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Porous Ag–CGO cermets as anode materials for ITSOFC using CO fuel

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Abstract

A novel route was developed for preparing Ag–CGO porous cermets as the anode materials for intermediate-temperature solid oxide fuel cells (ITSOFCs) using Ce_{0.8}Gd_{0.2}O_{1.9}(CGO) electrolyte. Porous CGO was prepared by leaching MgO from MgO–CGO ceramics with acetic acid and then impregnated with AgNO₃ solution. Porous cermet that contained 45 wt% Ag with the optimal porosity of 48% was a promising anode material for ITSOFCs using CO as the fuel. It yielded an electrical conductivity of 1260 S cm⁻¹ at 923 K and a CO oxidation rate of 0.6 mmol min⁻¹ g⁻¹_{cat}, and it was catalytically stable under reaction condition for 50 h with negligible carbon deposition.

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1. Introduction

Fuel cells represent an environmentally friendly and efficient means of generating electric power [1]. Solid oxide fuel cells (SOFCs), which are all-ceramic devices that operate at high temperatures, have many advantages, including high efficiency in generating electricity, the lack of need for precious metals as the electrodes, and the use of nonhydrogen fuels, such as hydrocarbons, alcohols, CO and others [2,3]. CO is considered to be a good candidate fuel since it can be generated by the gasification of chars with CO₂ at 973 K [4], and chars can be produced from plants or their wastes by carbonization [5]. Additionally, the process of generating CO also provides a means of recycling CO₂. SOFCs with yttrium-stablized zirconia (YSZ) as the electrolyte typically have to be operated at 1173–1273 K to have an acceptable power output. The high operating temperature markedly limits the range of the materials that can be used in interconnects and parts of the plant. To solve this problem, many researchers have been developing new solid electrolytes with a higher ionic conductivity than YSZ at intermediate-temperatures (IT, 773–973 K) and doped ceria materials are promising [6]. For sustainable development, intermediate-temperature solid oxide fuel cells (ITSOFCs) using CO as a fuel at 773–973 K are meaningful. However, to the best of the authors' knowledge, ITSOFCs using CO fuel have not yet been systematically studied.

Although Ni-based anodes have been extensively used in SOFCs [7], they are limited in that the deposition of carbon on Ni surface poisons the electrodes of SOFCs when either hydrocarbon or CO is used as the fuel [8–10]. Therefore, various attempts have been made to replace Ni with Cu, which is commonly supported on porous CeO₂-based material [9,11–13]. Although carbon deposition was avoided, other problems were found [12,13]: (i) Cu is electrical conductor but inactive in hydrocarbon oxidation [13]. (ii) Additional CeO₂ (typically about 10 wt%) introduced as an oxidation catalyst on the electrode fills some of the pore

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volume and limits the volume of the voids that left for Cu. Consequently, the relatively low Cu content (about 16 wt%) corresponds to the low electrical conductivity of the anode [12]. (iii) The reduction of copper by hydrogen partially reduced the dense CeO_2 -based electrolyte, leading to a low open circuit voltage and low power output.

Doped ceria materials have been studied extensively as the electrolytes in ITSOFCs [14]. Additionally, the highest conductivities have been identified in materials doped with 10-20% of Gd (GDC or CGO) or Sm (SDC or CSO) [15-17]. This work investigates anode materials for ITSOFCs with CGO as the electrolyte using direct CO fuel. In principle, the materials must meet the following requirements: (1) high activity in CO electro-catalytic oxidation, (2) high electronic conductivity, (3) sufficient oxide ion conductivity, (4) no carbon deposition, and (5) mechanically and chemically compatible with the CGO electrolyte. Porous CGO is chosen as the anode skeleton and oxide ion conductor because it has high oxide ion conductivity and is compatible with a dense CGO electrolyte. A novel method was developed to prepare highly porous CGO by leaching MgO from mixed CGO-MgO ceramics. Metallic Ag is not only the best electronic conductor, but also an effective oxidation catalyst [18-20]. Ag is active in carbon oxidation but inactive in CO decomposition [21]. Although Ag has a lower melting point (1235 K) than Cu (1356 K), anode sintering is not likely to occur because the operating temperature of ITSOFC is only in the range 773–923 K. Therefore, metallic Ag was employed as the electronic conductor and electro-catalyst in this work.

2. Experimental

2.1. Sample preparation

2.1.1. Porous CGO disc

The CGO powder Ce_{0.8}Gd_{0.2}O_{1.9} was prepared by the sol-gel method following a procedure described elsewhere [22]. MgO powder was prepared by calcining $Mg(NO_3)_2$. 6H₂O (Acros) at 773 K for 4 h, and mixed with the CGO powder in various Mg/(Ce + Gd) molar ratios of $1.0 \sim$ 3.3. The mixture was ball-milled into fine powders, termed "CGMz", where "z" stands for the Mg/(Ce + Gd) molar ratio. The CGMz powder was then pressed uniaxially into green discs (13.05 mm in diameter) at 750 MPa. The green discs were sintered in air at 1773 K for 5 h; the sintered discs were denoted CGMz(S). The CGMz(S) discs were then stirred in a 60 v% acetic acid solution at 358 K for 8 h, rinsed in distilled water to remove Mg^{2+} , and finally dried at 473 K overnight. The leached discs were denoted CGMz(L). The leaching-out ratio of MgO (denoted LR_{Mg}) was calculated from the weight difference of the disc before and after leaching process:

$$LR_{Mg} = \frac{Wt \text{ of } CGMz(S) - Wt \text{ of } CGMz(L)}{Wt \text{ of } MgO \text{ in } CGMz(S)} \times 100\%$$
(1)

2.1.2. Ag-CGO porous disc

The leached discs with 96% LR_{Mg} and 68% porosity were used to prepare Ag–CGO cermets by impregnating CGMz(L) with an AgNO₃solution, drying at 393 K overnight, and then calcining at 773 K for 4 h. The resulting cermets were named *x*Ag–CGO, where *x* represents the weight of Ag as a percentage of the total weight of the sample.

2.2. Sample characterization

2.2.1. Structure and conductivity

The crystal structures of the powder and disc samples were examined using a PANalytical X-ray diffractometer (Cu K α radiation). The linear shrinkages of the sintered and leached discs were estimated from the diameter using Vernier calipers and a micrometer. The porosities of the disc samples were determined by mercury porosimetry (Pore Master 33). The electrical conductivities of the *x*Ag–CGO cermet discs were measured at 923 K in CO using the two-probe DC method (Autolab). The ionic conductivity of the dense CGO disc was determined at 923 K in air using AC impedance equipment (Autolab).

2.2.2. Catalytic activity

The disc samples (xAg–CGO) with a diameter of ca. 1 cm and a volume of 0.0907 cm³ were crashed into 40– 60 mesh, and tested for CO oxidation at 373–973 K in a plug-flow system with a quartz tube reactor (7 mm ID) at atmospheric pressure and a gas hour space velocity (GHSV) of 34,682 h⁻¹, which is obtained by dividing the volumetric velocity (mL/h) of inlet gas by the volume of catalyst (mL). The inlet gases comprised 10.74% air, 4.54% CO and 84.72% N₂ (O₂/CO molar ratio of 1/2) and had a total flow rate of 100 mL/min at 273 K and 1 atm. All of the components at the inlet and outlet of the reactor were analyzed using a Gas Chromatograph (Shimadzu GC-7A) with a carbon molecular sieve column and a thermal conductive detector.

The reaction rate of CO was calculated using the following equation:

$$rate(mol/min g) = \frac{flow rate of CO(4.54 mL/min) \times CO conversion(\%)}{22,400(mL/mol) \times Catal Wt (g)}$$
(2)

3. Results and discussion

The synthesized CGO powder was a single phase of ceria-based solid solution. The CGO dense disc sintered at 1773 K for 5 h was still a single phase of ceria-based solid solution, and had a relative density of 93% and an ionic conductivity of 0.0115 S cm⁻¹ at 923 K, indicating that the sintering condition was suitable for preparing CGO ceramics with high ionic conductivity.



Fig. 1. Effect of MgO loading on porosities of CGMx after leaching with 60 v% acetic acid at 363 K for 21 h (pellet pressing pressure \bigcirc : 750 MPa, X: 375 MPa).

Fig. 1 plots the effect of MgO loading on the porosities of the acid-leached CGMz(L) discs. The porosity increases with MgO content to about 60%, at which the Mg/ (Ce + Gd) ratio is 3.3, indicating that MgO is an efficient pore-former. Moreover, since the increase in pore volume with the Mg/(Ce + Gd) ratio became less pronounced as the MgO content increased further, the disc made with a Mg/(Ce + Gd) ratio of 3.3, CGM_{3.3}, was the subject of further study hereafter.

Fig. 2 presents the XRD patterns of the CGM_{3.3} disc after sintering at 1773 K for 5 h [CGM(S)] and that after acetic acid-leaching [CGM(L)]. Both MgO and CGO phases were observed on CGM(S), while only a single phase of CGO was observed on CGM(L), indicating that MgO in CGM_{3.3}(S) was almost completely leached out. Elemental analysis by ICP demonstrated that the CGM(L) sample contained less than 4 wt% MgO. Since MgO was reported to be 2% soluble in CeO₂ at 1873 K [23], a small amount of Mg²⁺ may have been dissolved in the CGO lattice. Additionally, Mg and Gd co-doped



Fig. 2. XRD patterns of CGM(S), acid leached CGM(L), and xAg–CGO porous cernet samples with various Ag contents (x).

ceria has been reported to have higher conductivity than Gd singly doped ceria [22,23]. At 923 K, the CGM(L) disc was measured to have a conductivity of 0.004 S/cm in air. These results show that porous CGO ceramics can be successfully prepared as anode materials of ITSOFCs by leaching MgO from a mixed MgO–CGO disc with acetic acid solution.

Fig. 3 plots the effect of acid-leaching period on the LR_{Mg} value, the porosity and the shrinkage of the CGM(L) disc. Both LR_{Mg} value and porosity increased with leaching period and approached constants (about 96% and 68%, respectively) after 8 h. However, no significant decline in disc diameter was observed during leaching. Restated, acid-leaching greatly increased the porosity of the disc without detectably shrinking it. Furthermore, the porosity of 68% is much higher than that of 50% obtained when graphite was used to form the pores as reported in the literature [12].

The highly porous CGM(L) disc was sufficiently porous to hold enough Ag to meet the requirements of electrical conductivity and electro-catalytic activity. Fig. 2 shows the XRD patterns of xAg–CGO cermets prepared from highly porous CGM(L). Both metallic Ag and cubic ceria phases were observed on all of the Ag-containing samples. As the Ag content increased, the intensity of the diffraction peaks that corresponded to metallic Ag phase increased, while those for the ceria phase decreased. At x = 36.7 wt%, the ceria phase was almost negligible, indicating that silver covered most of the CGO surface.

Fig. 4 plots the effect of Ag content on the porosity and electrical conductivity of the xAg-CGO discs. The porosity decreased as the Ag content increased. At x = 45 wt%, the porosity was 48%, which exceeded that (ca. 32%) of Cu-based anodes that were prepared followed similar procedure but used graphite as the poreformer [12,13]. The curve of electrical conductivity versus Ag content was an S-shaped curve. The steep rise in conductivity from 0.004 S cm⁻¹ to 1260 S cm⁻¹ in the range



Fig. 3. Effect of acid-leaching period on leaching-out ratio of MgO (abbreviated as LR_{Mg}), porosity and shrinkage of the disc sample CGM(S).



Fig. 4. Effect of Ag content (x) on the porosity and electrical conductivity in CO at 923 K of Ag–CGO cermets.

of 35–45 wt% Ag was caused by a switch in the conducting mechanism from ionic conduction to electronic conduction. The conductivity of 1260 S cm⁻¹ at x = 45 wt% markedly exceeded that of 100–300 S cm⁻¹ for an Nibased anode [24].

The catalytic activities of Ag-CGO cermets for CO oxidation were tested in a plug-flow system. Fig. 5 shows the dependence of CO conversion on reaction temperature. The reactions over two Ag-CGO cermets and CGM(L) all began at about 723 K, and the activities increased with the temperature. However, the activity of the samples that contained Ag increased markedly more than those without Ag, indicating that metallic Ag is catalytically more active than CGO ceramics. The two Ag-containing samples exhibited similar activities over the whole temperature range, suggesting that most of the CGM(L) surface had been covered by silver when Ag content exceeded 36.7%. These results are consistent with those of XRD studies. At 923 K, the CO conversion over the two Ag-containing samples reached about 96%, equivalent to a reaction rate of $0.6 \text{ mmol min}^{-1} \text{ g}_{cat}^{-1}$. Consider the same CO oxidation rate on the anode when CO reacted with oxide ions through the equation

$$\mathrm{CO} + \mathrm{O}^{2-} \to \mathrm{CO}_2 + 2\mathrm{e}^{-} \tag{3}$$

The generated current density can be estimated based on knowledge of the weight and diameter of the anode pellet.



Fig. 5. Effect of reaction temperature on CO conversion in oxidation reaction of CO at atmospheric pressure over *x*Ag–CGO catalysts.

Ag–CGO cermet is expected also to exhibit high electrocatalytic activity in CO oxidation by reacting with O^{2-} ions that are transported from the cathode through the CGO electrolyte to the anode.

The stabilities of the two Ag–CGO catalysts in CO oxidation were studied by recording the extent of CO conversion as a function of reaction time at 923 K. The CO conversions were maintained at about 96% over a reaction period of 50 h, indicating that the materials were quite stable under this reaction condition. The possibility of the deposition of carbon on these samples was also investigated by analyzing the total carbon yields from the effluent of the reactor at various reaction temperatures. The results show that the total carbon contents do not change significantly, suggesting that the carbon depositions on the Ag–CGO catalysts were negligible.

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Current density =
$$\frac{0.6 \text{ mmol min}^{-1} \text{ g}_{cat}^{-1} \times 0.32 \text{ g}_{cat} \times 6.02 \times 10^{23} \times 2e^{-} \times 1.602 \times 10^{-19} \text{ C/e}^{-}}{3.14 \times (0.998/2)^2 \text{ cm}^2} \approx 47,000 \text{ mC min}^{-1} \text{ cm}^{-2} = 790 \text{ mA cm}^{-2}$$

The current density of about 790 mA/cm² is quite high for an anode [9,11–13]. Since the CO oxidation over silver catalyst with O_2 has been suggested to involve reduction of Ag₂O/AgO species formed on the Ag surface [25], the

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