



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Development of anodes for direct oxidation of methane fuel in solid oxide fuel cells

Yelda Akdeniz ^{a,b,*}, Bora Timurkutluk ^{a,b}, Cigdem Timurkutluk ^{a,b,c}

^a Nigde University, Mechanical Engineering Department, 51245, Nigde, Turkey

^b Nigde University Prof. Dr. T. Nejat Veziroglu Clean Energy Research Center, 51245, Nigde, Turkey

^c Vestel Defense Industry, Universiteler Mah, Ihsan Dogramaci Bul, Titanyum Blok 17/B Teknokent ODTU, 06800, Ankara, Turkey

ARTICLE INFO

Article history:

Received 3 November 2015

Accepted 15 January 2016

Available online 14 April 2016

Keywords:

Solid oxide fuel cell

Direct methane fuel

Carbon deposition

Infiltration

Copper

Ceria

ABSTRACT

In addition to pure hydrogen, solid oxide fuel cells (SOFCs) can utilize hydrocarbons as a fuel. However, conventional Ni-based anodes exhibit an excellent catalytic activity towards the hydrocarbon cracking reaction and thus the carbon deposition occurs in the anode. The deposited carbons quickly deactivate the anode irreversibly by covering the active surface of the anode catalyst. As a result, a significant degradation in the cell performance can be seen. In this study, the anode structure is modified by the addition of copper (Cu) and ceria (CeO₂) to increase the coking resistance of the cell under direct methane fuel. In this respect, the anodes are infiltrated by different amounts of Cu and CeO₂ nitrates via the wet impregnation technique to investigate the effects of Cu and CeO₂ loadings on the carbon tolerance of the cell. The effects of the anode porosity and composition are also considered in the study. The carbon resistance thus the service life of the cell with Cu/CeO₂/Ni/YSZ anodes is found to be significantly higher than that of conventional Ni-based anodes under direct dry methane fuel.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Solid oxide fuel cells (SOFCs) are high efficient electricity generating devices. The chemical energy of hydrogen can be directly converted into electricity and useful heat energy in an electrochemical way. The high operation temperature allows the utilization of hydrocarbon fuels beside hydrogen whose storage and distribution problems remain unsolved. On the other hand, the natural gas rich in methane is readily available in our houses or offices through well-established infrastructure. Therefore, it can be considered to be a potential fuel

for SOFCs alternative to hydrogen. The SOFC component responsible for the fuel oxidation is the anode electrode. At hydrogen fueled SOFC operating conditions, in addition to its low cost [1–3], Ni-based anodes shows excellent catalytic activity [4–6], good chemical stability [7–9] and high electronic conductivity [10,11]. In the case of hydrocarbon fueled SOFC with Ni anode, however, carbon deposition is seen covering the anode active sites thus reducing the cell performance irreversibly.

To suppress the carbon deposition under direct methane fuel, the anode structure is generally modified by the addition

* Corresponding author. Nigde University, Mechanical Engineering Department, 51245, Nigde, Turkey. Tel.: +90 388 225 23 37; fax: +90 388 225 01 12.

E-mail address: yelda_ciflik@hotmail.com (Y. Akdeniz).

<http://dx.doi.org/10.1016/j.ijhydene.2016.03.169>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

of copper/ceria or both in the form of a nitrate solutions via infiltration/wet impregnation. Qiao et al. [12], for example, developed Ni–CeO₂–YSZ anodes for the direct oxidation of methane in SOFC. Ni(NO₃)₂ and Ce(NO₃)₃ solutions were infiltrated into the porous YSZ backbone with a thickness of 1000 μm and a porosity of 65–67% fabricated by tape casting on a dense YSZ electrolyte layer with 300 μm thickness. Pt or LSM cathode with 0.49 cm² active area was coated by screen printing on the other surface of the dense electrolyte. The cells with various Ni and CeO₂ loadings were prepared and tested under H₂ and dry CH₄ fuels. The cell with 5 wt. % CeO₂ and 25 wt. % Ni infiltrated anode showed the highest performance under both fuels. The calcination temperature of the infiltration was then studied and optimized as 1073 K for this anode composition. The carbon deposition tests were also performed for the anode infiltrated with 10 wt. % CeO₂ and 25 wt. % Ni. After 5 h of operation under dry methane fuel, SEM and EDX analyses showed no obvious carbon deposition. Therefore, CeO₂ addition was found to improve the stability of the anode under CH₄ fuel. Zhao et al. [13] fabricated Ni–Cu–SDC anode supported cells with SDC–YSZ bi-layered electrolyte and LSCF cathode and studied the amount of Cu loading on the carbonization resistance under dry methane fuel. All powders were synthesized except YSZ which was purchased and Cu was incorporated by infiltration. Five different 1 cm² active area cells with various Cu-loaded anodes were fabricated and tested. The cell performance under methane fuel increased up to a Cu loading of 3.32 wt. %. The further increase in the Cu content adversely affected the cell performance. This was explained by the reduced surface area of nickel by Cu which has no catalytic activity towards fuels. In addition, the porosity of the anode was found to decrease with increasing the Cu content. As a result, increase in the gas diffusion resistance was detected. Therefore, the optimal Cu loading in Cu–Ni–SDC anode was determined to be 3.32 wt. % which corresponds to two times of impregnation. The short term tests of the cell with optimized anode composition was also performed at 500 mAcm⁻² current density under dry methane fuel for 900 min and indicated only 1.4% reduction in the initial voltage. This was attributed to the improved carbon tolerance of the anode with Cu addition. Wang et al. [14] developed NiF–Cu alloy with a composition of 12 wt. % Ni, 3 wt. % Fe, 50 wt. % Cu and balanced ZrO₂ as an anode catalyst for direct methane fed SOFCs. Glycine nitrate process, physical mixing and impregnation techniques were used for the catalyst preparation. The effects of the anode catalyst preparation method on the electrochemical and coking behavior of the cell was determined. The results indicated that the cell with Cu-impregnated anode catalyst has the highest carbonization resistance when compared to other two and exhibits a stable performance under CH₄ fuel without any degradation.

Hornes et al. [15], on the other hand, focused on the infiltration of both CeO₂ and Cu. A substrate composed of a dense YSZ electrolyte layer sandwiched between two porous YSZ layers was fabricated by tape casting for this purpose. One porous layer was LSF infiltrated while the other was impregnated with Cu, Ni and CeO₂. The total amount of loading was adjusted to 60 wt. % CeO₂ and 40 wt. % Cu–Ni with an atomic ratio of 1 corresponding to the 40 wt. % of the anode. The active area of the cell was 0.35 cm². The cell was shown to

provide a stable power at 1073 K operation temperature and 90% peak power conditions for 100 h. Liu et al. [16] also considered Cu–Ni–CeO₂–YSZ anode and presented the optimization of the anode composition and catalyst loading. Different amounts of Cu, Ni and CeO₂ in the form of nitrate solutions were impregnated into porous YSZ backbone similarly. The impedance measurements on the symmetric cells with 1.8 cm² active area revealed that the optimum mole ratio of Cu–Ni is 5:5 while the weight ratio of Cu–Ni to CeO₂ should be 3:1. The best performance was obtained from the cell with 40 wt. % catalyst loading. The carbon tolerance of the anode was also determined by measuring the weight changes after testing at 750 °C under 3% humidified CH₄ for 10 h. The cell with optimized anode showed lower gained carbon weight (0.05 g g⁻¹) compared to that of the cell infiltrated with Ni only (0.23 g g⁻¹). There can be also found numerous studies in the literature on the development of Cu–CeO₂ based Ni-free anodes for hydrocarbon fueled SOFCs to avoid carbon formation [17–24]. Although they showed high carbon tolerance, the reported performances seem to be relatively low when compared to those of Ni-based anodes.

In literature, since the powders used for the cell fabrication are generally synthesized by the authors, the microstructure of the anodes to be modified varies from study to study. As a result, the optimum infiltration parameters reported are different in the literature. In this study, on the other hand, commercial powders are used for the cell fabrication. Therefore, the results can be expected to be more general, repeatable and sustainable. In addition, the investigated cells in literature are generally manufactured in button size (≤1 cm²) without considering the effect of the cell size. By fabricating large size cell with 16 cm² active area like in this study is thought to overcome the scaling up problems in the optimization procedure.

Experimental

Base cell fabrication

Standard tape casting and screen printing routes were conducted for the fabrication of electrolyte supported cells with 16 cm² active area. YSZ powders (Ytria stabilized zirconia, TZ-8YS, Tosoh, Japan) were mixed with certain amounts of dispersant (fish oil, Sigma–Aldrich, Munich, Germany), plasticizer (poly ethylene glycol, Sigma–Aldrich) and binder (butvar, Sigma–Aldrich). After the addition of the solvent composed of high purity ethanol and ethyl methyl ketone (both from Sigma–Aldrich), the mixture was ball milled for 24 h to obtain a homogenous tape casting YSZ electrolyte solution. The slurry was then tape cast on a mylar strip with a doctor blade gap of 170 μm. The tape was allowed to dry under atmospheric air for 30 min. Next, six electrolyte tapes were stacked together and pre-laminated under 5 MPa for 4 min via uniaxial hydraulic pressing. The full lamination of the electrolyte layer was completed after the isostatic pressing under 50 MPa pressure at 60 °C for 10 min. The electrolyte laminate was then cut by a laser cutter in the form of a square with 75 mm × 75 mm outer dimensions. After sintering at 1400 °C for 5 h, the thickness of YSZ electrolyte support was measured

Download English Version:

<https://daneshyari.com/en/article/1277055>

Download Persian Version:

<https://daneshyari.com/article/1277055>

[Daneshyari.com](https://daneshyari.com)