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Short communication

Determining the mechanical properties of solid oxide fuel cell by an improved work of indentation approach

Zhao Xiang*, Wang Fenghui, Hang Jianye, Liu Tiejun

Department of Engineering Mechanics, Northwestern Polytechnical University, Xi'an 710129, China

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ABSTRACT

The mechanical properties of electrolyte and anode represent the characteristic of anode-supported solid oxide fuel cells (SOFCs). The micro-scale film/substrate structure makes it difficult to measure the hardness and elastic modulus. In this work, a modified work of indentation method is proposed to determine the hardness and elastic modulus, and nanoindentation test is carried out for the half-cell structure of SOFCs (before and after reduction). The final large range of hardness from the proposed method is shown to be well agreement with the values determined by Oliver Pharr method. Because NiO-YSZ reduces to Ni-YSZ, the hardness of substrate is decreased by 48%, elastic modulus is decreased by 34.4%, respectively.

1. Introduction

Recently, SOFCs are receiving much attention because of their high energy conversion efficiency, low pollution and flexibility of fuels [1–4]. Among them the anode-supported cells are generally fabricated by co-firing the thin electrolyte on the anode substrate at 1300–1500. Due to the different thermal expansion coefficients and particular work environments, measuring the mechanical properties is always the first critical step to analyze their mechanical integrity. This is often considered difficult since the conventional techniques, such as the tensile, the three-point or four point bending technique, require extensive machining efforts [5].

The Oliver Pharr analysis [6] is commonly used to determine hardness and elastic modulus due to easy application. Unfortunately, if h_f/h_m (final indentation depth/peak load indentation depth) >0.7, the method overestimates the hardness by as much as 100% because of the effect of pile up [6]. Alternatively, because of the use of the energy dissipated or work done during the indentation [7–15], work of indentation methods can particularly be an attractive approach when a pile up effect is observed. The relationship between hardness and work can be written as:

$$H = \frac{kP_m^3}{9W^2} \tag{1}$$

where P is the maximum load, k is a constant that depends on the geometry of the indenter, and W is the total work or plastic work, as shown in Fig. 1. This equation assumes that the load-displacement relationship follows $P = Ch^2$, but the peak load indentation depth h_m is replaced by contact depth h_c when into use. These two assumptions have brought some incredible deviations no matter whether pile up exists or not. For example, the hardness of titanium nitride and bulk MgB_2 crystal determined by work of indentation are 50% of that of Oliver Pharr method [7,15], even though the pile up effect was not observed. Hence, it is necessary to establish a proper method which considered the load–displacement relationship is $P = Ch^n$, where C and n are power law fitting constants [16].

In this paper, a reformative work of indentation method is proposed to determine the hardness and elastic modulus of anode-supported cells. The pile up effect is discussed by comparing the results of indentation experiments data of YBCO using Oliver Pharr method, work of indentation and the proposed method.

2. Experiment procedure

The half-cell structure of SOFC was made by Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences (Ningbo, China). The anode-supported cells were generally fabricated by co-firing the thin electrolyte (YSZ) on the anode substrate (NiO-YSZ) at 1300–1500. The thickness of YSZ film and NiO-YSZ substrate was about 10 μm and 310 μm, respectively. For measuring the anode mechanical properties after reduction, NiO-YSZ/YSZ composite ceramic was reduced in H_2–4% N_2 at 800 to make Ni-YSZ/YSZ cermets.

Before indentation testing using Berkovich diamond in MTS Nano Indenter II, each specimen with dimension of 0.32 mm(height) × 11 mm(width) × 15 mm(length) was

* Corresponding author. Tel.: +86 029 88431019; fax: +86 029 88431019.
E-mail address: hope_888@mail.nwpu.edu.cn (Z. Xiang).

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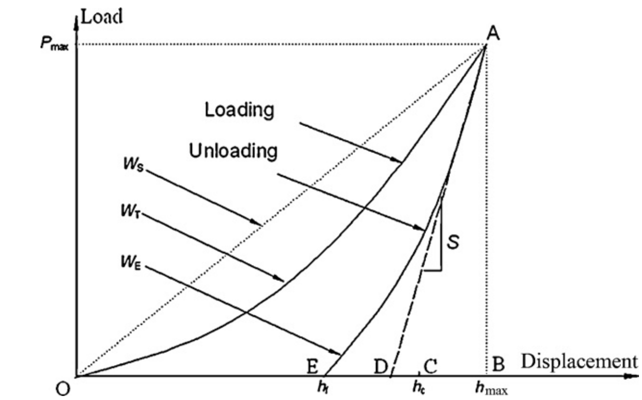

Fig. 1. Typical indentation cycle showing load–unload curves.

sandwiched in middle between epoxy. The system has load and displacement resolutions of 1 nN and 0.04 nm. Fig. 2 shows the cross-section of the test sample which polished before test. The indentation points are perpendicular to the half-cell structure interface of SOFC. Among six points, four points are on film side and two on anode side, respectively. The indenter was first loaded to the peak load 20 mN which was held constant for 10 s, then unloading terminated at 10% of the peak load with another 100 s holding period to allow any final time dependent plastic effects to diminish, and the specimen was fully unloaded. According to our early published study [17], the indentation point A1 which is far from the interface was held to avoid the substrate effect in hardness testing, and the film can be considered as bulk material due to the shallow indentation depth.

3. Theoretical consideration

3.1. Description of Oliver Pharr method

According to Oliver Pharr method [16], hardness is calculated by the following equation:

$$H = \frac{P_m}{24.56\ h_c^2} = \kappa \frac{P_m}{h_c^2}; \quad (A_c = 24.56\, h_c^2) \tag{2}$$

where P_m is the maximum load, $\kappa = 0.0407$ is the triangular pyramidal indenter with identical depth-to-area relationship, and the contact depth, h_c, is:

$$h_c = h_m - \varepsilon \frac{P_m}{S} \tag{3}$$

where h_m is the maximum displacement, $\varepsilon = 0.72$ for Berkovich indenter, and the elastic unloading stiffness, $S = dP/dh$, defined as the slope of the upper portion of the unloading curve during the initial stages of unloading (also called the contact stiffness), as shown in Fig. 1.

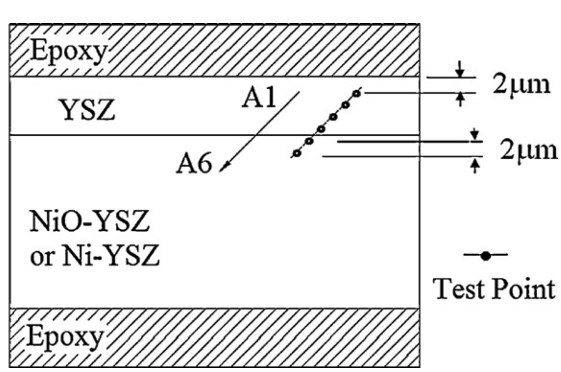

Fig. 2. Schematic of testing sample and indentation points of the experiments.

Once the contact area is determined, the specimen E can be derived by:

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} - \frac{(1-\nu_i^2)}{E_i} \tag{4}$$

where E_r is the reduced modulus which takes into account the fact that elastic displacements occur in both the specimen E and Poisson's ratioν, and the indenter, with elastic constants E_i and ν_i. The reduced modulus is estimated from:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \tag{5}$$

3.2. The work of indentation

Alternatively, hardness can also be calculated by the work of indentation approach. The calculations are directly performed by using the energy approach, without the need for the estimation of penetration depths, diagonals, projected areas or deformed volumes. The absolute (W_S), total (W_T), elastic (W_E) and plastic (W_P) energies, which based on the integral of the loading and unloading curves (Fig. 1), are calculated using the experimental data. The linear relationships between energetic quantities have been validated by literatures [10–13]: (a) variation of absolute energy (W_S) versus the other energies W_T, W_P and W_E, (b) variation of total energy (W_T) versus elastic and plastic energies and (c) variation of plastic energy (W_P) versus elastic energy (W_E). It is known that the energy ratios provide useful information on mechanical behavior and lead to determination of some specific energy constants [13]. In this method, the total work can be defined as follows:

$$W_T = \int_0^{h_m} P dh = \int_0^{h_m} Ch^2 dh = \frac{Ch_m^3}{3} = \frac{P_m h_m}{3} \tag{6}$$

where C is a constant which can be obtained from fitting the loading curve. If Eqs. (2) and (6) are combined, the hardness can be represented by:

$$H = \frac{3\kappa W}{h_c^2 h_m} \tag{7}$$

If h_m is replaced by contact depth h_c, the hardness of work of indentation can be rewritten as Eq. (1).

3.3. A new relationship between hardness and work energy

Considered the load–displacement relationship is $P = Ch^n$, Eq. (6) can be rewritten as:

$$W_T = \int_0^{h_m} P dh = \int_0^{h_m} Ch^n dh = \frac{P_m h_m}{n+1} \tag{8}$$

Combining Eq. (2) and Eq. (8), we get:

$$W_T = \frac{H h_c^2 h_m}{(n+1)k} \tag{9}$$

The relationship between contact depth and maximum displacement is given by Attaf [13]:

$$h_{c2} = \frac{2(\nu_E - 1)}{2(\nu_E - 1)} h_m \tag{10}$$

where ν_E is the elastic energy constants, defined as:

$$W_s = \nu_E W_E \tag{11}$$

The contact depth determined by Eq. (3) depends on the sensitive stiffness S and the correction factor ε. By contrast, Eq. (10) directly

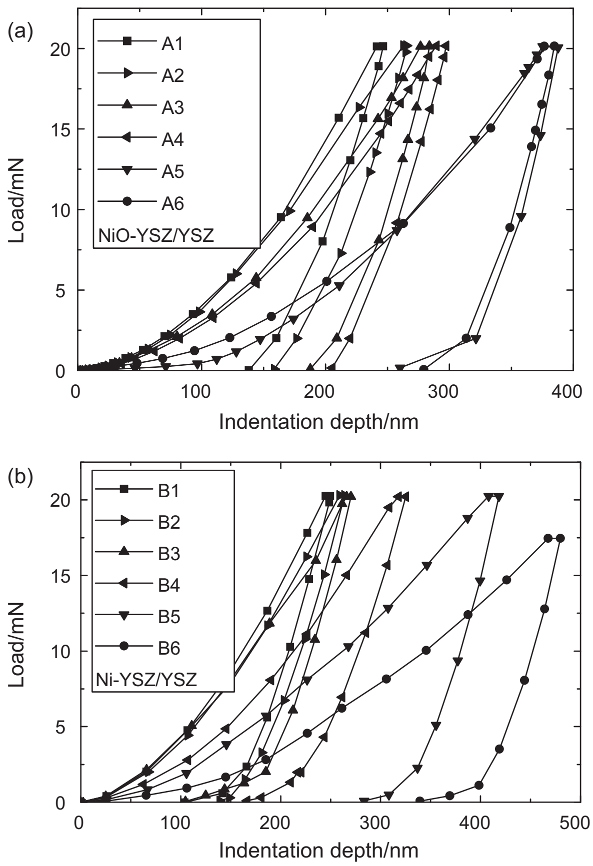

Fig. 3. Experimental indentation load–displacement curves (a) NiO-YSZ/YSZ and (b) Ni-YSZ/YSZ.

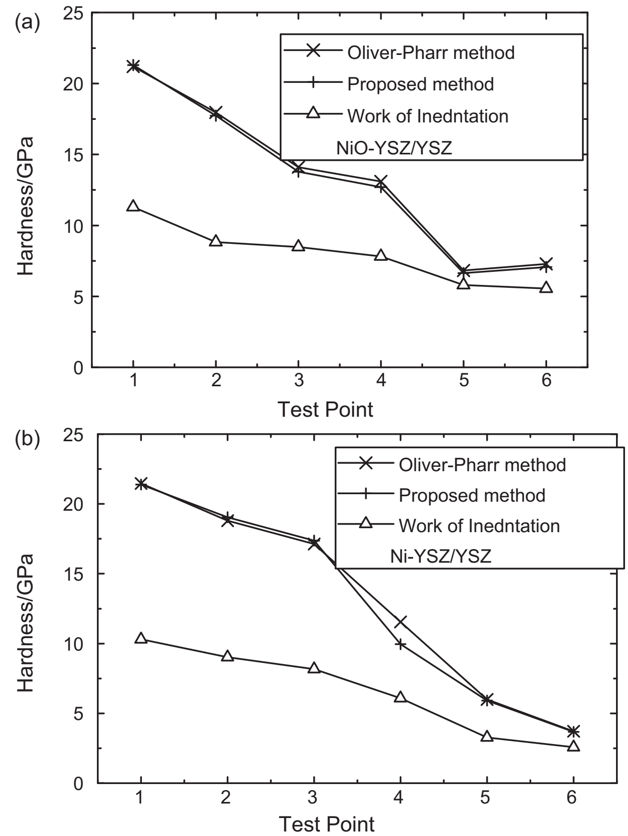

Fig. 4. Comparison of hardness values obtained by three methods for (a) NiO-YSZ/YSZ and (b) Ni-YSZ/YSZ.

gives the contact depth from the tangent of the unloading curve, with no need for correction. Then, the hardness can be calculated using Eqs. (8)–(11):

$$H = \frac{\kappa W(n+1)}{h_m h_{c2}^2} = \kappa \frac{P_m}{h_{c2}^2} \tag{12}$$

Furthermore, once we know the hardness by the modified work of indentation approach Eq. (12), elastic modulus can be determined by follow equation [6]:

$$\frac{W_T - W_E}{W_T} \cong 1 - 5\frac{H}{E_r} \tag{13}$$

4. Results and discussion

4.1. The characteristic of load–displacement curves

We begin the discussion of experimental results with an overview of the characteristics of the load–displacement curves for NiO-YSZ/YSZ and Ni-YSZ/YSZ. Fig. 3 presents the experimental data for both two materials for indentations made to peak load of 20 mN. The differences in hardness of NiO-YSZ/YSZ (or Ni-YSZ/YSZ) are apparent from the large differences in the depth. The hardest is YSZ film, and the softest region is in substrate. The whole results in terms of load, displacements and mechanical properties are presented in Table 1.

Although the penetration depth limits do not give us quantitative information about pile up of the sample, the experimentally measurable ratio h_f/h_m can be used to identify the expected indentation behavior of a given material [6]. The ratio h_f/h_m can be extracted easily from the unloading curve in a depth sensing indentation experiment. The natural limits for the parameter are $0 \leq h_f/h_m \leq 1$, the parameter will be a useful indicator of when pile-up may be an important factor. It is also noted that when $h_f/h_m > 0.7$, pile up effect on the sample is become significant.

The ratios h_f/h_m are listed in Table 1 for both two material systems, these results suggest that very little pile up are observed in most test points except A5 (NiO-YSZ) and B6 (Ni-YSZ). The contact depth h_c, computed using Oliver and Pharr method, are closed to h_{c2} which calculated by Eq. (10) in most situations.

4.2. Mechanical properties of half cell structure of SOFC by three methods

The hardness and elastic modulus of a bulk material can be obtained by Eqs. (12) and (13), respectively. The energetic quantities of NiO-YSZ/YSZ or Ni-YSZ/YSZ, as shown in Table 2, have no linear relationships among six test points (Fig. 2) due to the different distance between test points and interface. However, in order to get the hardness and elastic modulus of the film, it is just need to know the load-displacement curve (A1 or B1) which is far from the substrate [17].

Fig. 4 compares the hardness of each test point in two material systems, calculated by Oliver Pharr approach, the proposed method, and the work of indentation. It can be seen that the hardness obtained by the proposed method is closed to the values by Oliver Pharr approach, but the hardness obtained by work of indentation is about 50% of that of two other methods. Because test points A1 (or B1) and A6 (or B6) are all far from the interface, the hardness values of YSZ, NiO-YSZ and Ni-YSZ can be considered as 21.3 GPa, 7.07 GPa and 3.68 GPa, respectively. In addition, the hardness of substrate is decreased by 48% due to NiO-YSZ reduced to Ni-YSZ.

Subsequently, elastic modulus which calculated by three methods are given in Fig. 5. The elastic moduli, computed by the

Table 1
Experimental data for NiO-YSZ/YSZ and Ni-YSZ/YSZ.

Sample	Test point	n	h_f (nm)	h_m (nm)	P_m (mN)	h_c (nm)	h_{c2} (nm)	h_f/h_m
NiO-YSZ/YSZ	A1	1.8520	138.1	246.5	20.1	196.4	196.03	0.535
	A2	1.7684	158.5	265.4	20.2	214.0	215.36	0.597
	A3	1.8598	187.8	283.9	20.1	240.8	243.688	0.661
	A4	1.8793	205.4	297.2	20.2	250.7	254.499	0.691
	A5	2.4407	279.4	384.5	20.1	346.4	351.192	0.726
	A6	2.0309	260.2	376.8	20.1	335.1	340.205	0.691
Ni-YSZ/YSZ	B1	1.7536	121.0	249.5	20.3	196.2	196.549	0.485
	B2	1.7300	139.0	263.8	20.3	209.7	208.359	0.527
	B3	1.5979	136.2	270.5	20.2	219.1	217.614	0.503
	B4	1.8179	166.4	325.2	20.2	266.8	287.369	0.512
	B5	1.6656	283.6	418.5	20.2	370.5	372.701	0.678
	B6	1.9044	339.3	479.9	17.5	438.2	440.005	0.707

Table 2
Nanomechanical experimental data for NiO-YSZ/YSZ and Ni-YSZ/YSZ.

Sample	Test point	W_S (mN nm)	W_T (mN nm)	W_E (mN nm)	H_{OP} (GPa)	H_W (GPa)	E_{OP} (GPa)	E_W (GPa)
NiO-YSZ/YSZ	A1	2516.5	1803.1	855.4	21.20	21.30	269.31	224.46
	A2	2743.1	2054.7	870.2	17.96	17.73	278.36	209.36
	A3	2917.5	2079.5	724.0	14.11	13.78	241.41	197.92
	A4	3075.5	2182.6	772.6	13.09	12.70	224.26	179.36
	A5	4001.9	2514.4	643.4	6.82	6.64	204.32	129.65
	A6	3932.6	2572.3	696.0	7.29	7.07	182.24	130.68
Ni-YSZ/YSZ	B1	2579.6	1918.7	903.1	21.47	21.39	232.72	227.28
	B2	2727.3	2047.7	947.3	18.80	19.04	232.72	205.77
	B3	2776.5	2136.0	908.1	17.13	17.37	237.72	204.26
	B4	3357.2	2474.6	699.9	11.55	9.96	161.29	176.07
	B5	4331.9	3376.4	854.2	5.99	5.92	142.53	117.02
	B6	4290.1	3065.9	658.5	3.71	3.68	119.19	85.68

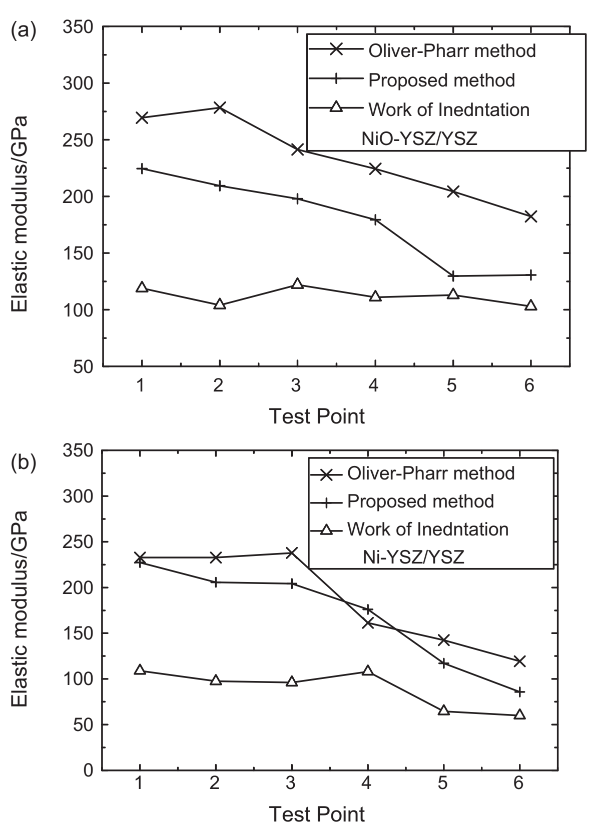

Fig. 5. Comparison of elastic modulus obtained by three methods for (a) NiO-YSZ/YSZ and (b) Ni-YSZ/YSZ.

proposed method, are lower than that by Oliver–Pharr method. The elastic modulus of YSZ, NiO-YSZ, and Ni-YSZ, given in Table 2, is about 227.28 GPa, 130.68 GPa, and 85.68 GPa, respectively.

4.3. Comparison of mechanical properties with pile up

The hardness values of two materials calculated by the proposed method are closed to the values obtained by Oliver Pharr method. But the ratios of h_f/h_m show very little pile up effect in hardness testing for the half-cell structure of SOFC. The indentation experiment data of YBCO polycrystalline superconductor sample, tested by elsewhere [7], is used to learn more about the proposed method when pipe up effect is observed. The ratios of h_f/h_m at different temperature are higher than the critical value 0.7. This result implies the existence of pile up effect in YBCO sample for each temperature. Fig. 6 shows the hardness calculated by three methods for YBCO

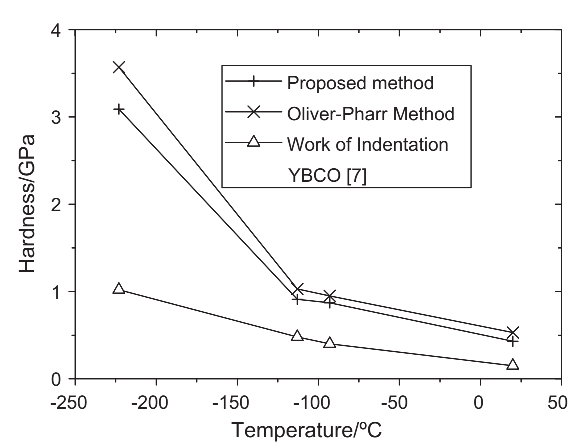

Fig. 6. comparison of hardness values obtained by three methods for YBCO sample.

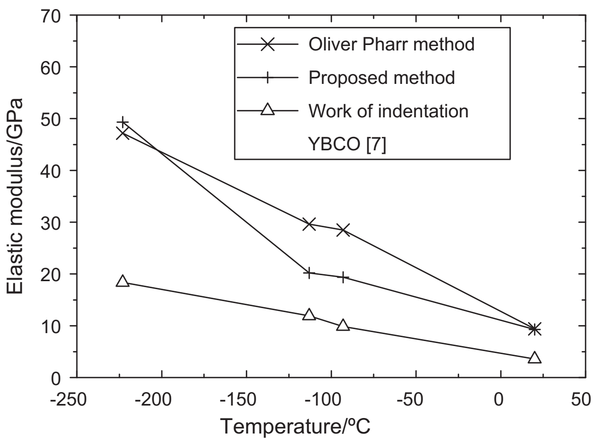

Fig. 7. comparison of elastic modulus obtained by three methods for YBCO sample.

sample. The hardness, calculated by the proposed method, is lower than that by the Oliver Pharr approach but higher than that by work of indentation especially at −223. As shown in Fig. 7, at room temperature, the elastic modulus, obtained by the proposed method (9.29 Gpa), is close to that (10.47 Gpa) given by some researches for YBCO sample tested by different methods [18].

5. Conclusions

In this study, a modified work of indentation was proposed to calculate the hardness and elastic modulus of the half-cell structure of SOFC. This method, directly performed by using the energy approach, avoids the pile up effect neglected in Oliver–Pharr method. Results from the indentation experiment to NiO-YSZ/YSZ and Ni-YSZ/YSZ show that, the hardness obtained by the proposed method exhibits well agreement with the values determined by Oliver Pharr method. The hardness and elastic modulus of YSZ film are higher than that of substrate NiO-YSZ or Ni-YSZ. With reducing to Ni-YSZ, hardness and elastic modulus of substrate can be decreased by almost 50%.

Pile up effect was discussed by comparing the results of indentation experiments data of YBCO. It showed that the proposed method works well even though pile up is observed.

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