Journal of Power Sources 246 (2014) 430–437

Contents lists available at ScienceDirect

Journal of Power Sources

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

Method for *in situ* carbon deposition measurement for solid oxide fuel cells

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HIGHLIGHTS

- A method for measuring carbon deposition in SOFC anodes *in situ* is developed.
- Only carbon deposits that have intimate contact with nickel can be gasified.
- >99.8 mass % of carbon with residence times up to 100 h can be gasified.
- Quantification of gasified carbon shows good agreement with TGA measurements.
- The observed effect of increased steam content is in agreement with the literature.

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form
17 July 2013
Accepted 27 July 2013
Available online 7 August 2013

Keywords:
Solid oxide fuel cell
Carbon deposition
Coking
Nickel
Steam
Quantification

ABSTRACT

Previous methods to measure carbon deposition in solid oxide fuel cell (SOFC) anodes do not permit simultaneous electrochemical measurements. Electrochemical measurements supplemented with carbon deposition quantities create the opportunity to further understand how carbon affects SOFC performance and electrochemical impedance spectra (EIS). In this work, a method for measuring carbon *in situ*, named here as the quantification of gasified carbon (QGC), was developed. TGA experiments showed that carbon with a 100 h residence time in the SOFC was >99.8% gasified. Comparison of carbon mass measurements between the TGA and QGC show good agreement. *In situ* measurements of carbon deposition in SOFCs at varying molar steam/carbon ratios were performed to further validate the QGC method, and suppression of carbon deposition with increasing steam concentration was observed, in agreement with previous studies. The technique can be used to investigate *in situ* carbon deposition and gasification behavior simultaneously with electrochemical measurements for a variety of fuels and operating conditions, such as determining conditions under which incipient carbon deposition is reversible.

1. Introduction

Solid oxide fuel cells (SOFC) are high temperature (550–1000 °C) electrochemical devices that generate combined heat and electricity with potential system efficiencies nearly double that of combustion based energy systems. SOFCs can consume relatively low cost and readily available fuels such as methane. Methane can be directly fed to the fuel cell together with steam in a process called direct internal reforming (DIR), which improves system efficiency and reduces system cost compared to externally reforming the fuel prior to its use in the fuel cell [1]. DIR is made possible by the fact that part of the SOFC anode is commonly composed of Ni, a material frequently used for industrial steam reforming and cracking catalysts [2].

Traditional yttria-stabilized-zirconia (Ni–YSZ) anodes are susceptible to coking when exposed to dry hydrocarbon fuels at SOFC operating temperatures. The formation of solid carbon is the result of an imbalance between competing formation and gasification reactions [3]. Atomic carbon (C_α) deposits originate from the dissociation of hydrocarbons and CO, which creates various morphologies of carbon that block pores and reactive sites [4], cause metal dusting [5,6], bulk expansion [7], and fracturing of electronic and ionic conducting pathways [8]. Carbon deposition can be suppressed by feeding large amounts (>60 vol%) of steam with the fuel. However, large steam concentrations reduce the Nernst potential, efficiency, and SOFC performance. External steam generators and associated water storage increase system cost and complexity, and prevent SOFCs from being well-suited for

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http://dx.doi.org/10.1016/j.jpowsour.2013.07.106

transportation and remote power applications. Therefore, it is useful to understand how Ni-based anodes perform under drier conditions.

A number of anode material sets have been developed to minimize or eliminate carbon deposition from directly feeding dry hydrocarbon fuels, including using precious metals such as Ru with Ni [9], scandia-stabilized-zirconia (ScSZ) instead of YSZ [10], infiltrated Cu and CeO_x [11], ceramic-based anodes [12], and nickel/gadolinia-doped-ceria (Ni–GDC) anodes [13]. However, many of these solutions use rare earth materials that have increased in price over recent years due to a reduction in Chinese export quotas [14]. BaO nanoislands on traditional Ni–YSZ anodes have been shown to promote water-mediated carbon removal reactions that create stable electrochemical performance in dry C_3H_8 for at least 100 h [15]. However, depositing a thin film of BaO on metal supported SOFCs is difficult due to the high temperatures required. Thus, in order to design a metal supported fuel cell with Ni-based anodes, an understanding of coking conditions is still important. Because operating conditions have a great influence on coking in SOFC anodes, a technique that can be used to quantify carbon deposition while operating the cells at various conditions is of great interest for aiding in the design of more robust anode compositions, microstructures, or operating regimes. The technique should be applicable to nickel-based anodes as well as to anodes that either contain decreased amounts of nickel or only alternative materials, and it can be used to determine the effectiveness and stability against coking of proposed new anode compositions or designs.

Tools commonly employed for carbon deposition studies include thermogravimetric analysis (TGA) [4,7,10,16], evolved gas analysis (EGA) [17–19], and Raman spectroscopy [20]. In TGA setups, it is difficult to provide two different gas streams and 4 electrodes to the anode and cathode while minimally disrupting the mass measurements, and Raman spectroscopy is limited to mapping regions in which carbon is prevalent, as opposed to quantification. However, EGA can be used to both quantify the total carbon and to characterize the morphology using temperature programmed oxidation (TPO) [8,21–24] or hydrogenation (TPH) [25].

Quantification of carbon *in situ* in SOFCs creates the opportunity to gain insight into the relationship between carbon deposits and resulting degradation of performance, electrochemical impedance changes, and anode morphological changes. TPO cannot be used for *in situ* quantification of carbon because nickel is oxidized in addition to the carbon, and oxidation of nickel causes another SOFC degradation mode known as redox cycling [26]. Additionally, thermal cycling that results from repeated TPO or TPH would also cause cell degradation. As a result, a new, less destructive method must be developed.

A specific form of EGA, defined here as the quantification of gasified carbon (QGC) method, involves feeding a carbon gasification agent at a fixed temperature and integrating the evolved carbon mass flow over the gasification period. Gasification occurs when a gasification agent is introduced via the reactions listed in Table 1.

Table 1
Carbon gasification reactions.

(1) $C(s) + O_2 \Rightarrow CO_2$
(2) $2C(s) + O_2 \Rightarrow 2CO$
(3) $C(s) + CO_2 \Rightarrow 2CO$
(4) $C(s) + 2H_2 \Rightarrow CH_4$
(5) $C(s) + H_2O \Rightarrow CO + H_2$
(6) $C(s) + 2H_2O \Rightarrow CO_2 + 2H_2$

First, different gasification agents were surveyed for their propensity to oxidize nickel and applicability to the QGC method using thermodynamic calculations and experiments. CO_2 and H_2 were then evaluated for their ability to completely gasify carbon with up to 100 h of residence time in the SOFC anode prior to gasification. Next, the accuracy of the QGC method was assessed using coupled TGAEGA. Finally, *in situ* carbon measurements on an SOFC at varying molar steam/carbon ratios (S/C) were determined and found to match well with trends reported in the literature, thus further verifying the QGC method.

2. Experimental procedure

Three sets of experiments were performed: chemical reversibility of deposited carbon after 100 h (TGA), validation of the QGC method (TGA–QGC), and *in situ* measurement of carbon deposition (QGC–SOFC test equipment). All thermogravimetric analyses were performed using a Setaram Setsys 1750 CS Evolution TGA. An external manual 3-way valve was installed on the auxiliary gas port so that H_2 could be used with either CH_4, C_2H_6, or CO. *Ex situ* masses were measured using a Mettler Toledo AB204-S/FACT digital balance. The concentration of CO was measured using a Thermo Scientific Model 48i Gas Filter Correlation CO Analyzer containing an internal volumetric flow meter. Flow rates and CO measurements from the CO analyzer were calibrated using a gas delivery system produced in-house and a 1% CO/balance N_2 gas bottle. The gas delivery system is part of a complete SOFC test apparatus also produced in-house. H_2 was generated using a Parker Balston H2-800NA electrolyzer, and all bottled gases were acquired from Linde Canada.

2.1. Choice of QGC gasification agent

The choice of a gasification agent for the QGC method was based on thermodynamic equilibrium calculations and on the practicality of measuring evolved carbonaceous species. Equilibrium calculations helped determine both the gasification temperature and the propensity for NiO formation from exposure to the gasification agent. Chemical equilibrium constants for carbon gasification reactions (Table 1) and NiO producing reactions (Table 2) were calculated using Matlab R2008b as a front-end for the publicly available NASA-CEA equilibrium solver [27]. C(gr) represents graphite, and C(s) represents all solid phase carbon.

In addition to the thermodynamic equilibrium calculations, the oxidation kinetics of carbon and nickel were evaluated to test the viability of O_2 as a QGC gasification agent. 90 mg of graphite powder and 39.8 mg of nickel powder were used in the TGA. Nickel powder was produced by pre-reducing NiO powder (Novamet) with a D50 size by volume of 16 μm in a tube furnace. The graphite powder used (Alfa Aesar) falls in a sieve fraction of 171–841 μm. The temperature in the TGA was ramped to 900 °C at 1 °C min^{-1} with an air flow rate of 200 sccm.

Table 2
Reactions that generate NiO.

(1) $Ni + CO_2 \Rightarrow NiO + CO$
(2) $2Ni + CO_2 \Rightarrow 2NiO + C(s)$
(3) $Ni + CO \Rightarrow NiO + C(s)$
(4) $2Ni + O_2 \Rightarrow 2NiO$
(5) $Ni + H_2O \Rightarrow NiO + H_2$