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Designing a miniaturised heated stage for *in situ* optical measurements of solid oxide fuel cell electrode surfaces, and probing the oxidation of solid oxide fuel cell anodes using *in situ* Raman spectroscopy

E. Brightman,¹ R. Maher,² G. J. Offer,¹ V. Duboviks,¹ C. Heck,¹ L. F. Cohen,² and N. P. Brandon¹

¹Department of Earth Science and Engineering, Imperial College, London SW7 2AZ, United Kingdom

²Department of Physics, Imperial College, London SW7 2AZ, United Kingdom

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A novel miniaturised heated stage for *in operando* optical measurements on solid oxide fuel cell electrode surfaces is described. The design combines the advantages of previously reported designs, namely, (i) fully controllable dual atmosphere operation enabling fuel cell pellets to be tested *in operando* with either electrode in any atmosphere being the focus of study, and (ii) combined electrochemical measurements with optical spectroscopy measurements with the potential for highly detailed study of electrochemical processes; with the following advances, (iii) integrated fitting for mounting on a mapping stage enabling 2-D spatial characterisation of the surface, (iv) a compact profile that is externally cooled, enabling operation on an existing microscope without the need for specialized lenses, (v) the ability to cool very rapidly, from 600 °C to 300 °C in less than 5 min without damaging the experimental apparatus, and (vi) the ability to accommodate a range of pellet sizes and thicknesses. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4719955>]

I. INTRODUCTION

Electrochemical measurements provide real-time data on solid oxide fuel cell (SOFC) performance and degradation kinetics, but there is a limit to the amount of mechanistic or chemical information that can be deduced from these measurements. Micro structural analysis such as SEM, and surface compositional analysis techniques such as Auger electron spectroscopy (AES) are useful for visualizing the microstructure and permanent chemical modifications on the active surfaces, but these techniques are limited to post-test analysis of *ex situ* samples, and it would be very difficult to perform such analysis on an SOFC anode *in situ*. However, it is important to be able to measure as much information as possible during fuel cell operation *in situ* in order to understand critical electrode processes and draw more detailed conclusions from the electrochemical measurements.

Raman spectroscopy is a molecularly specific, non-invasive optical technique capable of providing valuable chemical information such as reaction kinetics, reaction intermediates, temperature distributions and material oxidation state.¹ It has shown itself to be a useful technique for probing surface chemistry in SOFC operating conditions.²

Cheng *et al.*³ examined samples in an atmospheric heated stage capable of operating up to 500 °C, compared the results with those from samples exposed to fuel gases and then cooled the samples to room temperature for *ex situ* analysis, to show that misleading results may be obtained from the latter, due to compositional changes occurring during cooling. Maher *et al.*¹ also used a commercially available high temperature atmospheric stage, which was capable of heating to 1000 °C. They demonstrated the use of Raman spectroscopy to measure surface temperature and redox kinetics of SOFC anode materials in fuel environments.

However, these “*in situ*” experiments were performed at simulated operating conditions in a single atmosphere on materials not integrated in an operating fuel cell. In contrast Liu *et al.*⁴ demonstrated the first experiments enabling *in situ* Raman spectroscopy under practical operating conditions, followed by Pomfret *et al.*^{2,5–7} who demonstrated an apparatus for *in situ* Raman spectroscopy on operating fuel cells, which could be referred to as *in operando*. Pomfret *et al.*^{5–7} demonstrated the successful measurement of carbon deposition from hydrocarbon fuels at various current densities, and observed transient graphitic carbon during hydrocarbon oxidation on the anode compared with build-up of carbon at open circuit conditions. The practical considerations involved in constructing and using an *in operando* SOFC Raman apparatus are highly challenging.

The apparatus used by Pomfret *et al.*^{2,5–7} and latterly Eigenbrodt *et al.*^{8–10} involved a long-working distance objective with an SOFC mounted in a closed-end quartz tube situated in a furnace. The heated stage used by Maher *et al.*¹ has the advantage of fitting on a microscope-mounted mapping stage enabling 2D spatial mapping of the surface, while the apparatus described by Pomfret *et al.*^{2,5–7} enables the study of operational fuel cells and the effects of cell bias on surface properties.

This paper describes the development of a novel miniaturised heated stage for *in operando* optical measurements on SOFC electrode surfaces. This design combines the advantages of the previously reported designs, namely, (i) integrated fitting for mounting on a mapping stage enabling 2D spatial characterisation of the surface, (ii) a compact profile that is externally cooled, enabling operation on an existing microscope without the need for specialized lenses, (iii) fully controllable dual atmosphere operation enabling fuel cell pellets

to be tested *in operando* with either electrode in any atmosphere being the focus of study, (iv) combined electrochemical measurements with optical spectroscopy measurements with the potential for highly detailed study of electrochemical processes, (v) the ability to cool very rapidly, from 600 °C to 300 °C in less than 5 min without damaging pellets or the experimental apparatus, and (vi) the ability to accommodate a range of pellet sizes and thicknesses.

In order to demonstrate the viability of the experimental apparatus, this paper describes preliminary results for *in situ* Raman spectroscopy on an operating SOFC. Established state-of-the-art nickel-based anode materials, such as nickel/yttria stabilized zirconia (Ni-YSZ) and nickel/gadolinia doped ceria (Ni-CGO) cermets, have many advantages, such as low cost, high conductivity, and good catalytic activity. However, durability and impurity tolerance remain major challenges requiring an enhanced understanding of electrochemical processes. The main causes of anode degradation are carbon deposition, sulphur poisoning, and redox cycling. In this paper a preliminary study of oxidation state of a Ni-CGO cermet electrode during reduction is presented.

II. DESIGN OF THE SOFC TEST APPARATUS

The design remit for the test apparatus included a broad range of requirements. These break down into geometrical requirements, temperature requirements, material requirements and measurement and gas supply ports.

A. Geometrical

The dimensions of the existing spectroscopic apparatus in which the test apparatus is to be used dictated the outer dimensions of the test apparatus. The available space on the Raman microscope allows the apparatus to extend to an outer diameter of 100 mm and a total height of 70 mm. The fuel cells intended for testing are up to 22 mm in diameter, and so the inner core of the apparatus was designed to fit this size. This therefore sets the radial dimensions of the test apparatus to an inner diameter of 22 mm and the outer diameter smaller than 100 mm, while the maximum total height must be no more than 70 mm. Within this space must be fitted the heating element, insulation and any water-cooling apparatus required, as well as ports for gas and electrical access.

B. Measurement

The purpose of the test apparatus is to allow *in situ* Raman spectroscopy on a working fuel cell. This therefore necessitates two separate gas chambers, each with its own gas inlet and outlet. They must be properly sealed and thermally balanced, although the cathode side may be open to ambient air for simplicity under some conditions. For optical access a quartz window must form at least part of the top wall of the upper chamber. Furthermore, inlets for the electrical connections to the electrodes and thermocouples need to be integrated in both chambers.

C. Temperature

SOFCS have an operating temperature of 500–1000 °C, whereas the objective of the Raman spectroscope must not be exposed to temperatures much over 80 °C. The microscope objective intended for use has a working distance of 9 mm, which is therefore the maximum distance between the analyzed electrode of the fuel cell and the outside of the quartz glass. Furthermore, there has to be space between the window and the objective in order to allow a flow of gas over the quartz glass and avoid conduction of heat directly to the objective. This then dictates the possible distance between the fuel cell and the glass window forming the top surface of the test apparatus. Additionally, there has to be a proportionally high amount of insulation around the actual fuel cell in order to keep it at a constant temperature and to decrease the amount of heat dissipated to the outside. The outer surface of the test apparatus therefore requires water cooling. A further consideration is that the heating element will need to be capable of controlling the temperature to at least 600 °C and within <5 °C control error.

D. Materials

Due to the high temperatures and thermal gradients involved, the number of materials that can withstand these conditions is limited, since relaxation processes weaken materials at these temperatures. At the same time, they have to be as inert as possible in both reducing and oxidising atmosphere at high temperatures in order to avoid poisoning the fuel cell components which may affect the results. The materials should have small thermal expansion coefficients to avoid further stress on the ceramic parts (especially the fuel cell itself) during operation. Additionally, in order to allow safe handling of the test apparatus the design must be capable of being taken apart and reassembled without difficulty. This includes replacement of parts (especially the quartz glass, which is quite fragile) and the exchange of the fuel cell and the components connected to it. Therefore, a non-permanent sealing method is desirable.

III. PROTOTYPE DESIGN

The design is shown in cross section in Figure 1. Parts are made out of 316 stainless steel, due to its ease of machining, with a quartz window and compressive Thermiculite gasket seals (Flexitallic Ltd., UK), which enables ease of disassembly between experiments. The basic structural framework of the design consists of an inner core containing the fuel cell in a sandwich-like configuration between two parts, an inner cap and inner base plate, which are surrounded by the heating element. This is surrounded by insulation and a larger cylindrical outer cap and outer base plate, which are compressed together and provide the pressure required for the sealing gaskets, as well as forming a casket to contain the insulation. The outer cap is in contact with the cooling jacket and cooling top. Holes are drilled in the sides and the base to provide access to both chambers of the fuel cell for gas tubes, electrical connections, and thermocouples (not shown in Figure 1), and a

FIG. 1. Cross section drawing of the *in situ* SOFC test apparatus with optical access.

6 mm hole is drilled in the top for optical access. The quartz window sits between the inner and outer caps and is sealed with Thermiculite gaskets under pressure. Current collection is made with gold mesh held in place by a coiled Inconel wire spring, electrically isolated with a thin piece of ceramic.

A. Heating and cooling

The heating element consists of a 0.31 mm nichrome RW80 resistance wire (resistance-wires.co.uk) wound around the inner cap, using an alumina-based ceramic paste (Ceramabond 503, Aremco, USA) to provide electrical insulation and thermal conduction as well as to fix the wire in place – this is not shown on the drawing for clarity. The length of wire used has a resistance of $9\ \Omega$. This was used in conjunction with a proportional integral differential (PID) controller, solid state relay, and a 48 V power supply, giving a maximum possible power output of 256 W. The actual average power used is controlled by the PID controller and depends on the efficiency of the insulation and minimization of thermal bridges within the apparatus. In order to keep the outer surfaces of the apparatus at an acceptable temperature, water cooling is necessary. A cooling top was made, which fits on top of the apparatus, as shown, and is combined with a coiled copper tube around the sides through which water is pumped for cooling.

B. Gas and electrical ports

The inner cap of the apparatus includes five 2 mm holes, which allow access for gas inlet and outlet, PID input thermocouple, data-logging thermocouple, and gold wire for electrical connection to the upper chamber. 1/16" stainless steel tubing is used to support the thermocouples and to attach the gas supply/exhaust with standard Swagelok fittings. The gold wire is supported by an alumina tube to prevent short-circuiting of the fuel cell.

The lower chamber containing the cathode is currently left open to surrounding air, with a single gold wire attached to a gold mesh for current collection. However, the apparatus has been made with five holes on the lower side as well as on the upper side, which enables the modification to study SOFC cathodes by switching round the orientation of the fuel cell and delivering hydrogen to the lower chamber. In addition, at high continuous currents depletion of the oxygen in

the air must be considered, and the system has been designed to allow forced air flow over the cathode if necessary.

C. Sealing and fixing

For ease of disassembly/reassembly, Thermiculite compressible gaskets are used for the main sealing medium (Flexitallic Ltd., UK). These were cut from a sheet of the material using a punch and die set. Additionally, the gas and thermocouple ducting was sealed at the outer end with silicone rubber sealant, and fixed at the inner end with Ceramabond alumina paste. The gold wire was also sealed in place with alumina paste.

The manufacturer's guidelines for the Thermiculite gaskets recommend a static pressure of $20\ \text{N mm}^{-2}$ on the gasket. In order to maintain this pressure at the high temperatures involved, special high temperature creep resistant steel (ASTM A453 Grade 660 duplex stainless steel, Mellish Engineering Services Ltd., UK) was used to make custom screws for the core unit, while titanium screws were used for the large cap fixings (Pro Bolt Ltd., UK).

D. Thermal modelling

Before production of the prototype, the performance of the cooling system was modelled using Solidworks Flow Simulation 2011 software. A cut plot of temperature distribution is shown in Figure 2. Nichrome resistance wire wound around the inner cap is defined as a heat source with a constant temperature of $700\ ^\circ\text{C}$. Value for the water flow through the inlet of the cooling top and coiled copper tubes was obtained experimentally for the Eheim water pump and was set to 7 ml/s. The model included heat conduction in solid components as well as heat conduction, convection, and radiation heat transfer in all fluids. All outer walls were set to be adiabatic, except for the bottom side of the base plate where radiation was additionally defined to represent heat exchange with the environment.

The microscope for *in situ* Raman experiments has a short working distance and therefore the lens has to be placed about 1 cm away from quartz window of the test apparatus. Simulation results indicate that the air temperature in this region approaches $80\ ^\circ\text{C}$ when the temperature of the heat source approaches $700\ ^\circ\text{C}$. The safe operational temperature limit for the microscope lens is $80\ ^\circ\text{C}$, and it would therefore be necessary to incorporate an active air-cooling system of the objective to be able to carry out experiments at higher temperatures.

The low thermal conductivity of the Thermiculite gaskets ensures good thermal isolation between the inner and the

FIG. 2. Thermal model of the Raman Rig using COSMOS FloWorks 2008.

outer caps as shown in Figure 2. However, significant heat is lost through the base plate and overall thermal isolation could be improved if an additional layer of Thermiculite was placed between the inner core and the base plate.

IV. EXPERIMENTAL TESTING

Electrolyte supported button cells with a diameter of 20 mm, thicknesses between 1 mm and 100 μm , and electrode areas between 1 and 14 mm diameter can be tested in the described configuration. Electrolyte supported button cells were fabricated by die-pressing and sintering a thick (1 mm) YSZ electrolyte (Tosoh, Japan), followed by screen printing and sintering an 11 mm diameter LSM-YSZ cathode (Fuel Cell Materials, USA), followed by screen printing and sintering an 11 mm diameter NiO-CGO anode (Fuel Cell Materials, USA), both with an active area of 0.95 cm^2 . The counter electrode was open to ambient air, whilst the anode was within the sealed environment between the pellet and quartz window.

A. Assembly and testing

Figure 3 shows photographs of the test apparatus during assembly. Each functional component of the assembly was initially tested separately, i.e., the heating/cooling performance was tested without any gas flow or electrochemical connections; the gas flow was tested for leaks; and the electrochemical performance was tested at operating temperature before fully testing the system with Raman spectroscopy *in situ*.

B. Validation of thermal performance

Thermocouples were used to monitor the temperature in the core of the assembly and also near the outside of the quartz window in order to monitor the accuracy of the temperature controller and the efficacy of the insulation/cooling system. The temperature performance of the assembly with PID control is shown in Figure 4. It can be seen that the outer tempera-

FIG. 4. Temperature of the core and objective with core temperatures of 600 °C and 700 °C.

ture above the window remains below 100 °C, which is within the acceptable range, as this was without any forced convection over the surface. The maximum rate of cooling achievable is also very high, as shown in Figure 5. It is possible to cool the system by switching off power to the heating element from 600 °C and achieve initial cooling rates of greater than 80 °C/min for the first 200° of temperature change with no damage to the experimental apparatus. With the pellets used in this example there were no visible signs of damage to the pellets, although micro-cracks could have formed. This rate of cooling may be useful in certain experiments where there is a benefit from quenching reactions quickly so that reaction products or intermediates that may be unstable at high temperatures, but are stable at lower temperatures, can be examined *ex situ*. It would be necessary to design each experiment carefully to ensure that the cooling rate would not damage the pellet samples. Alternatively the cooling rate can be controlled using the normal PID process.

FIG. 3. Photo montage showing the Raman Rig design and assembly.

FIG. 5. Temperature of the core under maximum cooling rate from 600 °C.

C. Gas leak testing

Because of the location of the sealing gaskets inside the assembly, it was not possible to use conventional bubble-solution leak test fluid for leak testing the apparatus. The apparatus was tested for gas-tightness by measurement of the flow rate from the exhaust port and comparison with the input flow rate. It was found that a good seal was achieved with only moderate tightness of the compressive screw fixings; this made it easier to avoid over-tightening which was found to cause the quartz window to shatter when too much torque was used. The best results were achieved when a new seal was used for each experiment.

D. Verification of electrochemical performance

After verifying the thermal performance and gas-tightness of the apparatus, an SOFC pellet was tested to validate the electrochemical performance of the setup. A NextCell™ electrolyte supported button cell (Fuelcellmaterials, USA) was tested at 600 °C, the electrochemical performance at different current densities is shown in Figure 6, and an example electrochemical impedance spectrum is shown in Figure 7. It can be seen that good electrochemical performance, for a YSZ pellet at low temperature, can be achieved, and clean and well-defined electrochemical impedance spectroscopy can be performed.

E. Raman characterisation

The system has been designed to be compatible with standard commercially available confocal Raman microscopes. To ensure compatibility we have tested the system extensively with two different Raman systems, a Renishaw RM 2000 and a Horiba Jobin Yvon LabRAM HR 800. These systems allow a wide variety of materials to be investigated as a function of laser wavelength and power.

The Renishaw RM 2000 is CCD spectrometer is equipped with the required lasers, filters and gratings to al-

FIG. 6. Electrochemical performance of the NextCell™ at 600 °C operating under 50% H₂ and 50% N₂ at 25, 50, 75, and 100 mA cm⁻² corrected for electrolyte resistance at open circuit potential calculated from Figure 7.

FIG. 7. Electrochemical impedance Nyquist plot of the NextCell™ at 600 °C operating under 50% H₂ and 50% N₂ at open circuit potential, frequency range between 100 kHz and 1 Hz on a logarithmic scale.

low spectra to be collected using 488, 514, 633, 780, and 830 nm excitation. The laser is focused through the quartz window onto the surface of the pellet for *in situ* characterisation using either a $\times 20$ or $\times 50$ long working objective. This allows the laser to be focussed to a spot of ~ 4 or $1.5 \mu\text{m}$ diameter. Scattered light is then collected through the same objective in the usual backscattering geometry. The LabRAM is very similar in setup to the RM 2000 although it only has access to 514 and 633 nm lasers. Both systems have high resolution motorised stages to which the miniaturised SOFC can be mounted. This allows detailed Raman data to be obtained from active surfaces as a function of position for *in situ* measurements.

While the system has been tested using all incident wavelengths available, we only show results obtained using the 514 nm laser focussed using the $\times 20$ here for demonstration purposes.

V. RESULTS AND DISCUSSION

After verifying the thermal performance and gas-tightness of the apparatus, and after initial preliminary electrochemical tests on the laboratory bench away from the Raman equipment, the full assembly was tested as a complete setup with Raman spectroscopy. Figure 8 shows a white light image of an unreduced anode surface at room temperature, along with an extended Raman spectrum of the surface. The spectrum is dominated by the strong CGO fundamental peak, with the NiO peak and NiO magnon peak also visible. The magnon peak disappears as the cell is heated up between 200–300 °C.

The cell was heated in N₂ flowing at 100 ml min⁻¹. The temperature was ramped at 5° min⁻¹ up to 600 °C. The cell was then exposed to 25% H₂ and 75% N₂ (both gases humidified through a water bubbler at room temperature) flowing at 100 ml min⁻¹ in order to reduce the anode. Static Raman spectra centred on the NiO peak were continuously collected

FIG. 8. (Left) White light image of unreduced anode surface; (right) extended Raman spectrum of unreduced NiO-CGO anode at room temperature.

during the reduction to monitor the oxidation state of the NiO at the surface. These spectra are shown in Figure 9. At the same time, the open circuit potential (OCP) of the cell was also monitored and is plotted in Figure 10 overlaid with the integrated NiO Raman peak intensity. The OCP is plotted as-measured, i.e., a negative value, due to the water equivalent being in a reducing atmosphere. There is some correlation as would be expected between the two measurements; however, there are also some differences that will now be addressed, but which may merit further investigation.

After a “break-in” period of about 200 s, which can be mainly attributed to the time taken for the H_2 to reach the anode, the open circuit potential appears to develop in two stages. Between 200 and 400 s the OCP reduces to about 40% of the eventual value, followed by a sharp drop to >90% of the OCP between 400 and 450 s. The OCP then gradually approaches the final value of -1.07 V over a much longer period of around 1000 s. The trend for the Raman peak intensity initially increases during the same time period as the initial slower reduction measured electrochemically.

FIG. 9. NiO peak monitored during reduction at 600 °C in moist 25% H_2 , 75% N_2 .

The peak then disappears quickly, but this sharp drop in the Raman measurement occurs a short time after the sharp drop in electrochemical potential. This trend has been repeated and verified.

The OCP is dependent on the equilibrium of the redox reaction between H_2/H_2O at the working electrode, and O_2/O^{2-} at the counter electrode. This reaction equilibrates as soon as there is an electrically conductive path at the anode, i.e., as soon as enough NiO is reduced to Ni at the three-phase boundary – this is observed as the sharp drop in OCP in Figure 10. However, the results suggest that this electrically conductive path is formed before all of the NiO is reduced in the electrode.

These preliminary experiments demonstrate the potential of this novel test apparatus for *in operando* surface chemical characterisation of SOFC electrodes. Further experiments are ongoing to investigate degradation in CO containing fuels, and a second apparatus is under construction incorporating various design improvements, which will enable investigation of H_2S poisoning during SOFC operation.

FIG. 10. The integrated NiO peak area from Figure 9 overlaid with the monitored OCP of the cell.

VI. CONCLUSION

A novel test apparatus for *in situ* Raman micro spectroscopy has been designed and built, and proof-of-concept experiments have been successfully carried out comparing the electrochemical potential with the intensity of the NiO Raman peak during the anode reduction. Raman spectra were also measured under current load on the cell. Previous *in situ* test apparatus have been either restricted to single-atmosphere non-electrochemical measurements, or required an expensive long-working distance or thermally shielded lens objective which was not capable of mapping a 2-D area. The test apparatus also has the ability to cool very rapidly, from 600 °C to 300 °C in less than 5 min. The new apparatus described in this paper has great potential for a wide range of experiments, including investigation of reaction kinetics and mechanisms as our preliminary measurements demonstrate. The new apparatus also represents a significant advance in the miniaturisation of SOFC pellet cell test rigs, and significantly reduces the space required to conduct experiments, as large external furnaces are no longer needed.

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