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Influence of microstructure on nano-mechanical properties of single planar solid oxide fuel cell in pre- and post-reduced conditions

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The present work investigates, both the macro- and nano-mechanical properties of all the three component layers e.g., anode, cathode and electrolyte of a planar single solid oxide fuel cell (SOFC). The flexural fracture strength experiments in three point bending mode are employed in both pre- and post-reduced conditions to study the macro-mechanical failure behavior of the single cell. Further, the nanoindentation technique is utilized in both pre- and post-reduced conditions to evaluate the nanomechanical properties e.g. nanohardness, Young's modulus, mean contact pressure, relative stiffness and relative spring back at scale in both pre- and post-reduced conditions. The nanohardness and Young's modulus of the pre-reduced anode are considerably degraded after reduction as NiO gets converted to Ni. However, as expected; those of the pre-reduced electrolyte and cathode are only slightly decreased after reduction because there are no chemical conversions involved. Further, the experimentally obtained data of nano-mechanical properties, is explained with the application of the well established Weibull statistics as the microstructures with characteristically present pores and defects are highly heterogeneous in nature. The characteristic values of the various nanomechanical properties are analyzed using Weibull distribution for the anode, electrolyte and cathode layers of the SOFC in both pre- and post-reduced conditions.

1. Introduction

Fuel cell technology is emerging as a key alternative to the traditional power supply system, as it has potential for high efficiencies and low emission of pollutants [1–4]. Among various types of fuel cells, the planar design of solid oxide fuel cell (SOFC) is identified to be the most promising candidate because of its fuel flexibility [5,6]. Stacking of several single SOFCs, (series/parallel) is required to produce applicable amount of power for commercial applications. To maximize the contact between the interconnects and electrodes, typically these stacks are subjected to reasonably high clamping pressures e.g., 65–70 kPa [7]. Thus, for a single cell's architecture; it is essential to address the issue of the mechanical integrity before any stack operation can be undertaken. It is well known that in general, in most of the reported works on planar design SOFC the anode, electrolyte and cathode layers had been chosen as NiO-8YSZ, 8YSZ and lanthanum strontium manganite (LSM), respectively [7–11].

It is very important to understand that these brittle individual layers of the single cell have widely different Young's moduli. So, there can be enough of the elastic mismatch stress that could impair the mechanical integrity of a single cell [12]. In addition, since, such a whole multi-layer assembly of a typical single cell cools down from the sintering temperature e.g., 1400 °C to the room temperature e.g., 30 °C, there can be concurrent presence of thermally induced residual stresses due to the thermal expansion mismatch between the anode, electrolyte and cathode layers.

Therefore, it shows clearly that no matter whether it is an elastic mismatch stress, a thermally induced residual stress or a misfit strain active at the stack interfaces, their spatial extents may encompass the local microstructural length scale on the one hand and the macrostructural length scale on the other. It is in this context, that the examinations of the mechanical integrities of the various component layers of the single SOFC at the scale of the local microstructure as well as at the macro scale become an issue of paramount scientific and technological importance.

Macro and Micromechanical properties of individual components of an SOFC as well as half cell have been reported by several

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researchers [13–32]. Kumar et al. have evaluated macro- and micro-mechanical properties on half cell (i.e. anode and electrolyte) by ball on ring flexural strength test and nanoindentation techniques, respectively [13]. Mechanical properties of different types of electrolytes such as bulk and tape-casted 8YSZ, and screen printed gadolinium doped ceria (GDC) are measured by several groups. The screen printed GDC is reported to have the lowest value for hardness and modulus of elasticity [14–16]. The Young's modulus of different types of cathode materials i.e., calcium-substituted lanthanum chromites (LCC) and strontium-substituted lanthanum chromites (LSC), Sr-substituted $LaMnO_3$ (LSM) and LSCF (lanthanum strontium cobaltite ferrite) are determined using depth sensitive indentation measurements at different indentation loads [17,18,22,29]. Among several candidate materials of cathode, LSM is observed to have the lowest modulus of elasticity. The Young's modulus of cathode also depends on the porosity of the component [32]. In addition, the nanohardness of NiO-8YSZ based mixed electrode is reported as a function of porosity in both pre- and post-reduced conditions [9,23–27,31]. To provide an overview of the global status of knowledge, the literature data on mechanical properties e.g., hardness and Young's modulus of different individual component layers of the SOFC e.g., the anode, cathode and electrolyte are summarized in Table 1. The survey of literature (Table 1) depicts that the mechanical properties are strongly sensitive to the variations in the materials chemistry, processing methods, residual porosity and measurement techniques. In addition, significant variation of data are reported by various researchers even for the nominally similar materials e.g., anode, cathode or electrolyte. Further, the measurements reported in literature are performed on individual component layers and half cells.

To the best of our knowledge the detailed simultaneous evaluations of the mechanical properties from the macro scale to the nanoscale on all the three component layers of a complete single solid oxide fuel cell i.e., in cathode-electrolyte-anode architecture in situ; in both pre- and post-reduced conditions, have not yet been reported. As these layers have inherently hetergeneous microstructure, generally there is wide scatter reported in literature data (Table 1). But unfortunately, the issue of any statistical analysis of such prevalent scatter in the experimental data has been not yet addressed in literature.

Therefore, the main objectives of the present work are to evaluate in both pre- and post-reduced conditions of the single SOFCs: (a) the macro scale failure strength in three point flexural tests with respectively the anode, cathode and electrolyte layers placed deliberately in the tensile side to examine if that makes any significat difference in the failure strength of the whole assembly, (b) study of the related fracture mechanisms by extensive fractography and (c) detailed evaluations of the nanomechanical properties e.g. nanohardness and Young's modulus for all the three component layers at the scale of the microstructure utilizing the nanoindentation technique and correlations of the same with the microstructural parameters. Also, in the present work, the Weibull statistical analysis technique is employed to understand the reliability of the mechanical properties.

2. Materials and methods

In the present work, the anode, electrolyte and cathode layers are chosen as NiO-8YSZ (40–60 v/v), 8YSZ (Tosoh, Japan) and lanthanum strontium manganite (LSM), respectively. The mixture of NiO-8YSZ is treated with alcohol, plasticizer and binder to form a well dispersed stable suspension. The suspension is ball milled for about 24 h before it is tape casted. Similar procedure is followed to prepare the electrolyte with 8YSZ. Several layers of tapes (green) with layer of electrolyte are laminated together under high pressure, in an uniaxial press, at room temperature. The multilayer laminated structure of adequate thickness, is then, sintered in air at about 1400 °C. The sintered structure consisting anode and the electrolyte, is known as the half cell. The LSM cathode is screen printed over the electrolyte layer. Finally, the entire assembly is sintered in air at about 1100 °C for four hours to complete the fabrication of a single solid oxide fuel cell [8,33].

The microstructural characterizations are carried out by the field emission scanning electron microscopy (FESEM; Supra VP35 Carl Zeiss, Jena, Germany) technique. Further, for a single cell in both pre- and post-reduced conditions the flexural fracture strengths are measured by the three point bending tests. Three point bending tests are carried out with the following three different configurations e.g., (a) anode/electrolyte/cathode, (b) electrolyte/anode and (c) cathode/electrolyte/anode as shown in Fig. 1. In each of these three cases the first layer is kept deliberately at the tensile side of the respective whole assembly architectures of the three point bend specimens ($40 \times 10 \times 1.5$ mm) exposed to the loading train in an UTM (Model 5500R, Instron, UK). As mentioned earlier, these experiments are deliberately conducted just to examine whether there is any significant change in the average flexural fracture strength values of the entire whole assembly due

Table 1
Literature data on hardness and Young's modulus of the three component layers e.g., the anode, the electrolyte and the cathode of SOFC.

Electrodes/electrolyte	Composition	Processing method	*H* (GPa)	*E* (GPa)	Load (mN)	Porosity (%)
Half cell (anode supported) [13]						
Electrolyte	8YSZ	Tape casting	12	218	100	Dense
Anode						
Pre-reduction	NiO-8YSZ	Tape casting	3	97	100	27
Post-reduction	Ni-8YSZ	Tape casting	0.73	33	100	44
Electrolyte [14]	GDC[a]	Screen printing	1.9	27.2	49	–
Electrolyte [15,16]	8YSZ	Bulk	20–14.2	260–210	5–500	Dense
Electrolyte [21,25,28,32]	8YSZ	Tape casting	21–12	260–157	3–100	Dense
Anode						
Pre-reduction [23–27,31]	NiO-YSZ	Tape casting	8.5–3	220–40	3–100	0–38
Post-reduction [20,26–28,31]	Ni-YSZ	Tape casting	0.73	200–20	100	0–52
Cathode [18,22]	LCC[b]	–	–	180–110	5 kg	~10
Cathode [18]	LSC[c]	–	–	170–160	5 kg	~10
Cathode [19,30,32]	LSM	Bulk	–	41–35	–	29
Cathode [17,29]	LSCF[d]	Bulk	6	188–139	2 kg to 1 N	3–6

[a] GDC: gadolinium doped ceria.
[b] LCC: calcium-substituted lanthanum chromites.
[c] LSC: strontium-substituted lanthanum chromites.
[d] LSCF: lanthanum strontium cobaltite ferrite.