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<http://dx.doi.org/10.1109/ICSENS.2015.7370102>

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Ranaweera, Manoj Prasanna, Indae Choi, and Jung-Sik Kim. 2016. "Cell Integrated Thin-film Multi-junction Thermocouple Array for In-situ Temperature Monitoring of Solid Oxide Fuel Cells". figshare.
<https://hdl.handle.net/2134/20014>.

Cell integrated thin-film multi-junction thermocouple array for in-situ temperature monitoring of Solid Oxide Fuel Cells

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Abstract— A thin-film multi-junction thermocouple array was developed and tested for multi-point simultaneous temperature measurements from an operating SOFC stack. The array requires only $\{N+1\}$ number of wires/ thermo-elements for N number of independent temperature measuring points. Hence, it requires less number of lead wires than any available contact-temperature sensors require for the same number of measurements. Because the multi-junction thermocouple array operates on the same principle of a conventional thermocouple, the Seebeck effect, it shares all the merits of a thermocouple. A thin-film multi-junction thermocouple array was sputter deposited on the cathode of a SOFC test cell and tested and evaluated up to 1050°C from 20°C. Temperature measured from the thermocouple array was compared with that from a commercial thermocouple placed adjacent to it during the test; they were in very good agreement within the entire temperature range that a SOFC stack generally operates.

Keywords—multi-junction thermocouple; SOFC; thin-film thermocouple

I. INTRODUCTION

Solid Oxide Fuel Cell (SOFC) is an electrochemical energy conversion device that directly converts the chemical energy of a fuel (mainly, hydrogen and lighter hydrocarbons) into electricity without combustion and produces steam as a byproduct. They normally operate at a temperature range from 600°C - 900°C. When the heat energy of this high temperature steam is also used to produce further electricity through a suitable bottoming cycle (such as gas turbine and/or steam turbine), the overall efficiency of the plant can reach as high as 80%[1],[2]. Thus, SOFC is a promising technology for future clean energy generation with less or no environmental pollution. However, premature degradation of cells and stack significantly hinders the wire-spread of this technology. Among various factors, thermal cycling at high temperature and uneven temperature distribution contribute significantly to premature degradation by creating severe mechanical failures such as delamination and cracking of cell components and sealing. A comprehensive knowledge on cell level temperature distribution of an operating SOFC stack is important to understand these phenomena and thereby to successfully mitigate them.

Several experimental approaches made on measuring the temperature distribution of SOFC stacks are recorded in literature. Among them, the thermocouple thermometry appears to be the widely employed technique while, electrochemical impedance spectroscopy (EIS) [3] and Infrared (IR) thermometry[4] were also used with specially arranged stacks. In general, IR imaging is an excellent technology to reveal temperature distribution over a surface with greater spatial resolution. However, the lack of visibility into inner cells of a stack does not enable it to be used in standard multi-cell stacks. Despite the strong abilities of EIS in evaluating SOFC's performance, it may not be the best technology to reveal local temperature variations with traceable locational information. Therefore, thermocouple thermometry is probably the best for stack temperature measurements not only because it has been used for the task but also it has the required characteristics to survive in the harsh operating conditions inside a SOFC stack.

Razbani et al [5][6] embedded 5 K-type thermocouples (ϕ 0.5mm) into the middle of a 5-cell (110mm x 86mm) short stack to measure the temperature from 4 corners and the middle of a cell. Further, they state that researchers at Jülich GmbH were able to measure the temperature profile of a 5kW SOFC stack by embedding 36 thermocouples into the stack. Guan et al.[7] and Bedogni et al.[8] have also used thermocouples to measure gas flow temperature at inlet and outlet of a stack. Although these approaches could yield successful results within their respective scopes, the inability to measure the temperature closer to reactions cites on the cell is a significant drawback commonly noticed in these approaches. Therefore, authors devised to use cell integrated thin-film thermocouples (TFT) to get better details on cell level temperature distribution.

TFT finds a number of applications in different application domains[9]-[18]. More importantly, TFT can measure temperature with as high as 10nS responsiveness[19]. However, unlike most of those applications that already employ TFT; SOFC requires temperature measurement with greater spatial resolution because of potential significant temperature variations that exist across a cell[20]. Since each sensing point of a thermocouple is formed by intersecting two thermo-elements, integrating a large number of thermocouples onto the cell potentially covers a large area from reaction sites

and thus causing a significant disturbance to the normal operation of the cell/stack. In order to overcome this drawback while sharing the merits of TFT, authors investigated the potential of multi-junction thermocouples that shares some thermo-elements to reduce the number of thermo-elements required in multi-point temperature sensing. This paper discusses the fabrication, testing, and the results of a multi-junction thermocouple fabricated on a SOFC electrode.

II. FABRICATION AND TESTING

A. Material Selection

From among different high temperature thermocouple materials, the K-type materials (Alumel - Ni:Al:Mn:Si 95:2:2:1 by wt. and Chromel - Ni:Cr 90:10 by wt.) were chosen for thermo-elements. These materials have NIST¹ standardized performance up to 1372°C and they are more economical to test than other high temperature noble metal thermocouples. (Although K-type materials are good enough for concept verification and feasibility testing purposes, they are not very suitable to apply in SOFC stacks under non-laboratory conditions because of the presence of Chromium, which is a poisonous material for SOFC cathode). The external wires to collect the signals were chosen from the same material as the film to prevent formation of an intermediate junction with a third material, which may otherwise induce an additional electromotive force.

B. Sensor Fabrication

A multi-junction thermocouple array having 4 sensing points was fabricated on the cathode of $\phi 52\text{mm}$ commercial test cell (KERAFOFOL®). The cathode (made of LSM) is always porous and the anode (made of NiO – YSZ) becomes porous only when NiO is reduced to Ni. Therefore, cathode was chose as the substrate to deposit the array. It is important to test the thermocouple array's survivability on a porous substrate as both the electrodes are porous in an operating SOFC.

The substrate was prepared by first cleaning with acetone and then with deionized water followed by drying in a furnace at 150°C for 10 minutes. This preparation process ensures that the substrate is free from any dirt, grease, and moisture. Sputter deposition with Quorum QT150ES sputter coater was chosen as the fabrication technique. Film thickness is a critical parameter that influences the sensitivity of TFT[21]-[23]. However, the sensitivity of K-type thin-film thermocouples is independent of the film thickness when the it is greater than 140nm[24]. 16 cycles of sputter deposition with sputter current of 150mA and cycle time of 120S could yield films with thicknesses sufficiently greater than this threshold.

Fig. 1 shows the fabricated multi-junction thermocouple array. The pattern was obtained by using two masks hand-cut from transparent binding sheets. The Alumel thermo-element was first deposited and then the Chromel thermo-elements. The width of each thermo-element is about 1mm. The plastic sheet warped from the cutting edges due to temperature inside the sputter chamber and hence, no proper edge definition on deposited films could be achieved. The labels A to E represent

Fig. 1 Thermocouple array on the cathode of $\phi 52\text{mm}$ test cell (KERAFOFOL®)

the connection pads (3mmx 3mm) and S1 to S4 represent the 4 sensing points. The voltage measured across E-D, E-C, E-B, and E-A represents the temperature at S4, S3, S2, and S1 respectively.

An Alumel wire ($\phi 0.25\text{mm}$) was connected to pad E and 4 Chromel wires ($\phi 0.25\text{mm}$) were connected to pads A to D. Silver paste (from Sigma-Aldrich) was applied at the connection pads to ensure better electrical connectivity between the wire and the film. Silver paste was cured at 130°C for 40min as per manufacturer's instructions. Although silver provided a good electrical connection between the films and the external wires, it does not provide a sufficient mechanical strength holding the wires onto the substrate. Therefore, once the silver paste was cured, high pure Alumina adhesive (EQ-CAA-2-LD, MTI Corporation, USA) was applied over the connection pads to provide sufficient mechanical strength for the joint to ease handling. Since Alumel and Chromel forms oxide layer at temperatures beyond 800°C[25], the same Alumina layer was continued over the films covering entire set of films as an oxygen contact barrier to prevent potential oxidation of films. Curing Alumina at 250°C for 30 min yielded a very strong layer of Alumina. The wires were sent through ceramic beads to prevent any short circuiting during handling. The resistance across the distal ends of wires were measured before commencing the experiment and the they are given in Table 1

C. Sensor Testing

The thermocouple array was placed in a box furnace and a commercial thermocouple was also fixed keeping its tip about 1cm adjacent to the cell for comparison purposes. Furnace was heated at a rate of 400°C/ hour while having set the maximum temperature to 1050°C. Two temperature

Table 1 Resistance across external wires

External wire connection	Resistance (Ω)
A-E	20
B-E	16
C-E	13
D-E	11

¹ National Institute of Standard and Technology

interruptions were introduced during heating to investigate a temperature discrepancy noticed during heating between the commercial thermocouple and the thin-film array. Once the set temperature was reached, the furnace was rapidly cooled by slightly opening the furnace's door. Temperatures from both thermocouple array and commercial thermocouple were recorded at 3s intervals using NI-9213 thermocouple data logger and a LabVIEW program that authors developed. The resistances were measured after the experiment across the same distal ends of the external wires as before: all of those showed open circuit status. Resistance on the cathode surface was also measured and it was approximately $120\Omega/\text{cm}$ across any arbitrary two points on the cathode.

III. RESULTS AND DISCUSSION

Fig. 2 shows the temperature measured from 4 sensing points of the array (S1 to S4) and from the commercial thermocouple (TC). The wavy-like heating pattern up to about 450°C is an intrinsic characteristic of the furnace during early stage of the heating process. The two abrupt temperature changes around 680°C and 850°C are the two temperature interruptions introduced during heating. The results show that the temperature measured from the array is in a reasonably good conformity with that from commercial thermocouple. Further, the enlarged section of the graphs in Fig. 2 demonstrates the array's ability to independently measure temperature from its sensing points despite sharing a common thermo-element among them.

The second sensing point (S2) shows an unusual sudden rise in temperature beyond 1000°C in heating and then starts

catching up the others' readings when cooling down nearly at the same temperature at which it started diversion. The experimental setup does not provide any explanations or evidences on such localised temperature peaks on the cell. Therefore, it is more likely a result of momentary failure occurred somewhere between the data logger and S2 sensing point along thermo-element B. However, the experiment did not provide any insight into the exact cause of the failure. However, it happened well beyond the required temperature range.

The near-constant lag of thermocouple array's reading with respect to the thermocouple's reading during near-steady heating period is another important feature observed from results. Authors would like to consider two hypotheses to explain this "temperature lag":

- (1) Characteristic differences between thin-films and bulk materials

Thin-film's Seebeck coefficient can generally be different from those of bulk materials[26]. NI9213 data logger is calibrated to work with NIST approved emf data, which are based on bulk material properties. Therefore, there can be an intrinsic difference between temperatures measured from a commercial thermocouple and from the thin-film thermocouple array.

- (2) The effect of thermal inertia

The SOFC test cell has higher thermal inertia than the surrounding air. Therefore, the test cell does not change its temperature at the same rate as the surrounding air does. Therefore, at a given instance of time, the air might be at

Fig. 2 Performance of the multi-junction thermocouple array
(Legends: TC – Commercial thermocouple S₁–S₄: four points from array)

slightly higher temperature than the cell, particularly, during heating. The commercial thermocouple measured air temperature while the thermocouple array measured the cell temperature. Hence, it is possible for the array's temperature to slightly lag the thermocouple's temperature.

Fig. 3 shows the temperature difference between the array and the commercial thermocouple (calculated by subtracting array's temperature from thermocouple's temperature) plotted against thermocouple's temperature. The graph was obtained by 5th order polynomial curve fitting in order to make the trend prominent by filtering out any local fluctuations. As this graph shows, the temperature difference has a non-linear relationship with the temperature from commercial thermocouple. (Thermocouple's reading can be considered as sufficiently accurate measurement of the true temperature.) Usually, the thermo-electric emf produce by a K-type thermocouple is highly liner. Thus, if the aforementioned first hypothesis is correct, the temperature difference should be nearly constant. On the other hand, the two intentional interruptions caused the thermocouple's graph to almost overlap the array's graphs (see Fig. 2). This phenomenon can easily be explained in thermal of thermal inertia: when the system cools rapidly, the air responds quickly due to its low thermal inertia (so as the thermocouple). However, the substrate still remains hotter than the air due to its higher thermal inertia. As a result, thermocouple's temperature reading goes down passing the array's temperature reading making them overlap. After critically evaluating these scenarios, it is justifiable enough to infer that the temperature difference noticed between the commercial thermocouple and the array is due to the thermal inertia difference between the air and the substrate.

The complete electrical disconnection between external wires was further investigated to see any failure of the thin-film fabricated on the porous substrate. Two thermocouples were fabricated by twisting Alumel and Chromel wires ($\Phi 0.25\text{mm}$ each) together as shown in Fig.4. External wires to thermocouple "B" were directly connected by twisting those with thermo-elements in a similar way that the junction is formed. One of the external wires to "A" was connected through Silver paste while the other was directly connected by

Fig. 4 Twisted-wire thermocouples
(A: connection through silver, B: direct connection)

twisting. All connections points were covered with Silver paste and once silver was hardened, Alumina was applied over it to replicate the conditions at the thin-film connection pads. The as-fabricated resistance of each thermocouple, measured across the distal ends of external wires, was less than 20Ω . The two thermocouples were heated to 1000°C in the same furnace. The same resistance measurement carried out once the thermocouples cooled down to room temperature indicated complete electrical disconnection of A while B showed a matching resistance to its previous measurement. This confirms that the cause of electrical disconnection of thin-film thermocouple array lies at the connection point.

IV. CONCLUSIONS

The multi-junction thermocouple array, sputter deposited on the cathode of a commercial SOFC test cell, measured temperature with satisfactory accuracy within the operating temperature range of a SOFC (600°C to 900°C). Each sensing point could measure temperature independently from the others even when there is only very minor temperature difference between junctions. Thin-film thermo-elements could survive on the porous cathode during the entire operation. Therefore, the feasibility of cell integrated thin-film multi-junction thermocouples to measure cell temperature distribution of SOFC with reduced number of thermo-elements is experimentally confirmed. The alumina layer could successfully protect the thin-films during the experiment. However, suitability of Alumina as a protective sheath during long term operation may need to be further investigated.

The thermocouple array could not demonstrate any level of repeatability because of a failure at the connection points where, the external wires connect to the thin-films. Although the Alumina at the connection point could connect the external wires to the substrate with excellent mechanical strength, the use of Silver as a connection agent is identified to be unsuccessful, particularly, after cooling down. Therefore, the

Fig. 3 Temperature difference between the array and thermocouple

connection mechanism needs to be investigated further and more durable electrical connection needs to be developed in order to use the proposed thin-film multi-junction thermocouple array in operating SOFC stacks.

V. ACKNOWLEDGEMENT

Authors would like to gratefully acknowledge the financial support from the Engineering and Physical Sciences Research Council (EPSRC) to carry out this research.

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