



Effect of steam content on nickel nano-particle sintering and methane reforming activity of Ni–CZO anode cermets for internal reforming SOFCs

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ABSTRACT

In this work, the reforming activity of Ni–Ce_{0.75}Zr_{0.25}O₂ (Ni–CZO) solid oxide fuel cell (SOFC) cermet anodes for steam reforming of methane has been investigated in the absence of electrochemical effects and the results were compared with Ni–Ce_{0.9}Gd_{0.1}O₂ (Ni–CGO) cermet anodes. From X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM/EDS) and CHN analysis on the spent Ni–CZO anode cermets, it was found that a decrease in reforming activity at higher steam-to-carbon ratios (S/C) was due to sintering of nickel nano-particles rather than re-oxidation or sintering of bulk nickel and carbon formation. Time-on-stream analysis demonstrated a higher reforming activity for Ni–CZO cermet anodes compared to Ni–CGO cermet anodes. While the initial sizes of nickel nano-particles were similar (5–10 nm) for both cermet anodes, after the operation under steam-rich conditions (S/C = 1.5) the nickel nano-particles on Ni–CGO were found to be significantly larger (20–40 nm) than those on Ni–CZO (15–25 nm). Under steam-lean conditions (S/C = 0.5), the size of nickel nano-particles remained below 10 nm for both cermet anodes during the operations, indicating that the effect of sintering of Ni nano-particles on the performance was negligible. The reforming activity is still higher for Ni–CZO cermet anodes than Ni–CGO cermet anodes, which could be attributed to higher concentration of ex-solved nickel nano-particles as well as lower Ce⁴⁺/Ce³⁺ reduction energy of CZO than CGO support.

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1. Introduction

A solid oxide fuel cell (SOFC) is a device that converts the chemical energy of the gaseous fuels, such as hydrogen and natural gas, to electricity through electrochemical processes. SOFCs are considered as one of the most promising energy converters due to its high efficiency, design modularity and environmentally friendly nature [1–4]. Besides, one of the main advantages of SOFC over other fuel cell systems is the adaptability of the internal steam reforming of methane (ISRM), which could potentially increase the overall system efficiency, minimize reforming components and provide effective cooling [5]. Two major challenges in this area are: (i) suppressing carbon formation (ii) moderating the reforming rate to avoid large thermal gradients along the anode gas flow direction [6,7]. At higher operating temperatures and steam-to-carbon (S/C) ratios, the reforming reaction is very fast compared to the electrochemical oxidation of hydrogen [8], which could result in large temperature gradients during the fuel cell stack operations. This inhomogeneous temperature distribution could cause thermally induced stresses and possibly a mechanical failure of the material

[7]. To overcome this problem, the application of tailored anode catalysts which possess moderate steam reforming rate along with a high activity with respect to the electrochemical oxidation is essentially required [9].

Recently, for hydrocarbon fuels, Ni-based anode composites with various support materials such as doped-ceria and scandia-stabilized-zirconia have been extensively studied to understand the role of these support materials in controlling carbon deposition [10–12]. It is known that doped-ceria is an effective catalyst for steam reforming and the oxidation of hydrocarbons, and also enhances the anode performance by promoting charge-transfer reactions at the triple-phase boundary (TPB) due to its high mixed ionic-electronic conductivity and ability to suppress the carbon formation [13–19]. Among various doped-ceria materials, zirconia-doped ceria exhibits the improved thermal stability and compatibility with the electrolyte based on yttria stabilized zirconia [20]. Specifically, the presence of Zr⁴⁺ ions in the lattice improves both oxygen storage capacity (OSC) and conductivity of ceria [21], and also increases the adsorption capacity for H₂ and CO [22], which may increase the rate of electrochemical oxidation of these species. Ceria–zirconia solid solution has been also widely used as an “active support” in the heterogeneous catalysis [23]. The role of this support in high catalytic activity is strictly correlated to its superior OSC, i.e. the ability to act as an

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