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Performance and long-term stability of nickel/yttria-stabilized zirconia anode-supported solid oxide fuel cell in simulated biosyngas

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ABSTRACT

Here solid oxide fuel cells (SOFCs) technology and microwave-induced pyrolysis of sewage sludge (MWPSS) are combined to recover energy from waste by taking biosyngas as these medium. The biosyngas from the MWPSS with high concentration of H_2 and CO is a novel fuel alternative for SOFCs to generate electricity other than the counterparts from air gasification and anaerobic digestion of biomass. The maximum power densities of the nickel/yttria-stabilized zirconia (Ni/YSZ) anode-supported SOFC in simulated biosyngas are 0.324 and 0.485 W/cm^2 reaching up to 91.5 and 86.3% of the same cell in H_2 at 973 and 1023 K, respectively. The gradual degradation and following stability of the cell performance are observed from an 1100 h long-term operation at 1023 K. The postmortem characterization indicates that carbon deposition on the anode surface is greatly related to the degradation. Finally, the changed thermodynamic propensity of the simulated biosyngas is attributed to be responsible for the special long-term stability analyzed by anode process models and carbon-hydrogen-oxygen ternary diagram. In summary, the results indicate that the biosyngas from the MWPSS is feasible and applicable as the medium for energy recovery from the sewage sludge by SOFCs technology in high efficiency with appropriate gas cleaning systems.

1. Introduction

In recent years, the production of sewage sludge from both municipal and industrial wastewater treatment plants has been increasing significantly worldwide and the related application attracts ever-growing attentions and interests. As far as in China was concerned, the yields of sewage sludge (moisture content of 80 wt %) discharged from about 3000 waste water treatment plants have reached up to approximate 61.6 million tons in the single year of 2012 [1]. Because the sewage sludge usually contains toxic pollutants, pathogens and other microbiological pollutants (such as heavy metals, polychlorinated biphenyls and dioxins, etc.), the environmental safety and human health will be at stake if its disposal is inappropriate. As a matter of fact, tremendous capitals have been spent on its transportation, treatment, and final disposal in order to eliminate the potential hazard over environmental safety and human health, which accounted for a big part of the operation cost of a wastewater treatment facility. However, the current situation of sewage sludge treatment is still a big concern in most cities in China and needs to be taken seriously [2].

Conventionally, the sewage sludge is disposed by means of incineration, landfilling, ocean disposal or taken as soil conditioner in agriculture [3]. However, from the point of view of environmental protection, the sewage sludge treatment process needs to be sustainable, i.e. resource and energy in the sewage sludge ought to be recovered and utilized efficiently especially under the circumstances of global fossil fuel shortage. Lots of emerging methods have been proposed and adopted to recover the resource and energy from the sewage sludge in consideration of utilizing the organic compounds in the sludge [3,4]. Among them, treating the sewage sludge by pyrolysis is being taken as a potential promising solution owing to its advantages such as energy-saving and

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resource recoverable (such as bio-char, bio-tar and biosyngas) [5]. Electric furnace and microwave taken as the heat source are usually chosen to decompose the sewage sludge with different heating routines. Meanwhile, it has been verified that microwave pyrolysis is economically viable and highly efficient for the sludge pyrolysis [6,7]. With the assistance of microwave receptors, the microwave-induced pyrolysis of sewage sludge (MWPSS) has been investigated extensively by our group and many other researchers [8–10]. Generally, the current investigations are mainly devoted to the methods or processes of the MWPSS in their microwave reactor. While the utilization of the products generated from the MWPSS is rarely reported. In order to develop effective methods for the utilization of these pyrolysis products (especially for the biosyngas) and further promote the development of the MWPSS, we here proposed a combination of solid oxide fuel cells (SOFCs) technology and the MWPSS to generate electricity.

Biosyngas was reported as one on the main microwave-induced thermal decomposition products of the sewage sludge. Its yield including multiple components such as H_2, CO and a small amount of hydrocarbon gas, etc. could reach up to 0.4 L/g which accounted for about 40% of the sludge in mass [11]. Although combustible components in the biosyngas can be taken as the raw material for chemical feedstock, the purification and separation of gases would compromise its application. The direct utilization of the biosyngas in combustion engines is inhibited due to its low heating value as well as the contaminants in the outlet gas such as NO_x, SO_x and halide et al. [12]. Therefore, the application of the biosyngas in high efficiency is of importance with regard to the pyrolysis treatment of the sewage sludge. It is well known that directly converting the chemical energy into electricity by solid oxide fuel cells (SOFCs) is an intriguing and promising method, which are unlimited by Carnot cycle [13], can transform the chemical energy into electricity in high efficiency and with low emission at almost the same temperature as that for the MWPSS. Recently, there have been some reports of the SOFCs fed with simulated biosyngas or biosyngas from biomass (wood or sewage sludge) gasification [14–17]. They focused on the performance of the SOFCs and the evaluation of the adverse impacts (carbon deposition, sulfur poisoning and corrosion) on the anode due to impurities (tar, sulfur- and chlorine-containing compounds etc.) [18,19]. In addition, high efficiency was widely verified by either the integrated biomass gasification-SOFC systems or models of combined heat and power (CHP) system [20–22]. More importantly, successful operation of the SOFCs in hydrocarbons has stimulated great interests in utilization of carbonaceous gas as fuel [23]. Therefore, it is feasible and reasonable to integrate the MWPSS with the SOFCs technology to recover the energy from sewage sludge efficiently and environmentally friendly with the biosyngas as their medium.

In this paper, we proposed the combination of the SOFCs technology and the MWPSS in which the biosyngas was utilized as the medium. At first, the gas composition of the simulated biosyngas was set according to the characteristics of the biosyngas generated from the MWPSS. Secondly, we focused on the investigations on the electrochemical performance and long-term stability of the Ni/YSZ anode-supported SOFC with the biosyngas feeds. Finally, based on the postmortem characterization of the long-term tested cell, the possible reasons of two-stage power output were analyzed by anode process models and carbon-hydrogen-oxygen ternary diagram.

2. Experimental details

2.1. Biosyngas preparation and its composition analysis

In this investigation, the biosyngas was collected from the MWPSS. The sewage sludge for the MWP was derived from the filter press in sewage treatment plants located in Harbin, Heilongjiang China. The MWPSS was performed in a quartz tubular reactor which was placed inside a microwave cavity. The final pyrolysis temperatures were from 773 to 1073 K with interval of 100 K. Other details of the biosyngas producing procedures please refer to our previous papers [8,24]. The simulated biosyngas stored in a gas cylinder was purchased from a gas company (SHANGHAI YAOYI GAS CO., LTD). The primary compositions of the biosyngas were determined by the total ion chromatogram (TIC) peaks from Agilent gas chromatograph (6890GC)-mass spectrometer (5973MSD). The temperature program for the GC column (HP-PLOT MoleSieve 5A, 30.0 m × 320.00 μm × 12.00 μm) was that dwelling the sample at 308 K for 5 min and then elevating the temperature up to 573 K at the rate of 10 K/min followed by dwelling it for another 3 min. The total heating period was about 34.5 min. Both the carrier gas (He) velocity and the column flow rate were fixed on 1.0 mL/min and the interface temperature was 553 K. Concentrations of H_2, N_2, CH_4, NH_3 and HCN were identified by using the GC 9790II(ZheJiang, China) with two thermal conductivity detectors (TCDs) because the peak signal of these gases was lower than the background of TIC. Both GDX-301 and Porapack Q column were kept at 343 K. The temperature of TDCs was fixed at 393 K.

2.2. Single cell fabrication

The Ni/YSZ anode-supported SOFC was adopted and its electrolyte and anode were fabricated by tape casting with commercial NiO powders (mean diameter 0.67 μm, Qingdao, China) and YSZ powders (mean diameter 40 nm, E-type, TOSOH, Japan). For further details of the tape casting please refer to our previous paper [25]. The porous cathode layer (LSM/YSZ, Fuel cell materials, USA) with a mean diameter of 4.5 mm was obtained by screen printing and subsequent sintering at 1473 K for 2 h. The single cell components thickness profiles were 776 μm for Ni/YSZ anode, 32 μm for YSZ electrolyte and 19 μm for LSM/YSZ cathode, respectively. The porosity of the anode was determined by the Archimedes method [26].

2.3. Electrochemical test and characterization of SOFC

The schematic diagrams of experiment system and single cell are shown in Fig. 1. In this study, the electrochemical tests of the Ni/YSZ anode-supported cell in simulated biosyngas were performed after tests in H_2 with steady open circuit voltages (OCVs). The simulated biosyngas free from humidifier was directly fed to the single cell at the flow rate of 30°sccm (standard cubic centimeters per minute) the same as H_2 flow rate. The flow rates were controlled using air rotameter with a correction factor in terms of the physical properties of the simulated biosyngas. The cathode was exposed to the ambient air. The operating temperatures of the cell were fixed at 973 and 1023 K. The current–voltage curves were measured using an Arbin fuel cell testing system (S-Series FCTS, USA). A LK2100A (Tianjin, China) electrochemical system was employed for electrochemical impedance spectroscopy (EIS) measurement in the frequency range of 0.1 Hz–100 kHz with the applied amplitude of 10 mV under open circuit.

Temperature programmed oxidation (TPO) was used to evaluated the quantity of carbon deposited on the cell after the long-term operation. Oxidation of the carbon was conducted by flowing 50 mL/min of a mixed gas (10% O_2, argon gas as the balance) in an element analyzer (Vario EL cube, Germany) with a heating rate of 10 K/min from 298 to 1423 K. On the other hand, the weight of the carbon accumulated inside the alumina tube near the anode was obtained from the weight change of the test tube before and