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A novel method for preparing highly porous gadolinia-doped-ceria ceramics

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Abstract

Highly porous $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) was prepared with a novel method by acid leaching MgO from MgO–CGO ceramics (CGM) with acetic acid solution. Effects of leaching conditions and MgO content in CGM were studied. Under proper conditions (60 vol% acetic acid solution, 358 K, 8.5 h), MgO in CGM ceramics can be effectively leached out, but no CGO can be dissolved. The porosity of the sufficiently leached pellet increases with the increasing MgO content, but too much MgO can result in the collapse of the leached pellet. The suitable value of MgO/CGO is about 3.3. With the novel method, a highly porous CGO pellet was prepared with a porosity of 68% which is much higher than that (∼50%) with graphite as pore former.

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1. Introduction

Porous ceramics have many applications, such as fuel-cell electrodes [1]. In the works [2,3] developing copper-based, ceramic–metallic (cermet) composites for direct oxidation of hydrocarbon fuels in intermediate temperature solid oxide fuel cells (ITSOFCs) with $Ce_{0.8}Sm_{0.2}O_{1.9}$ (CSO) as electrolyte, the synthesis of a porous CSO matrix is the first step in fabrication. Unlike traditional Ni–CSO cermets, which can be formed simply by cosintering NiO and CSO powders and subsequently reducing NiO to nickel, it is difficult cosintering mixtures of copper oxides and CSO powders because Cu_2O and CuO melt at temperatures below those necessary for CSO sintering. To avoid this problem, Gorte and co-workers [2,3] prepared Cu–CeO_2–CSO cermets by impregnating soluble salts of copper and cerium into a porous CSO structure after the CSO

electrolyte layer had been sintered. Because the cermet anode should be ∼50% metal to ensure electronic conductivity and should still remain highly porous to allow diffusion of fuel to the electrolyte interface, high initial porosity is desirable for the porous CSO before the addition of copper oxides.

There are several standard methods for preparing porous ceramics. Most commonly, the porous structures are produced by sintering powders made up of different particle sizes [4]. In this case, a porous network is formed by the spaces between the necked powders, and it is difficult to achieve porosities greater than ∼45%. Higher porosities can be achieved through the use of pore formers [5,6]. Here, sacrificial compounds, such as graphite or starch, are added to the green body and are removed during calcination, leaving behind a porous ceramic. Using graphite as pore former, Gorte and co-workers [2,3] have prepared a porous CSO ceramic at 1773 K for copper-based anode, and found that the porosity could only achieve ∼50%. In addition, Gorte and co-workers [7] have created another method to prepare porous yttria-stabilized zirconia (YSZ) by using NiO as pore former. This method involves cosintering NiO–YSZ green tape at 1800 K, reducing with H_2 at 973 K for 10 h, and leaching Ni from the formed Ni–YSZ cermet with

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2.2 M HNO_3 at 353 K. Using this method, the porous YSZ achieved a porosity of 55–70%. However, this method cannot be applied to the preparation of porous CSO and other doped ceria because, in the acid leaching step, the hot and strong nitric acid can result in considerable dissolving of doped ceria, and that the hydrogen reducing step can cause partial reduction of the doped ceria electrolyte layer, which in turn causes lower open circuit voltage and lower power output of the fuel cells.

Similar to CSO, $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) has been widely studied as ITSOFC electrolyte and found even better than CSO in ionic conductivity [8–10]. In order to develop highly porous anode for direct hydrocarbon ITSOFCs with CGO as electrolyte, it is necessary to develop an effective way to prepare highly porous CGO ceramics.

In this work, we developed a novel method to prepare highly porous CGO by acid leaching MgO directly from MgO–CGO ceramics with acetic acid solution. The effects of MgO content and acid leaching conditions were studied. Using this method, highly porous CGO ceramics with porosity of 68% were prepared.

2. Experimental

2.1. CGO powder preparation

The starting materials were the nitrate salts of reagent grade (Acros) and used as purchased. An aqueous solution of Ce^{3+} and Gd^{3+} with Ce/Gd = 4 was prepared in a beaker. Then, citric acid (CA) and polyethylene glycol (PEG) with the weight ratio of CA/PEG = 60 were added until the molar number of citric acid was equal to the total number of the metal ions in the beaker. The mixed solution was evaporated under stirring at 353 K until the solution gelled. The gel was dried at 378 K, ground and calcined in air at 973 K for 4 h, and then ground again to form CGO powder.

2.2. Porous CGO pellet preparation

MgO powder was prepared by calcining $Mg(NO_3)_2 \cdot 6H_2O$ (Acros) at 773 K for 4 h, and mixed with the CGO powder in a molar ratio of x = MgO/CGO = 1.0–3.3. The mixture was ball milled into fine powder and pressed uniaxially into green pellets with a stainless steel die (diameter: 13.05 mm) under 750 MPa. The green pellets were sintered in air at 1773 K for 5 h into dense pellets [termed as $CGM_x(S)$], leached with acetic acid solution (60 vol%) at about 358 K for a sufficient time (>8 h), rinsed with distilled water to remove Mg^{2+}, and finally dried at 473 K over night. The leached pellets were termed as $CGM_x(L)$. The leaching-out rate of MgO (termed as LRMg) was calculated by the weight difference of the pellet before and after the leaching.

2.3. Sample characterization

The diameter and thickness of all the pellet samples were measured with vernier caliper and micrometer for the calculation of pellet volumes and linear shrinkages with
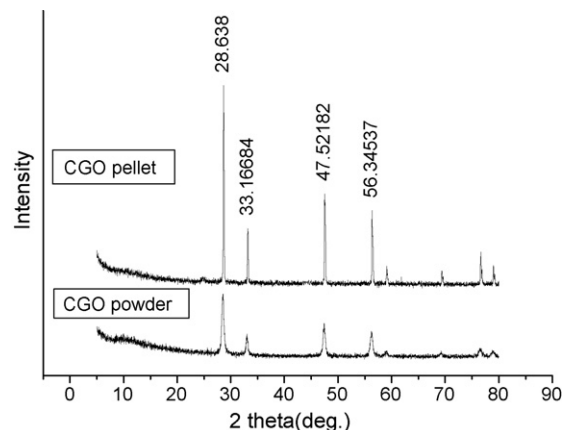

Fig. 1. XRD patterns of CGO powders (calcined at 973 K for 4 h) and pellet (sintered at 1773 K for 5 h).

respect to the green pellets. The linear shrinkages of sintered and leached pellets were calculated only with the diameter data. The porosities of the pellet samples were measured by mercury porosimetry (Pore Master 33). The compositions of pellet samples and filtrate from the acid leaching process were analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jarrell-Ash, ICAP9000). Before the analysis, pellet samples need to be dissolved hydrothermally in a HF and HNO_3 solution at 453 K for 15 h. The crystal structures of the samples were identified at room temperature using a PANalytical X-ray diffractometer (Cu Kα radiation). Scanning electron microscopy (SEM) analysis of the cross-section of pellet samples was conducted on a Hitachi S-2400 electron microscope. The relative density of the dense CGO pellet was measured by Archimedes' method. The ionic conductivity of the dense CGO pellet was measured in air with AC impedance equipment (Autolab).

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized CGO powder and the dense pellet which was prepared with the
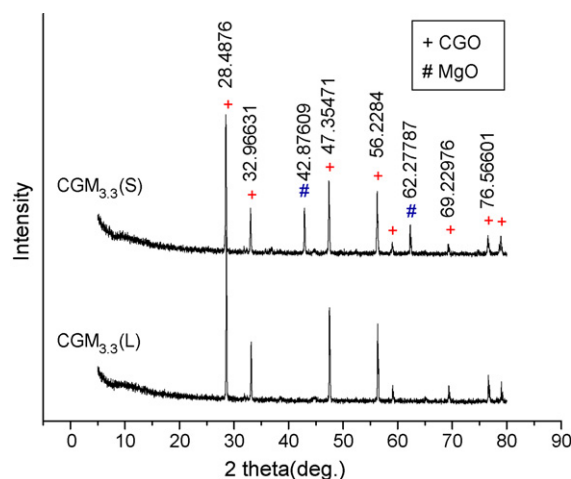

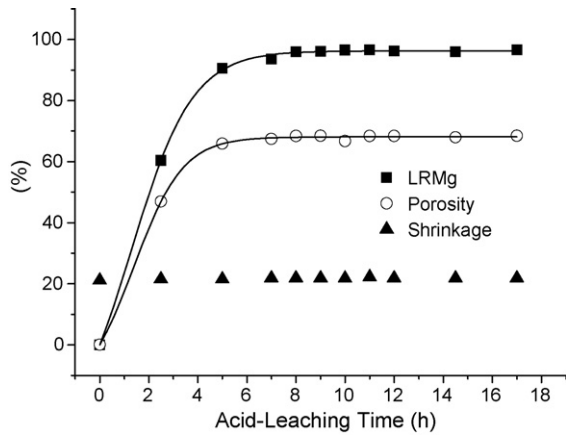Fig. 2. XRD patterns of $CGM_{3.3}(S)$ and $CGM_{3.3}(L)$.

Fig. 3. Effect of acid leaching time on LRMg, porosity, and shrinkage of $CGM_{3.3}(S)$ pellet (pellet 0.4 g; 60 vol% acetic acid 25 ml; 358 K).
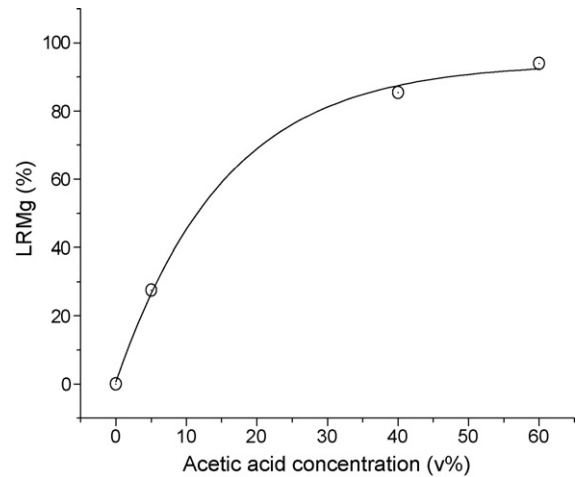

Fig. 5. Effect of acetic acid concentration on the LRMg at about 358 K, for 8.5 h ($CGM_{3.3}(S)$: 0.4 g; acetic acid: 25 ml).

powder by pressing under 750 MPa and sintering at 1773 K for 5 h. The powder and the pellet had the same XRD patterns as that of standard pure ceria except that the pellet had sharper peaks (due to higher sintering temperature and better crystallization) than the powder. These results suggest that both the powder and the pellet are single phase of ceria-based solid solution. The relative density (91%) and ionic conductivity (at 973 K, 0.0321 S cm^{-1}) of the dense CGO pellet indicate that the CGO powder is suitable for preparing dense electrolyte and porous anode, and that the sintering conditions are acceptable.

Fig. 2 shows the XRD patterns of the $CGM_{3.3}(S)$ and $CGM_{3.3}(L)$. $CGM_{3.3}(S)$ was observed two phases, MgO and CGO. Since MgO had been reported to have a solubility of 2% in CeO_2 at 1873 K [11], little MgO might also be dissolved here into the CGO lattice. After sufficient acid leaching, the sample $CGM_{3.3}(L)$ was observed only in one phase of CGO. Composition analysis by ICP revealed that the remnant MgO in $CGM_{3.3}(L)$ was less than 4 wt.%, and that no Ce^{3+}, Ce^{4+}, and Gd^{3+} were detected in the filtrate from acid leaching process. These results suggest that MgO in $CGM_{3.3}(S)$ can be effectively leached out, but no CGO can be dissolved.
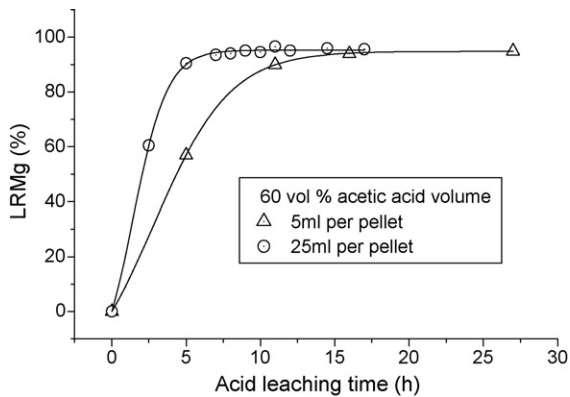
Fig. 3 shows the effect of acid leaching time on the shrinkage, the porosity, and the LRMg of the pellet. Although the shrinkage did not change apparently with time, both LRMg and porosity increased apparently with time and approached constants (about 96 and 68%, respectively) after 8 h. These results suggest that MgO in CGM(S) pellet can be effectively leached out, and that the acid leaching process cannot cause further shrink, but can cause great increase of porosity. Fig. 4 shows the effect of acetic acid volume on the acid leaching efficiency of the $CGM_{3.3}(S)$ pellet. The more the acetic acid solution, the shorter the sufficient leaching time is. If a $CGM_{3.3}(S)$ pellet (0.4 g) is leached with 25 ml acetic acid solution (60 vol%) at 358 K, the sufficient leaching time is about 8 h. Fig. 5 shows the effect of acetic acid concentration on the LRMg of $CGM_{3.3}(S)$ pellet. With acid concentration increasing, the LRMg increased rapidly at first and then approached constant at the concentration of about 60 vol%.

Fig. 6 shows the effect of the MgO content in $CGM_x(S)$ pellet on the porosity of the sufficiently leached pellet $CGM_x(L)$. The porosity increased with the increasing MgO content, and approached 68% at $x = 3.3$. When $x > 3.3$, the
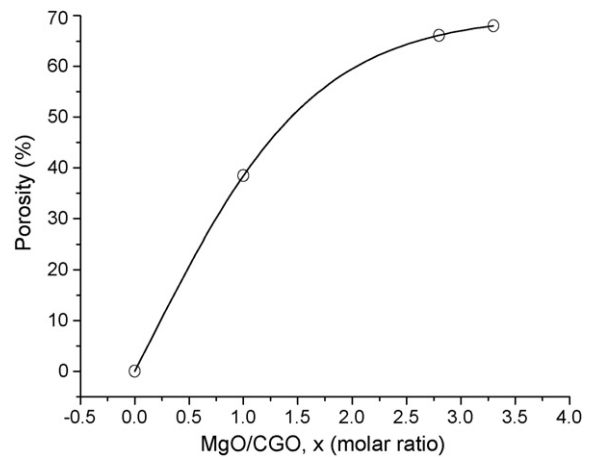

Fig. 4. Effect of acetic acid volume on the acid leaching efficiency of $CGM_{3.3}(S)$ pellet (0.4 g) in 60 vol% acetic acid solution of 25 ml (circle) and 5 ml (triangle) at 358 K.

Fig. 6. Effect of MgO content (x) in $CGM_x(S)$ on the porosity of sufficiently leached sample $CGM_x(L)$. Acid leaching conditions: $CGM_x(S)$ pellet 0.4 g, 60 vol% acetic acid 25 ml, 358 K, 21 h. LRMg $\approx$ 97%.
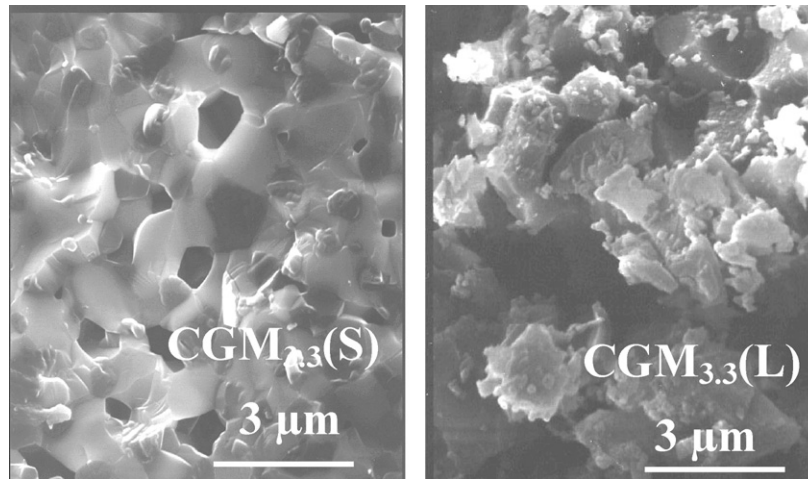
Fig. 7. SEM micrographs on the cross-sections of CGM$_{3.3}$(S) and CGM$_{3.3}$(L) pellets.

CGM$_x$(L) pellet had a little higher porosity but much lower strength. The proper x was found about 3.3.

Fig. 7 shows the SEM micrographs on the cross-sections of CGM$_{3.3}$(S) and CGM$_{3.3}$(L) pellets. Although smaller pores were still observed in CSM$_{3.3}$(S) pellet, much more and larger pores were observed in the CSM$_{3.3}$(L) pellet due to the removing of MgO. These results are consistent not only with the porosity and LRMg results but also with the average pore size results [about 0.6 μm for CGM$_{3.3}$(S) and 1.7 μm for CGM$_{3.3}$(L)]. These large pores are beneficial to the preparation and function of the porous anode.

In literatures [2,3], porous CSO had been made with graphite as pore former, but its porosity could only achieve 50%. This low porosity might be explained as follows. During the sintering process from room temperature to 1773 K, the graphite started to burn at about 900 K and burnt out at about 1273 K [12], the pores thus produced might further shrink or even vanish during the rest sintering in higher temperature range (about 1273–1773 K), consequently, the porosity of the final product of porous CSO was low. In our present work, MgO was used as pore former. Since MgO could not burn during sintering, the pores produced by MgO through acid leaching at 358 K could be all reserved. Therefore, the porosity of the final porous CGO was quite high.

4. Conclusions

In summary, a new method was developed to prepare highly porous CGO by acid leaching MgO from MgO–CGO ceramics with acetic acid solution. The effects of acid leaching conditions and MgO content were studied. Under proper leaching conditions (60 vol% acetic acid, 358 K, 8.5 h), MgO in MgO–CGO ceramics can be effectively leached out but no CGO can be dissolved. The porosity of the sufficiently leached sample increases with the increasing MgO content, but too much MgO may result in the collapse of the leached samples.

The proper MgO/CGO (molar ratio) is about 3.3. Under the proper conditions, highly porous CGO pellet can be made with a porosity of 68%, much higher than that (50%) with graphite as pore former.

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