Co-generation of energy and ethylene in hydrocarbon fueled SOFCs with Cr_3C_2 and WC anode catalysts

Shao-Hua Cui[a,b], Jian-Hui Li[b,c], Jing-Li Luo[b,*], Karl T. Chuang[b], Li-Jie Qiao[a]

[a]Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China
[b]Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada, T6G 2G6
[c]National Engineering Laboratory for Green Chemical Productions of Alcohols–Ethers–Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Abstract

Electricity and ethylene were co-generated in proton-conducting solid oxide fuel cells using Cr_3C_2 and WC as dehydrogenation anode catalysts, $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY) as electrolyte, and $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) as cathode catalyst. Characterization was carried out using electrochemical method, X-ray diffraction (XRD), temperature-programmed reaction (TPR) and X-ray photoelectron spectroscopy (XPS) techniques. Tungsten carbide anode catalyst was identified to be unstable in hydrogen fuel, whereas, chromium carbide anode catalyst exhibited chemical and electrochemical stability in both hydrogen and ethane environments during the test at the operating temperatures from 650 °C to 750 °C. The power density and ethylene yield of the chromium carbide-based fuel cell increased significantly with the increasing operating temperatures.

1. Introduction

Ethylene is a major intermediate in petrochemical industry and is produced mostly by the conventional steam cracking of ethane at high temperature. However, this commercial process inevitably produces the undesired products that include the greenhouse gas and some significant pollutants [1]. Oxidative dehydrogenation of ethane has been explored as an alternative for converting ethane to ethylene in recent years. However, this method is unlikely to be feasible because ethane can easily be oxidized to CO_x, which results in the low selectivity of ethylene [2].

Solid oxide fuel cells (SOFCs) as the effective energy conversion systems have received extensive attention in the past two decades due to their process simplicity, fuel flexibility and potential for reducing the environmental impact [3]. To generate electricity with low cost and environmental friendliness, direct use of hydrocarbon fuels becomes a much more appealing approach for SOFC technology [4]. In our previous studies, ethane fueled proton-conducting SOFCs have been developed to co-produce ethylene and electricity with high efficiency and low emission of greenhouse gas and/or other pollutant gases [5,6]. A proton-conducting SOFC generates electricity through the dehydrogenation of ethane to ethylene and protons over the anode catalyst, while the protons are conducted through the proton-conducting electrolyte to the cathode side, and reacted with oxygen to produce water. During this process, electrons are conducted through an external circuit. The conventional Ni-based anode material is not suitable for the hydrocarbon fueled SOFCs due to its low redox stability and susceptibility to carbon deposition [7]. Noble metals, such as Pt and Ru, show high and stable activity for ethane dehydrogenation. However, they are expensive and can easily be poisoned by CO and carbon deposition under the fuel cell operating condition [8].

It is well known that transition metal carbides exhibit good catalytic activity in various chemical reactions with analogous

*Corresponding author. Tel.: +1 780 4922232; fax: +1 780 4922881.
E-mail address: jingli.luo@ualberta.ca (J.-L. Luo).

performance of noble metal catalysts [9–11]. In particular, the excellent catalytic and electrocatalytic properties of group VIB transition metal carbides (Cr, Mo, W) have received much more attention because of their potential application as alternative catalytic materials to replace the noble metals [12,13].

In an early study, we discovered that ethylene and electricity could be co-generated from ethane when molybdenum carbide was employed as the anode catalyst in a proton-conducting SOFC [14]. Following the previous work, the present study has investigated the ethane fueled protonic SOFCs using Cr_3C_2 and WC as anode catalyst, with $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) as the cathode catalyst, and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY) as the electrolyte for co-generation of ethylene and electricity. The electrochemical performance, catalytic activity and stability properties of the anode catalyst materials were also studied.

2. Experimental

2.1. Materials preparation

The anode catalysts, chromium carbide (Cr_3C_2) and tungsten carbide (WC), used in this study were obtained from Aldrich without any pre-treatments. The electrolyte material $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZY), and the cathode material $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) perovskite nanopowders were prepared using the citric acid–nitrate combustion method. The process can be exemplified by the preparation of BCZY powders. Stoichiometric amounts of Ba$(NO_3)_2$ (Alfa Aesar, 99%), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.5%), $ZrO(NO_3)_2 \cdot 6.6H_2O$ (Alfa Aesar, 99%) and $Y(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%) were first dissolved in deionized water as metal precursors. Then, citric acid (Alfa Aesar, 99.5%) as chelating agent and NH_4NO_3 (Aldrich, 99.5%) as oxidant agent were added at a molar ratio of citric acid:total metal ions:NH_4NO_3 of 1.5:1:3. The resulting solution was adjusted to about pH 8 with ammonium hydroxide (Acros, 28–30% NH_3 in water) and heated on a hot plate to evaporate solvent until brown foam was formed and then ignited. The as-combusted powder was calcined in air at 1000 °C for 6 h to obtain the desired BCZY powders and at 800 °C for 5 h to get the LSF powders. Detailed descriptions have been reported elsewhere [6].

2.2. Fuel cell fabrication and testing

Dense BCZY electrolyte pellets were fabricated via a pressing method and sintered in air at 1500 °C for 10 h. The thickness of the dense BCZY electrolyte was about 800 μm. Both anode and cathode were intimate mixtures of commercial WC, Cr_3C_2 and LSF with BCZY powders. The mixtures mentioned above were finely powdered in a planetary ball milling. The electrodes inks were prepared by mixing the powders with α-terpineol (Alfa Aesar): isopropanol = 2:1 as a solution containing 5 wt% poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, Mw = 70,000–100,000, Aldrich) and 5 wt% ethyl cellulose (Aldrich). Each electrode ink was screen printed onto the corresponding face of the electrolyte to form a membrane electrode assembly (MEA) with the thickness of 50 μm and the circular area of 1 cm^2, and then

presintered in 10% H_2–He atmosphere at 920 °C for 4 h to achieve strong bonding between the electrolyte and electrode materials. After the MEA was sintered, 1 cm^2 gold and platinum pastes were painted onto the sides of the anode and cathode, respectively, which were then sintered to form the current collectors.

The fuel cell reactor set up and testing system were described previously [15,16]. The MEA was placed between two coaxial alumina tubes to form the anode and cathode compartments. Before all single cell tests, the anodes were reduced in-situ in 10% H_2 balanced He (10% H_2–He, Praxair) at a rate of 100 mL min^{-1} as the temperature was increased from room temperature to 750 °C at 1 °C min^{-1}. The cathode side of each MEA was not sealed within a tube, and its compartment was supplied with air flow of 75 mL min^{-1}. Pure hydrogen (H_2, Praxair) and ethane (Praxair) were fed at a rate of 75 mL min^{-1} to the anode. The system was stabilized after each change of temperature and feed, before recording measurements.

Fuel cell tes was performed with standard DC and AC electrochemical techniques using a Solartron instrument (SI1287 EI). The polarization resistance of the cell was measured using electrochemical impedance spectroscopy (EIS) that was controlled by Zplot electrochemical impedance software over the frequency range from 1 MHz to 0.1 Hz at open circuit voltage (OCV) with 10 mV AC amplitude.

The outlet gases from the anode chamber were analyzed using a Hewlett-Packard model HP5890 gas chromatograph (GC) equipped with a packed bed column (packing: Porapak QS) operated at 80 °C by a thermal conductivity detector. The ethane conversion and ethylene selectivity were calculated according to the previously reported method [17,18].

2.3. Characterization of cells

A RIGAKU RU-200B Rotating anode X-ray diffraction (XRD) system with a Cu target was used to analyze the phase composition of all synthesized powders under a scan rate of 2° min^{-1}. The commercial software Jade® 5.0 was used to identify the phase structure. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical AXIS 165. A monochromatic Al Kα source ($h\nu$=1486.6 eV) was used at a power of 210 W, with a base pressure of 3×10^{-8} Pa in the analytical chamber. Spectra were referenced to the C 1s binding energy of 284.4 eV, and were fitted using Gaussian–Lorentzian peak shapes and Shirley baselines. H_2-TPR was performed on a flow apparatus using a 5% H_2/Ar mixture flowing at 20 mL min^{-1}. The heating rate was 10 °C min^{-1}. Hydrogen consumption was monitored by a TCD detector after removing the formed water.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows the XRD patterns of WC and Cr_3C_2 anode catalyst before and after the treatments in C_2H_6 at 750 °C for