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A facile method of preparing Fe-loaded activated carbon fuel for direct carbon solid oxide fuel cells

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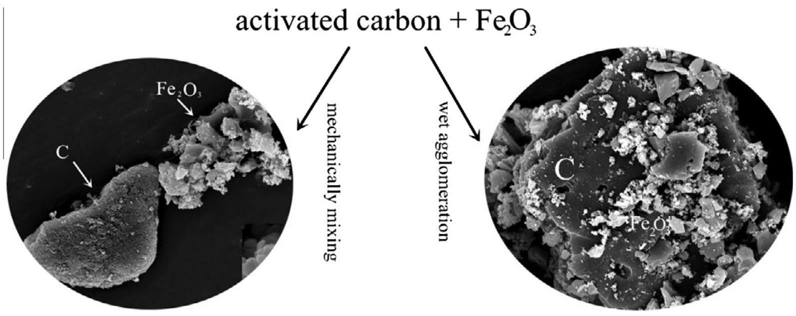
HIGHLIGHTS

- A wet agglomeration process is developed to make Fe-loaded carbon fuel for DC-SOFCs.
- The process improves the DC-SOFC output from 134 to 196 mW cm^{-2} at 850 °C.
- Carbon fuel prepared by agglomeration enables longer DC-SOFC discharging time.
- Agglomeration process is superior to others in cost, time, and environment.
- DC-SOFC with the agglomerated carbon gives high fuel utilization.

GRAPHICAL ABSTRACT



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ABSTRACT

A wet agglomeration process is developed for preparing Fe-loaded carbon fuel for direct carbon solid oxide fuel cells (DC-SOFCs). This technique involves a simple mechanical mixing of carbon and Fe_2O_3 powder, along with a proper amount of polyvinylbutyral (PVB) ethanol solution as binder. A DC-SOFC with carbon fuel prepared by this technique is tested and its performance is compared with DC-SOFCs, respectively operated with pure carbon, carbon mechanically mixed with Fe_2O_3, and carbon prepared with the conventional impregnation technique. Experimental results show that its output performance is comparable to that of the cell with carbon fuel prepared by the impregnation technique and is better than those of cells, respectively with pure carbon and carbon mechanically mixed with Fe oxide as the fuels. The microstructures of the variety of carbon, the impedance spectra of the corresponding DC-SOFCs are measured and the superiority of the wet agglomeration process in preparing the Fe-loaded carbon for DC-SOFCs is analyzed in detail.

1. Introduction

With the rapid development of the global economy, environment pollution and energy demand have become two major challenges for human beings [1]. As fossil fuels, especially coal in China, are and will still be the major energy sources in the foreseeable future, it is necessary to develop efficient and clean technology to conserve the resources and reduce pollutant emission [2]. Direct carbon fuel cell (DCFC) is an energy conversion device that can directly convert the chemical energy of carbon into electrical power, through electrochemical process, with high efficiency and low pollution [3]. Therefore, it is a promising technology of using coal cleanly and efficiently.

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Several kinds of electrolyte have been applied in DCFCs, such as molten hydroxide [4–7], molten carbonate [8–12], and solid oxide [13–18], among which, solid oxide electrolyte is the only solid state electrolyte that may avoid issues of high temperature liquid electrolyte such as leaking, corrosion, and degradation caused by CO_2 in the air. However, some liquid metals [13,19,20] or molten salts [15,16,21] have been filled into the anode chamber of solid oxide electrolyte DCFCs for carbon delivering. While such hybrid DCFCs may be robust and can be operated continuously with carbon provided along with flowing liquid metal or molten salt, they still have the problem of high temperature liquid. Gür et al. have developed a fluid bed solid oxide DCFCs, in which carbon or coal is provided into solid oxide fuel cells (SOFCs) with Ar or CO_2 as carrying gas [22–24]. In recent years, increasing attentions have been paid to the direct carbon solid oxide fuel cell (DC-SOFC), which is a SOFC operated directly on solid carbon fuel without any liquid medium or feeding gas [25,26]. It works through the coupling of the electrochemical oxidation of CO at the anode

$$CO + O^{2-} = CO_2 + 2e^- \tag{1}$$

and the Boudouard reaction at the carbon fuel

$$CO_2 + C = 2CO \tag{2}$$

This mechanism of DC-SOFCs has been verified by Xie et al. [27]. Because the configuration of a DC-SOFC is simple and the energy density of carbon is high, DC-SOFCs have been recommended as a potential high performance battery [28,29].

Loading catalyst that can promote the Boudouard reaction, on the carbon fuel, can significantly improve the performance of a DC-SOFC [14,26,30]. One of the efficient catalysts is iron. With activated carbon loaded with 5 wt.% Fe as fuel, a Ni–YSZ anode-supported DC-SOFC stack has given an output power density of 460 mW cm^{-2} at 850 °C [28].

The conventional way to load catalyst on activated carbon fuel for DC-SOFCs is impregnation [26,28,31], in which iron nitrate solution is mixed with activated carbon powder followed by drying at 80 °C and heat treating with flowing Ar at 700 °C. This method is complicated (3 steps), costly, and with NO_x pollution. To promote the widespread application of DC-SOFCs, it is necessary to develop some clean and low-cost techniques for preparing catalyst loaded carbon fuel.

In this paper, we report a facile, economic and environment-friendly method for preparing Fe-loaded carbon fuel for DC-SOFCs, with which it is easy to realize large-scale industrial production. The method involves a simple wet agglomeration process, i.e., mechanically mixing activated carbon, iron oxide powder, along with a proper amount of binder. The performance of a DC-SOFC operated with the carbon fuel prepared by this method is compared with those of the DC-SOFCs with carbon fuels prepared by some other techniques. The microstructures of the carbons and the output performance, impedance spectra, discharging characteristics and fuel utilization of the corresponding DC-SOFCs are examined and analyzed in detail.

2. Experimental

2.1. Fabrication of SOFCs

Solid oxide fuel cells with a configuration of Ag–GDC/YSZ/Ag–GDC (GDC: gadolinium doped ceria, $Ce_{0.9}Gd_{0.1}O_{2-\delta}$, Ningbo Institute of Materials Technology & Engineering, China; YSZ: yttria stabilized zirconia, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, Tosoh Corporation, Japan) were fabricated as follows: First, YSZ powder was pressed into pellets (each of 0.6 g in weight and 20 mm in diameter), followed by sintered at 1400 °C in air for 4 h to densify the pellets (each of 0.5 mm thick and 1.6 mm in diameter). A Ag–GDC (weight ratio of 70:30) slurry was prepared by mixing GDC powder (purity $\geqslant$ 99.5%, particle size d50: 0.5–3 μm) and silver paste (DAD-87, with 70 wt.% Ag, Shanghai Research Institute of Synthetic Resins, Shanghai, China) through grinding in an agate mortar until the slurry was uniform [32]. The Ag–GDC slurry was painted respectively on both sides of the YSZ pellets, followed by drying in an oven and annealing at 880 °C in air for 4 h. The cathode area of all the cells was controlled to be the same of 0.9 cm^2. Ag paste was used to paint grids on both of the anode and cathode for current collection.

2.2. Preparation of carbon fuel

Activated carbon (Activated Charcoal, 8–16 mesh, Aladdin) was crushed into carbon powder by an electric grinder, and then sieved through a sieve (77 mesh) to get granules under 0.212 mm in diameter. Four kinds of carbon fuel were prepared (Table 1). The first kind, denoted as C-1, was pure activated carbon. The second kind, C-2, was activated carbon mechanically mixed with commercial Fe_2O_3 (A.R., Tianjin Kemiou Chemical Reagent Co., China). 0.5 g of the carbon and 0.036 g of the Fe_2O_3 were mixed and the mixture was ground in an agate mortar for 5 min. The third kind, C-3, was prepared by the so-called wet agglomeration process [33]. Similar to the process for preparing C-2, 0.5 g activated carbon was mixed with 0.036 g Fe_2O_3. Then 0.5 mL PVB ethanol solution (concentration: 6 wt.%) was added into the mixed powder drop by drop under grinding until it became agglomerated and homogeneous. Afterward, it was dried under an infrared lamp for 0.5 h. For the fourth kind, denoted as C-4, Fe catalyst was loaded on carbon by the conventional infiltration technique [28,31]: Carbon powder was immerged into $Fe(NO_3)_3$ solution under stirring and let stand overnight so that carbon powder could adsorb Fe^{3+}, followed by heating at 90 °C until the water of the mixture was evaporated. Then the residue was heat-treated at 700 °C for 60 min under Ar atmosphere to decompose the nitrate. The mass ratio of C:Fe of all the four kinds of fuel was controlled to be the same, 95%:5%.

2.3. Cell assembling and characterization

Ceramic adhesives (High temperature ceramic adhesives & pastes, P/N 552, Aremco Products, INC., USA) was used as sealing and jointing materials to connect each of the single cell pellets to

Table 1
Activated carbon fuels prepared by different techniques and the performances of the corresponding DC-SOFCs operated on these fuels.

Preparing technique	C-1 Pure	C-2 Mechanically mixed with Fe_2O_3	C-3 Wet agglomeration	C-4 Conventional impregnation
OCV at 850 °C/V	0.88	0.89	0.96	0.98
MPD at 850 °C/mW cm^{-2}	132	140	196	212
Discharging current at 0.7 V/A	0.10	0.12	0.20	0.22
Discharging time/h	12.4	10.9	10.3	5.7
Fuel utilization/%	28	29	46	28