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Evaluation of waste paper as a source of carbon fuel for hybrid direct carbon fuel cells

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ABSTRACT

Magazines and newspapers, as two kinds of municipal solid waste, were investigated as the fuel feedstock in a hybrid direct carbon fuel cell. These carbon sources, together with a reference carbon source-activated charcoal, were characterized by such techniques as X-ray diffraction spectra, X-ray photoelectron spectroscopy, and thermal gravimetric analysis, among others. The results indicate that the carbon from magazine waste paper was more abundant in calcite and magnesium calcite, with more oxidation degree of carbon and higher thermal reactivity, compared with the other two carbon sources. Then, the cell performance fed with such carbon sources was tested in a homemade device. The cell fed with magazine waste paper carbon showed the highest performance among the three carbon sources, with a peak power density of 172 mW/cm^2 at 650 °C. The cell performance results indicated that waste paper carbon sources, with a surface containing certain inherent impurities (calcite and magnesium calcite) and a high oxidation degree of carbon, could favor the thermal gasification of carbon fuel, and thus considerably enhance cell performance, especially for the operating temperatures below 700 °C. This study demonstrated that waste paper carbon sources could be promising fuel feedstock for hybrid direct carbon fuel cells.

1. Introduction

DCFCs (Direct carbon fuel cells) have been regarded as a desirable technology for power generation in the consumption of solid carbon fuels, such as coal [1,2]. The overall reaction in a DCFC is quite simple, as shown in Eq. (1):

$$C + O_2 = CO_2 \tag{1}$$

So far, many types of DCFCs have been developed, of which, hybrid DCFCs have inspired researchers to conduct intensive studies [3,4]. In a hybrid DCFC, oxygen is reduced in the cathodic reaction, as shown in Eq. (2):

$$O_2 + 4e^- = 2O^{2-} \tag{2}$$

The mechanism of the anodic reaction in a hybrid DCFC is quite complex, due to the media of molten carbonate. The possible reaction paths are shown in Eqs. (3)–(6) [1,3]:

$$C + 2O^{2-} = CO_2 + 4e^- \tag{3}$$

$$C + O^{2-} = CO + 2e^- \tag{4}$$

$$C + 2CO_3^{2-} = 3CO_2 + 4e^- \tag{5}$$

$$C + CO_3^{2-} = CO + CO_2 + 2e^- \tag{6}$$

The generated CO can be further oxidized via Eqs. (7) and (8):

$$CO + O^{2-} = CO_2 + 2e^- \tag{7}$$

$$CO + CO_3^{2-} = 2CO_2 + 2e^- \tag{8}$$

The CO_3^{2-} ion can be regenerated via Eq. (9), to keep the electric charge of molten carbonate neutral [5]:

$$CO_2 + O^{2-} = CO_3^{2-} \tag{9}$$

The rate of the overall reaction in a hybrid DCFC is controlled by the anodic reaction, which is the carbon electro-oxidation, as shown in Eqs. (3)–(8) [6]. In addition, the activation of the carbon fuel dominates the carbon electro-oxidation [7,8]. Therefore, the

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Nomenclature

AC	activated charcoal
AC-imp	alternative current impedance
ac_r	atomic concentration of element r
ac %	atomic concentration
$CO_{0.5x}$	oxidation degree of carbon
DCFCs	direct carbon fuel cells
DC-SOFCs	direct carbon-solid oxide fuel cells
DTG	derivation profiles of TGA
EIS	electrochemical impedance spectroscopy
I–V	current–voltage
MCD	maximum current density
MDF	medium density fiberboard
MPC	magazine paper carbon
MSW	municipal solid waste
NC	newspaper carbon
OCP-t	open circuit potential-time
OCV	open circuit voltage
PPD	peak power density
Q	constant phase element
R1	ohmic resistance
R2	activation polarization resistance
R3	concentration polarization resistance
SDC	Samaria doped Ceria

Greek symbols

θ	diffraction angle (°)

performance of hybrid DCFCs could be enhanced by improving the activation of the carbon fuel through promoting the carbon electro-oxidation in the anodic reaction. Many approaches, including the exploration of new carbon sources as fuel, have been used to activate the carbon fuel in hybrid DCFCs. For instance, Irvine et al. utilized the processed MDF (medium density fiberboard) as fuel for hybrid DCFCs, Zhu et al. studied the effect of particle size on the activation of the carbon fuel for hybrid DCFCs [7,9]. Moreover, Konsolakis et al. studied the thermal-produced biochars as carbon fuels and Zondlo et al. investigated the pretreated biomass as fuel sources for hybrid DCFCs [10,11]. In addition, the carbon fuel modifications were reported by Deleebeeck et al., who enhanced the performance of hybrid DCFCs via adding Ag_2O in the carbon/carbonates slurry and Jian et al. employed liquid antimony anode to study the refueling DCFCs [12,13]. To activate the carbon fuel, the aforementioned DCFCs were operated at high temperatures (over 700 °C), which consume large amount of heat energy and propose strict requirements to the cell facilities [14–16]. While the carbon sources as active carbon fuels for DCFCs operating at low temperatures (below 700 °C) were rarely reported. Therefore, the exploration of promising fuel feedstock for DCFCs operating at temperatures below 700 °C remains as an issue to be solved.

MSW (Municipal solid waste), as a significant feedstock of biomass fuel, possesses truly high potential as the fuel feedstock for DCFCs due to its easy availability, low cost, and high energy content (19,800 kJ/kg), especially for the MSW after pyrolysis or compaction [17]. The energy content of pyrolyzed MSW is competitive to that of coals (30,200 kJ/kg) [6,17]. Waste paper, in terms of weight, accounts for nearly half composition of the MSW, and possesses the abovementioned properties of MSW. It is highly expected that waste paper would be suitable feedstock for DCFCs. Therefore, it is well worthy to study the feasibility of waste paper as a fuel feedstock for DCFCs.

In this work, we report an evaluation study of waste paper as a source of carbon fuel for hybrid DCFCs. The evaluation of cell performance was focused at operating temperatures below 700 °C and compared with the recent literature reports. Two kinds of waste paper sources from MSW – outdated magazines and newspapers – were used to prepare the carbon fuels via the pyrolysis process. The prepared carbon fuels were investigated in a hybrid direct carbon fuel cell with SDC (Samaria doped Ceria) electrolyte. Activated charcoal, a nearly pure carbon source, was also tested as carbon fuel for comparison. The study has demonstrated that the waste paper carbon fuel considerably enhanced cell performance at temperatures below 700 °C. The result suggested that waste paper from MSW could be promising fuel feedstock for hybrid DCFCs operating at temperatures below 700 °C.

2. Experimental

Two feedstocks of waste paper carbons were used in this study, namely outdated magazines and newspapers. The MPC (magazine paper carbon) and the NC (newspaper carbon), obtained from the pyrolysis of the aforementioned feedstocks, were used as the anode fuel for study. A nearly pure carbon source-AC (activated charcoal) was chosen as the reference carbon source.

2.1. *Preparation of waste paper carbon fuels*

The waste paper carbons were prepared by the pyrolysis of the feedstocks. Two types of pyrolysis were used in this study - direct pyrolysis and carbonate-wetting pyrolysis [9]. Direct pyrolysis was conducted to prepare the waste paper carbons, while carbonate-wetting pyrolysis was conducted to prepare the carbon fuels in the cell performance test.

2.1.1. *Direct pyrolysis*

The outdated magazines were crushed into small pieces, and then put into a tube furnace for pyrolysis [18]. In each batch, ~4 g magazine papers were first dried at 100 °C for 3 h, and further decomposed in an environment of pure N_2 at 650 °C for 10 h to produce the MPC. The same processes were applied to generate the NC. The acquired waste paper carbons were dried at 80 °C in an oven and weighed before characterization. Direct pyrolysis was conducted on five batches for each feedstock, the carbon yields from which were investigated. The results of the carbon yields of each feedstock are listed in Table 1. It can be calculated from the table that the average yield of the MPC and NC was 31.37% and 30.66%, respectively.

Table 1
The results of the carbon yields of the outdated magazines and newspapers after direct pyrolysis.

Item	Magazine/g	MPC/g	Yield/%	Newspaper/g	NC/g	Yield/%
1	3.6017	1.1183	31.05	3.8091	1.1446	30.05
2	3.7704	1.1997	31.82	3.7882	1.1808	31.17
3	4.0021	1.3211	33.01	4.3016	1.3163	30.60
4	4.0936	1.2629	30.85	4.1785	1.2715	30.43
5	3.9798	1.2003	30.16	4.0539	1.2587	31.05