



Research paper

The usefulness of walnut shells as waste biomass fuels in direct carbon solid oxide fuel cells

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ABSTRACT

Raw and charred walnut shells were investigated as solid fuels in direct carbon solid fuel cells operating within the temperature range 600–850 °C. Char was prepared by means of thermal processing of pulverised shells in a quartz reactor within a temperature range of 400–850 °C. Elemental analysis identified high carbon and marginally low sulphur contents in char obtained from biomass-derived solid waste. With increased temperatures, a greater degree of carbonisation of raw material was observed in the char, along with reduced sulphur and hydrogen contents. XRD and Raman spectroscopy investigations showed that the char samples were characterised by a disordered carbon structure. The particles were characterised by the presence of smaller isometric particles as well as a porous structure. Thermogravimetric analysis performed in a pure CO₂ gas atmosphere within a temperature range of 25–850 °C demonstrated a substantial loss of mass due to CO production via the Boudouard reaction. Tests showed that DC-SOFCs supplied by char obtained from walnut shells were characterised by stable operation with reasonably satisfactory levels of current and power density. A significant improvement was noted in the performance of a DC-SOFC supplied by all forms of char when CO₂, as opposed to N₂, was used as the shielding gas in the anode chamber.

1. Introduction

The increased demand for efficient and environmentally friendly energy systems and the direct conversion of gaseous fuels into electricity by fuel cells have received tremendous attention during the past decades. A recent classification distinguished five basic types of hydrogen-oxygen fuel cells: polymer electrolyte, alkaline, phosphoric acid, molten carbonate, and solid oxide (SOFCs) [1]. High-temperature SOFCs constructed mainly from ceramic materials have been the object of particular interest due to their flexibility in terms of fuel, their high level of efficiency, and high quality of exhaust heat [2–4]. Carbon-based fuels can also be used to supply SOFCs, both directly and indirectly. In this case, coal is gasified, and the resulting syngas, containing mainly H₂ and CO, is subjected to further processing, becoming enriched with additional amounts of H₂ as a result of the reaction

between water vapour and CO.

A direct carbon solid oxide fuel cell is an electrochemical device which directly converts the chemical energy of solid fuel into electricity and heat. In the case of DC-SOFCs, carbon can be directly electrochemically oxidised to:



as well as formed in a sequence of electrochemical reactions (2) and (3) as follows:



The Boudouard reaction, $\text{C} + \text{CO}_2 \rightarrow \text{CO}$ (4), involving CO₂ and C as reactants, is an additional source of the CO consumed in reaction (3).

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The complex course of reactions (1–3) may constitute a potential asset for this fuel cell, as it enables a choice of various design options leading to optimisation of its performance. It should be stressed that DC-SOFCs, like hydrogen-oxygen SOFCs, can be designed in planar or tubular geometry [5–8]. In addition, a DC-SOFC can operate using either a solid or a fluidised coal bed [9]. Some authors have demonstrated the potential for the use of various carbonaceous waste materials as fuels in solid oxide fuel cells; for example, waste coffee grains, corncobs, wheat, and coconuts can be used as solid fuels in DC-SOFCs to produce electricity. These authors obtained promising typical values of power output P_{\max} (60–150 mW/cm²) within the temperature range 800–900 °C [10–16]. Certain potential directions have been identified for the continued development of solid oxide fuel cells supplied by carbon-based fuels originating from biomass waste products. One strategy is focused on the application of new electrode materials (cathodes and anodes) and electrolytes better suited to work with direct carbon fuels. Li, Wei, et al. [17] demonstrated the potential for increased power output P_{\max} through the application of new anode materials such as La_{0.8}Sr_{0.2}Fe_{0.9}Nb_{0.1}O_{3-δ} and a modified layered ceramic electrolyte, SDC|SCSZ, obtaining power from a DC-SOFC within a range of 200–300 mW/cm². Some authors have indicated the considerable impact of a reverse Boudouard reaction in DC-SOFCs utilising biochar.

Cai [18] found that orchid-leaf char is a suitable fuel for all solid state DC-SOFCs. This type of biochar is very active in terms of the reverse Boudouard reaction, i.e. reaction (4), of which CO is an intermediate product. The activation polarisation of an anode reaction involving the oxidation of gaseous CO is lower than that of a reaction involving the oxidation of carbon particles. It was found that the porous structure of leaf char and the presence therein of biologically accumulated and uniformly distributed elements such as Ca, K, and Mg improve the gasification process in this kind of solid fuel. This finding was confirmed in electrochemical comparative tests of DC-SOFCs in which biochar from orchid leaves and charcoal modified by calcium were used as solid fuels. Higher levels of power output P_{\max} were obtained from a DC-SOFC when biochar was used as fuel.

Cai and Liu [19] confirmed the promising performance of DC-SOFCs operating on wheat straw char, which is renewable and economical. N. Jafri [20], in a review paper, analysed the impact of general physicochemical properties of solid fuels such as proximate and ultimate analysis parameters, heating values and surface areas of solid fuels, H/C and O/C atomic ratios, and disordered vs ordered carbon particles. These properties are important in the process of pyrolysis of waste biomass as well as for its performance as solid fuel in different types of direct carbon fuel cells. It is difficult to determine which type of direct fuel cells operating within different temperature ranges (alkaline 200–400 °C, molten carbonate 500–750 °C, solid oxide fuel cells 700–900 °C; the electrochemical performance of the last-named type possesses some specific unique features of its own) is closest to the point of practical application in various power systems [21].

Irrespective of these promising results, which clearly show the potential of waste biomass in sustainable electricity generation in fuel cells, it is necessary to understand the relationship between the chemical composition, structure, and physicochemical properties of this kind of biomass and its performance in direct carbon solid fuel cells.

The aim of this paper was to determine the impact of the physicochemical properties of walnut shells on their electrochemical reactivity in DC-SOFCs.

2. Experimental

2.1. Preparation of raw samples and char

Walnut shells were selected for investigation as potential solid fuel for DC-SOFCs. Two kinds of samples were investigated: raw ground powders and char obtained from previously ground samples. In the first

stage of the experiments, the shells were first coarsely ground and subsequently subjected to thorough grinding in a coffee mill. A portion of these materials was processed for further analytical and electrochemical investigations. In the second stage, char was prepared from ground raw powders. The char applied as solid fuel was obtained by means of the thermal processing of pulverised shells in a quartz reactor at 400 to 850 °C for over 1 h in an argon atmosphere. Following carbonisation, all samples were ground in a mortar.

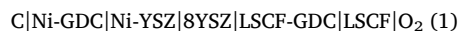
2.2. Analytical methods of carbon evaluation

The raw ground waste biomass samples and the obtained char were subjected to elementary and technical analysis. Proximate analysis (C, H, S) was carried out with an ELTRA CHS-580 analyser. Technical analysis included the determination of levels of moisture, ash, and volatile compounds. The phase compositions of the carbon samples thus obtained were evaluated using X-ray diffraction analysis (XRD) with reference to the ICDD database. Raman studies were carried out using a Horiba Jobin Yvon LabRAM HR micro Raman spectrometer equipped with a CCD detector. An excitation wavelength of 532 nm was used, with a beam intensity of approximately 10 mW. Acquisition time was set at 30 s. Scanning electron microscopy (Nova NanoSEM 200 FEI, Netherlands) coupled with an EDS system (EDAX, Netherlands) was used to characterise the morphology and chemical composition of carbon particles used as solid fuels. The measurements and observations were conducted in low vacuum conditions (60 Pa) with a secondary electron detector (LVD); the accelerated voltage was 10–18 kV. The chemical composition of the investigated samples was determined using standardless analytical algorithms; the element concentrations were normalised to 100%. Thermal effects occurring during heating of the solid carbon fuel within the temperature range 25–1000 °C in argon gas flow were measured using the DTA/DSC and TG methods (SDT 2960, TA Instruments). The samples (ca 50 mg) were ramped up at a rate of 10 K/min in an alumina crucible. Analysis of solid fuel mass losses (thermogravimetry analysis) was also performed in a CO₂ gas atmosphere, using a DynTHERM HP-ST (Rubotherm) apparatus.

H₂-TPR studies were carried out on a ChemBET 3000 analyser (Quantochrome). Hydrogen consumption was monitored with a TCD detector. For a typical run, the sample (25 mg) was placed in a quartz U-shaped tube reactor and conditioned at 100 °C under He flow (30 ml/min) for 1.5 h. Next, the sample was cooled to room temperature (RT) under He flow and an H₂-TPR experiment was performed in 5 %H₂/Ar (30 mL/min) within the temperature range RT–750 °C (ΔT = 10 °C/min).

2.3. Electrochemical oxidation of solid fuels in electrolyte-supported button solid oxide fuel cells

The electrochemical oxidation of carbon particles was studied in button solid oxide fuel cells which varied only in terms of cathode materials:



For the purpose of this experiment, 8YSZ denotes an electrolyte of 8 mol% Y₂O₃ in ZrO₂ in the form of ceramic tape with an approximate thickness of 160 μm. LSCF and LSM are monophasic La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ and La_{0.8}Sr_{0.2}MnO₃ cathode materials, respectively. LSCF-GDC is a composite cathode material composed of LSCF and 5 mol% Gd₂O₃ in CeO₂ (10GDC) with a weight ratio of 1:1. LSM-GDC is also a composite cathode material composed of LSM and 5 mol% Gd₂O₃ in CeO₂ (GDC) with a weight ratio of 1:1. All cathode layers were fabricated using the screen printing method. Ni-GDC and Ni-YSZ are cermet anodes consisting of 50 vol% of Ni distributed in an 8YSZ or GDC matrix. The geometric area of the surfaces of the active electrode

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