



Mechanism of enhanced performance on a hybrid direct carbon fuel cell using sawdust biofuels

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HIGHLIGHTS

- The outstanding performance is obtained in sawdust biofuels.
- The power output of sieved sawdust is superior to that of pyrolyzed sawdust.
- The anode reaction mechanisms of sawdust are discussed.
- The mechanisms of catalytic effects of Li-K carbonate salts are modified.

ARTICLE INFO

Keywords:

Hybrid direct carbon fuel cell
Sieved and pyrolyzed sawdust
Electrochemical performance
Reaction mechanism

ABSTRACT

Biomass is expected to play a significant role in power generation in the near future. With the uprising of carbon fuel cells, hybrid direct carbon fuel cells (HDCFCs) show its intrinsic and incomparable advantages in the generation of clean energy with higher efficiency. In this study, two types of biomass treated by physical sieve and pyrolysis from raw sawdust are investigated on an anode-supported HDCFC. The structure and thermal analysis indicate that raw sawdust has well-formed cellulose I phase with very low ash. Electrochemical performance behaviors for sieved and pyrolyzed sawdust combined with various weight ratios of carbonate are compared in N₂ and CO₂ purge gas. The results show that the power output of sieved sawdust with 789 mWcm⁻² is superior to that of pyrolyzed sawdust in CO₂ flowing, as well as in N₂ flowing. The anode reaction mechanism for the discrepancy of two fuels is explained and the emphasis is also placed on the modified oxygen-reduction cycle mechanism of catalytic effects of Li₂CO₃ and K₂CO₃ salts in promoting cell performance.

1. Introduction

Along with the incredible development of the urbanization and industrialization, especially in China, the demand for fossil fuels including petroleum, natural gas and coal is increasing dramatically. The inevitable resource depletion is one of the driving forces for pursuing alternative energy sources. Biomass including food and non-food sources such as corn, wood chips, leaves and other organic waste is supposed to be an alternative renewable energy resource due to its low emission of NO_x and SO_x pollutants and readily availability [1,2]. Sawdust is a biomass, containing hemicellulose, cellulose, lignin and minor quantities of minerals. It is generated from wood manufacturing

process in large amounts every year as well as available from domestic and industrial refuse as well as agricultural residues. However, the utilization of sawdust is limited due to its low energy density and loose structure characteristics [3].

One of the most efficient ways to utilize sawdust are direct carbon fuel cells (DCFC), in which solid carbon energy is converted into electricity at 80% efficiency [4], higher efficiencies than most other conversion technologies. The molten carbonate and solid oxide electrolyte based DCFC prototypes have been extensively studied [5,6]. A recent design is the hybrid direct carbon fuel cell (HDCFC), which is a composite of a solid oxide fuel cell and molten carbonate fuel cell which gives higher power density by extending active reaction sites and

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limiting the cathode corrosion [7,8].

Several investigations into the effect of carbon types, anode microstructure, scaling up of geometric areas and electrochemical mechanisms on HDCFCs [9]. In initial development of the HDCFC concept proposed, Nabae [10] compared the specific surface areas of two carbon black materials (XC-72R and Super-S) on the cell performance. The best outputs from the Super-S carbon black fuels were 13.0 mWcm^{-2} at 900°C . This is followed by Jain et al. [11] demonstrating the scaling up the active area of YSZ electrolyte-supported cells to 4 cm^2 . The results also demonstrated that pyrolyzed medium density fibreboard (pMDF) was a promising fuel for HDCFC, achieving 50 mW cm^{-2} . Jiang et al. [12] further investigated the pMDF fuels on thin ($5 \mu\text{m}$) YSZ electrolyte which produced the highest power density of 878 mWcm^{-2} using lanthanum doped strontium cobalt (LSC) cathode. The excellent electrochemical performance was ascribed to lower ohmic and polarization resistance, less carbonate blocking at the gas/liquid/solid interfaces, faster gas diffusion and transportation, good cathode catalyst and flowing air at the cathode. Recently Elleuch et al. [13] showed the origin of CO , H_2 and CH_4 in the anode from complex chain chemical reactions of surface oxygen groups in olive wood charcoal and thus obtained a maximum power density of 105 mWcm^{-2} at 700°C . In recent research Hao et al. [14] evaluated magazine and newspaper waste papers carbon in HDCFCs. The cell fed with magazine waste paper carbon exhibited a higher performance with a peak power density of 172 mWcm^{-2} at 650°C . From these previous literature, biomass is supposed to be a promising fuel in hybrid DCFCs. Large amounts of organic groups in biomass at operating temperature emit fuel gas such as H_2 , CO and CH_4 , which is primarily contributed to the enhanced performance in DCFCs. However, the understanding of complex reaction in the anode compartment and mechanism of alkali metal carbonate catalytic effects lag behind the cell performance development.

In this study, sawdust selected as biofuels including sieved and pyrolyzed sawdust has been investigated in hybrid direct carbon fuel cells. Based on the structural and thermal characterizations of sieved sawdust and pyrolyzed sawdust, the comparative electrochemical performance with various mass ratios of carbon-carbonate mixture is optimized. Associated with off-gas evolution measured in flowing N_2 and CO_2 analyzed by gas chromatography, a deep insight into different reaction mechanisms is discussed to interpret the enhanced performance of two fuels. Furthermore, reasonable and modified mechanisms for catalytic properties of alkali metal carbonate in accelerating carbon gasification process in N_2 and CO_2 flowing are suggested.

2. Experimental

2.1. Preparation of sawdust fuels

The sawdust biomass used in this study was collected from wood processing workshop. To ensure the homogeneity of physical properties and reduce particle size, the raw sawdust was passed through 80 mesh sieve ($180 \mu\text{m}$). Then the sieved powders were pyrolyzed in tube furnace under flowing N_2 gas at 400°C for 2 h. The average yield of the pyrolyzed sawdust calculated over 5 batches was 30.4% as indicated in Table 1. The acquired carbon fuels including sieved and pyrolyzed

Table 1
Summarized results of sawdust pyrolysis.

Number	Sawdust/g	Pyrolyzed sawdust/g	Yield/%
1	1.72	0.50	29.07
2	2.37	0.72	30.38
3	3.27	0.98	29.97
4	5.97	1.81	30.32
5	6.64	2.15	32.38

sawdust mixed with different weight ratios of lithium-potassium carbonate eutectic ($62\text{mol}\%\text{Li}_2\text{CO}_3\text{-}38\text{mol}\%\text{K}_2\text{CO}_3$) were prepared as fuels for the cell performance test.

2.2. Characterization of sawdust fuels

The physicochemical properties of the sawdust are the key parameters to determine the cell performance. The X-ray diffraction patterns of the prepared samples were obtained by PANalytical X'Pert (Cu $\text{K}\alpha$ radiation). The morphology was examined via Scanning Electron Microscope (JSM-5600, Jeol). The thermal behaviors of carbon fuels evaluated by Thermo-gravimetric analysis (TGA) using a Thermo-gravimetric Analyzer (Netzsch-209). The TGA data was collected under N_2 or air atmosphere with a heating rate of 5°C min^{-1} from room temperature to 800°C .

During cell testing, the gas products were analyzed on an Agilent 3000 micro Gas Chromatograph equipped with two capillary columns and a backflush injector. The thermal conductivity detector (TCD) was calibrated by a standard gas mixture of H_2 , CH_4 , CO , CO_2 balance He, and also N_2 and air. All off-gas products were measured in the same condition.

2.3. Cell fabrication and performance test

$10 \times 10 \text{ cm}$ anode supported half-cells were prepared by tape casting to form a porous Ni/YSZ scaffold ($415 \mu\text{m}$) with black carbon as pore former, a Ni/YSZ active layer ($15 \mu\text{m}$) and a dense YSZ electrolyte ($17 \mu\text{m}$). These were laminated and co-sintered at 1400°C for 4 h in air. Then the obtained half-cells were laser cut into smaller 2.5 cm diameters button cells. A GDC interlayer ($2 \mu\text{m}$) was then coated onto the YSZ electrolyte by dip-coating and sintering at 1200°C for 2 h, to prevent reactions between the YSZ electrolyte and the GDC/LSCF composite cathode. The GDC/LSCF composite cathode ($25 \mu\text{m}$) and LSCF current collection layer ($25 \mu\text{m}$) was screen printed on the surface of the thin GDC interlayer with 1.1 cm in diameter, co-calcined at 1050°C for 4 h. The schematic diagram of HDCFC design and the SEM image of the cross-section of the anode-supported cell are shown in Fig. 1.

Before electrochemical measurements, silver paste was painted on each electrode surface as the current collector and the cells were sealed into the jig. During the heating operation the anode chamber was purged under N_2 at 10 ml min^{-1} as inert gas, while the cathode side was exposed to the ambient air. When the cell was ramping to the operating temperature (750°C), the flow rate was exchanged into 20 ml min^{-1} . The current density–voltage(I-V) curves were tested by an IM6 Electrochemical Workstation (ZAHNER, Germany) with four-probe configuration, described as previous work [8].

3. Results and discussion

3.1. Structural and thermal characterization

The XRD patterns of sieved and pyrolyzed sawdust are presented in Fig. 2. The pattern of sieved sawdust demonstrates characteristic wide reflections of the cellulose I crystalline phase [15]. The cellulose polymer is composed of ringed glucose units ($\text{C}_6\text{H}_{10}\text{O}_5$)_n, as indicated with the insert graph. No traces of crystalline mineral impurities were detected in sawdust. The broad diffraction peak (002) and another weak peak (001) in XRD pattern of pyrolyzed sawdust reveal that the amorphous carbon structure is formed after pyrolysis treatment at 400°C .

The thermal reactivity for various samples was investigated by thermogravimetric analysis (TGA) in this study, providing the simulation of pyrolysis of carbonaceous composition evolution during the heating segment, especially for sawdust pyrolysis *in situ* in HDCFCs, as shown in Fig. 3. The carbonate medium seems to be stable until the operating temperature (750°C) and the overall weight loss is about

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