Journal of Power Sources 233 (2013) 62–68

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

NiCu–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ anode materials for intermediate temperature solid oxide fuel cells using hydrocarbon fuels

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HIGHLIGHTS

- ► By doping Zr into ceria, thermal stabilities and activities of anodes are improved.
- ► The best performing anode is Ni–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ cermet.
- ► The best thermally stable anode is Cu–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ cermet.
- ► $Ni_{0.5}Cu_{0.5}$–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ anode achieves both high stability and high activity.
- ► Ni–Cu alloy–Zr doped CeO_2 can be promising candidate anode materials.

ARTICLE INFO

Article history:
Received 10 October 2012
Received in revised form
2 January 2013
Accepted 3 January 2013
Available online 12 January 2013

Keywords:
Solid oxide fuel cell
Anode
Ceria–zirconia
Intermediate temperature
Direct utilization of hydrocarbons

ABSTRACT

NiCu–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ based cermets are evaluated as anode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) using hydrocarbon fuels. Polarization curves and stability tests are conducted for direct methane SOFCs with various anode materials at 700 °C. The performances and thermal stabilities of the cells with $Zr_{0.1}Ce_{0.9}O_{2-\delta}$ based anodes are significantly higher than those using pure CeO_2-based anodes, indicating by doping 10 mol% Zr into CeO_2, the thermal stability and anode performance can be improved. Among the anode materials investigated, the best performing anode is Ni–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$. The cell using the $Ni_{0.5}Cu_{0.5}$–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ anode exhibits a similar performance to that with the Ni–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ anode, but experiences a much lower degradation after a short-term operation in weakly humidified CH_4. The cell using the Cu–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ anode shows the best stability, only 0.61% degradation after a 48 h operation, but a low performance as well. The results suggest that NiCu–$Zr_{0.1}Ce_{0.9}O_{2-\delta}$ based cermets could be promising candidate anodes for direct hydrocarbon IT-SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that directly convert the chemical energy of a fuel into electrical energy with high efficiency and low emission of pollutants. Though hydrogen represents an attractive clean fuel it is not readily available and its storage and transportation still present technological hurdles. Thus, direct utilization of hydrocarbons in SOFCs based on oxide ion conducting electrolytes would contribute to the more effective utilization of remaining fossil fuel reserves [1–3]. Anode materials are regarded as one of the most important components for direct hydrocarbon SOFCs. Ideally, the direct utilization of hydrocarbons without reforming, either external or internal, at anodes can not only enhance the fuel cell efficiency but also simplify the system. However, the conventional anode material for SOFCs, Ni–YSZ cermet, cannot be used for this application directly since Ni is a good catalyst for hydrocarbon cracking reaction [1]. Different alternatives such as Ni-, Cu–CeO_2-based cermets [4,5] and various perovskites [6–8] have been developed to overcome such deactivating effect for direct hydrocarbon SOFCs. Though perovskite anodes exhibit good resistances to carbon deposition and tolerances to sulfur contamination, their electrical conductivity and electro-catalytic activity are still lower than those of cermet anodes under the reducing environments. Ni–, Cu–CeO_2-based cermets have been widely studied and showed significant activities for direct utilization of hydrocarbon fuels in SOFCs [2–5]. Furthermore, these CeO_2-containing anodes can be easily compatible with electrolytes able to operate at intermediate temperatures like gadolinium-doped ceria (GDC) [1]. Murray et al. [2] have successfully operated a cell on dry methane by employing

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http://dx.doi.org/10.1016/j.jpowsour.2013.01.022

a nickel-containing CeO_2-based anode. Recently, the use of Cu–CeO_2 anodes has received much attention for direct utilization of a large diversity of hydrocarbons in SOFCs [4,5]. Cu is generally chosen as the electronic conductor due to its catalytic inertness for carbon formation. CeO_2 acts as an oxidation catalyst and a mixed ionic-electronic conductor (MIEC) under reducing conditions.

The catalytic activities of Ni-, Cu–CeO_2-based anodes strongly depend on the interaction between metal and oxide, that is, the strong metal–support interaction (SMSI). However, CeO_2 has the disadvantage of being less refractory, causing the loss of SMSI and catalytic activity at a relatively high temperature. He et al. [9] found that the area-specific resistance (ASR) of an SOFC using CeO_2 anode sintered at 723 K was about three times lower than that sintered at 1523 K. This was attributed to a loss of CeO_2 surface area due to particle sintering. Furthermore, under a reducing condition, the relatively big effective ionic radius of Ce^{3+} (0.114 nm) compared to that of Ce^{4+} (0.097 nm) can cause an expansion of the CeO_2 lattice and a concomitant structure instability [10]. One way to counteract this would be to add metal ions into CeO_2. Most of the related studies were on the substitution of a lower-valent metal ion, such as Tb^{3+} [11], Fe^{2+} [12,13] or Sm^{3+} [14] for Ce^{4+}. Doping CeO_2 with Tb^{3+} results in a lowering of the energy barrier for oxygen migration and a stabilization of specific surface area during high temperature calcinations [11]. But Ce seems to be less reducible to Ce^{3+} in the presence of Tb^{3+} and its electrical conductivity is rather low under reducing conditions, possibly due to the excess electrons being located on Tb in preference to Ce. Pe'rez-Alonso et al. [12] studied the chemical structures of co-precipitated Ce–Fe mixed oxides. They thought that these Ce–Fe mixed oxides were not suitable to become anode materials for SOFCs because doping CeO_2 with high Fe content induces the extremely low oxygen vacancy concentration [13]. Tavares et al. [14] studied Cu–$Ce_{0.8}Sm_{0.2}O_{1.9}$ (Cu-SDC) anode material for IT-SOFC and achieved an excellent cell performance in methane. However, the short-term stability tests showed an initial impairment of the anode performance and carbon formation.

Adding small Zr^{4+} (0.084 nm) into CeO_2 has proven very useful in stabilizing CeO_2 for oxidation or partial oxidation reaction of hydrocarbons [10]. The dissolution of ZrO_2 into the cubic fluorite lattice of CeO_2 strongly affects its catalytic behavior by lowering the activation energy for oxygen mobility within the lattice. This results in an increase in the oxygen storage capacity (OSC) and the concentration of Ce^{3+} which acts as the active site for oxidation of hydrocarbon [10,15]. Zr doped CeO_2 (ZDC) have exhibited a stable activity for direct oxidation of methane without carbon deposition at temperatures below 800 °C [16]. Larrondo et al. [16] examined the catalytic activity of ZDC for direct oxidation of methane by TPR method, aiming at their potential applications as anode materials for direct hydrocarbon SOFCs. They concluded that Zr can stabilize the reducibility of both surface and bulk CeO_2 sites. Ahn et al. [17] investigated the SOFC performance using Cu–$Zr_{0.4}Ce_{0.6}O_2$–YSZ anode material compared with that using Cu–CeO_2–YSZ anode. The latter showed a lower performance after both anode materials were calcined at 1273 K. Recently, Cimenti et al. [18] have investigated the direct utilization of methanol in SOFCs with impregnated Ni/YSZ and Ni–$Zr_{0.35}Ce_{0.65}O_2$/YSZ anodes at 1073 K. The performances and stabilities of anodes were remarkably improved by the presence of ZDC. The carbon deposition could be effectively mitigated by ZDC, whether the cells were operated at open circuit or under load (at 0.6 V). Though the CeO_2-based anodes have been studied extensively for direct hydrocarbon SOFCs, to the best of our knowledge, the investigations on use of ZDC anodes are rare. Baker et al. [19] have reported that by doping Zr into CeO_2 both the anode performance and thermal stability could be largely improved. The anode polarization could be reduced by more than half for ZDC electrodes with low Zr contents ($Zr_{0.1}Ce_{0.9}O_2$ and $Zr_{0.25}Ce_{0.75}O_2$), possibly due to the Zr^{4+} helping to enhance surface and bulk oxygen species mobility and the concentration of Ce^{3+} [20]. Therefore, a strategy of developing CeO_2-based anodes with good thermal stability and catalytic activity through doping with Zr would worth further pursuing.

Since the electronic conductivity of CeO_2 at intermediate temperatures is not adequate for use as anodes for SOFCs, and its anode performance can be largely enhanced by adding a catalytic component for C–H bond breaking in CH_4, the use of an active metal phase is necessary for CeO_2-based anode. The coupling of metal such as Ni, Cu and alloys with CeO_2 can provide enough electronic conductivity for the anodes and enhance the oxidation rate of hydrocarbons [21–23]. In contrast to Ni, Cu does not catalyze the cracking process and is effective as current collector under reducing conditions. However, Cu has several limitations related to its relatively low melting temperature, which makes the fabrication of Cu–CeO_2-based anodes difficult and limits the SOFC operation temperature to below intermediate temperature. Furthermore, Cu is also rather poor for hydrocarbon activation [24]. One approach for enhancing the catalytic properties of Cu and stabilizing the tendency of Ni for carbon formation is to use Ni–Cu alloys. Ni–Cu alloy–CeO_2-based anodes offer potential advantages with respect to typical Ni–YSZ anode for direct hydrocarbon SOFCs [21–23,25,26]. In the present work, we investigated the performances and stabilities of NiCu–$Zr_{0.1}Ce_{0.9}O_2$ based anodes for direct methane IT-SOFCs using GDC electrolytes at 700 °C, with NiCu–CeO_2-based anode as the reference material. Using GDC as the electrolyte gives the advantages of higher electrolyte conductivity, better adhesion, and thermal and chemical matching to the $Zr_{0.1}Ce_{0.9}O_2$ materials. The effects of the promotion by Ni–Cu alloy on electrochemical activity and stability for the anodes are also examined. This work extends the previous impedance studies on ZDC anode materials for direct oxidation of methane in SOFCs [19].

2. Experimental

2.1. Preparation of GDC, CeO_2, $Zr_{0.1}Ce_{0.9}O_{2-\delta}$ and $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ cathode

All reagents used in this work were obtained from Beijing Chemical Reagent Company. GDC of composition $Gd_{0.1}Ce_{0.9}O_{1.95}$ was prepared following a modified gel synthesis method [27]. The stoichiometric amounts of Gd_2O_3 and $Ce(NO_3)_3 \cdot 6H_2O$ were mixed in deionised water. After it was stirred thoroughly, a cross-linking agent consisting of N,N-methylene-bisacrylamide and monomer acrylamide solution was added. The mixture was ground using a planetary ball mill for 24 h and then vacuum deaerated. After that, the ammonium persulfate and tetramethyl ethylenediamine were added as the initiating agent and catalyst, respectively. The as-prepared slurry was stirred thoroughly again and dried gradually at 120 °C. The resulting dry precursor was calcined in air at 800 °C for 2 h in order to eliminate carbonaceous residues and obtain the GDC powder. Finally, the as-prepared GDC powder was ball-milled again for 12 h to achieve average particle distribution. A similar procedure was used for the preparation of CeO_2 and $Zr_{0.1}Ce_{0.9}O_{2-\delta}$ (ZDC) powders and $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot nH_2O$ were used as the starting reagents. $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) was prepared by the conventional solid state reaction process as described in our previous work [28,29]. Stoichiometric amounts of $BaCO_3$, Fe_2O_3, Co_3O_4, and Nb_2O_5 were mixed by ball-milling in ethyl alcohol medium for 48 h. Calcination of the precursor powders was performed at 1000 °C in air for 24 h. Finally, the synthesized oxide was ball-milled again for 24 h.