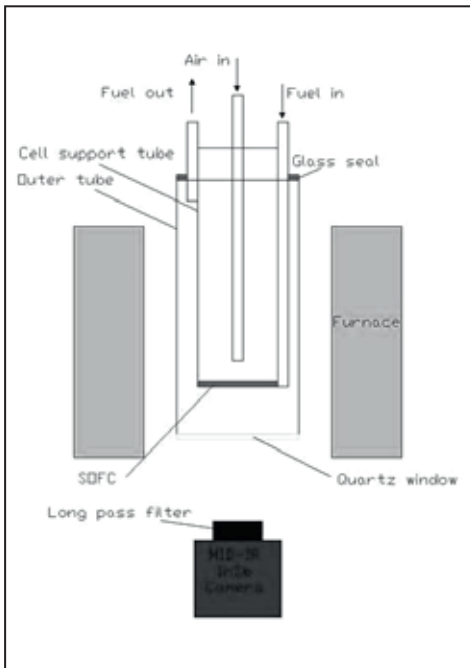


Fig. 4. Scheme of the test stand for infrared studies of fuel cells

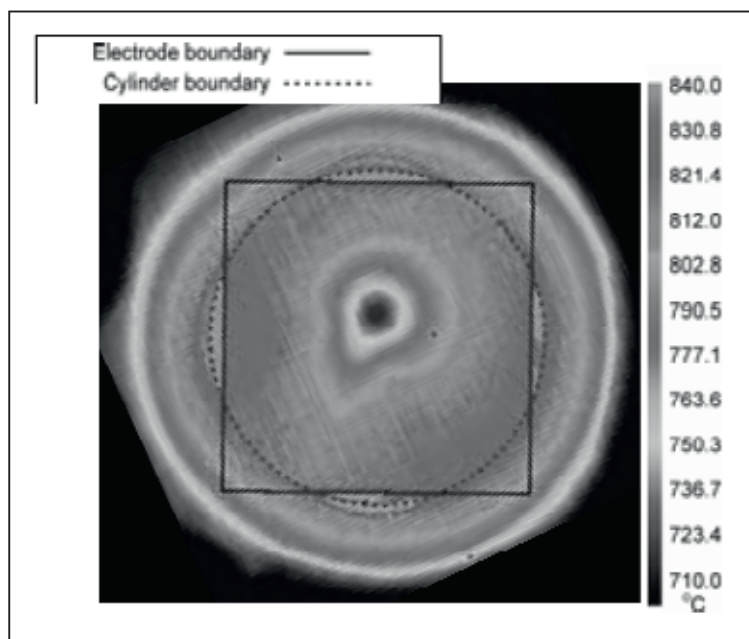


Fig. 5. the IR image for an electrolyte supported SOFC when exposed to a 'cold' air stream at its centre

that significant temperature variation results across the surface of the PEM due to changing current density, humidification and reactant composition. The work of Wang et al. (Hakenjos 2004: 8) demonstrates how electrode surface temperature increases with current density. Also, recent studies of SOFC cells support the potential of the method for testing thermal imaging of small (a few millimeters in diameter) cells (Pomfret 2010: 14; Pomfret 2013: 15).

Mid-infrared thermography is a method that allows the observation of the electrode surface cells and study of its temperature – providing much more detailed information of the processes taking place on the surface of working cell than using spot temperature measurement using thermocouples. Brett (Schöttl 2006: 18) has applied infra-red thermography to determine the temperature changes and spatial distribution associated with different current densities for electrolyte supported pellet cells. Temperature changes of up to 2.5°C were observed for heavily electrically loaded pellet cells.

Figure 5 shows the IR image for an electrolyte supported SOFC when exposed to a 'cold' air stream at its centre. Evidence of temperature distribution heterogeneity was observed (Schöttl 2006: 18). The solid line shows the interface between active catalyst and electrolyte area. A temperature gradient of over 9°C mm⁻¹ was recorded without the electrolyte cracking or electrode delaminating.

Conclusions

Dilatometry, Electrochemical Impedance spectroscopy, Current-voltage characteristics are common research methods of solid oxide fuel cells. However Infrared

imaging method enables to study processes running directly at the surface of the cell. This method in combination with electrical measurements allow much more complete information on the processes occurring in the fuel cell cells such as combustion of fuel.

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Abstract

Solid oxide fuel cells (SOFC) are high temperature electrochemical devices, which convert the energy of a chemical reaction directly into electricity. The long-term performance of fuel cells is strictly related to both the structural and electrical properties of anode materials. In order to achieve high mixed electronic-ionic conductivity and high activity of electrochemical reactions and hydrocarbon fuel reforming, it is necessary to select an appropriate chemical composition and a suitable method of preparation. To verify that the synthesized materials meet the requirements set down for them, it is necessary to use simple research methods to analyze them. The article presents a brief description of commonly used research methods (dilatometry, impedance spectroscopy, current-voltage characteristic) and the new prospective method such as infrared thermal imaging.

Key words: infrared thermal imaging, SOFC, solid oxide fuel cell, measurement techniques

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