Journal of Power Sources 186 (2009) 1–9

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Surface modification of carbon fuels for direct carbon fuel cells

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ARTICLE INFO

Article history:
Received 5 June 2008
Received in revised form
10 September 2008
Accepted 11 September 2008
Available online 27 September 2008

Keywords:
Carbon
Direct carbon fuel cell
Surface treatment
Electrochemical reactivity
Pre-treatment
Oxygen functional groups

ABSTRACT

The direct carbon fuel cell (DCFC) is a promising power-generation device that has much higher efficiency (80%) and less emissions than conventional coal-fired power plants. Two commercial carbons (activated carbon and carbon black) pre-treated with HNO_3, HCl or air plasma are tested in a DCFC. The correlation between the surface properties and electrochemical performance of the carbon fuels is explored. The HNO_3-treated carbon fuels have the highest electrochemical reactivity in the DCFC due to the largest degree of surface oxygen functional groups. The overall effect on changing the electrochemical reactivity of carbon fuels is in the order HNO_3 > air plasma ≈ HCl. Product gas analysis indicates that complete oxidation of carbon to CO_2 can be achieved at 600–700 °C.

1. Introduction

The direct carbon fuel cell (DCFC), the only fuel cell capable of converting solid carbon into electricity without a reformation process, is gaining increasing attention due to its high conversion efficiency with low pollution. Solid carbon fuels used in the DCFC can be produced easily from various sources that include coal, petroleum, natural gas and even biomass. Compared with other hydrogen-based fuel cells, the DCFC has the significant thermodynamic advantage of a near-zero entropy change at high temperature, i.e., the theoretical electrochemical efficiency of the DCFC ($\Delta G/\Delta H$) is almost 100% [1–7]. Even under practical conditions, about 80% efficiency can be reached in the DCFC system. The activities (chemical potentials) of both reactant carbon and the product carbon dioxide are fixed, and this results in a stable carbon anode potential during practical cell operation [2,3]. Finally, the DCFC has lower emissions compared with conventional power plants. In principle, the off-gas can be pure carbon dioxide, which can be directly collected for industrial use [1] or committed to storage.

Various electrolytes such as molten carbonates [2,3,8–13], molten hydroxides [7,14–17] and yttria-stabilised zirconia (YSZ)-based solid electrolytes [18,19] have been used in DCFCs. The latest development in DCFC technology is to utilize highly reactive carbon particulates dispersed in a molten carbonate electrolyte, which flows between the anode and cathode at high temperature [2,3,9,11,12]. The anode and cathode reactions may be expressed by Eqs. (1) and (2), respectively. The overall reaction and anode potential are given by Eqs. (3) and (4), respectively [2,12].

$$\text{Anodereaction}: C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^- \quad (1)$$

$$\text{Cathodereaction}: O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-} \quad (2)$$

$$\text{Overallreaction}: C + O_2 \rightarrow CO_2 \quad (3)$$

where the anode potential is given by

$$E_{\text{anode}} = E^{\circ} - (RT/4F)\ln[P^3_{CO_2}(w)] + (RT/4F)\ln[P^2_{CO_2}(r)P_{O_2}(r)] \quad (4)$$

and E° is the anode potential at standard conditions, R is the universal gas constant, T is the cell temperature, $P_{CO_2}(w)$ is the CO_2 partial pressure at the working electrode, while $P_{CO_2}(r)$ and $P_{O_2}(r)$ are the partial pressures of CO_2 and O_2 at the reference electrode, respectively.

Various carbon fuels have been tested in different DCFC apparatus to investigate the efficacy of carbon fuels in the anodic reaction. It has been found that disordered carbon is more reactive due to the existence of more edge sites and defects, and graphitic carbon with high electrical conductivity may also benefit the electrochemical reaction. The physical and chemical properties of carbon fuels

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doi:10.1016/j.jpowsour.2008.09.070

can thus influence their electrochemical performance. Weaver et al. [13] observed that carbon fuels with high surface area, such as devolatilized coal, are more accessible to the anode reaction, whereas Cooper's group [2,3] concluded that the effect of carbon surface area on discharge rate is not strong. Consequently, ways of improving the electrochemical reactivity of carbon fuels in the anode [i.e., reaction given by Eq. (1)] is still a major obstacle to the application of the DCFC.

Carbon materials are widely used in fuel cells as electrodes, electrocatalyst supports and hydrogen materials [20]. It is well known that the kinetics of the electrochemical processes involving carbon depend strongly on the surface characteristics of the carbons used. Surface treatments, including acid, heat, laser, plasma and electrochemical treatment, are usually applied to the carbon materials in order to enhance their electrochemical reactivity [21]. To our knowledge, no published study has been conducted on the relationship between the surface modification of carbon fuels and their electrochemical performances in a DCFC (rather than carbon electrodes). Thus, it was deemed appropriate to conduct a comparative investigation of the DCFC performance of two commercial carbon fuels including one activated carbon (AC) and one carbon black (CB) with different surface treatments employing HNO_3, HCl and plasma treatments. The electrochemical reactivities of these carbon fuels in the DCFC were systematically analysed, and correlated with physical and chemical characterization data on the surface chemistry and physics of the fuels.

2. Experimental

2.1. Preparation of carbon fuels

A commercial granular activated carbon (Calgon BPL, 0.25–0.45 mm particle size) and a carbon black sample (Koppers Continex N220, 0.1–0.2 mm particle size) were selected as the starting samples, which were designated as AC and CB, respectively. The acid treatment of AC and CB was by immersion in 4 M HNO_3 and 4 M HCl at room temperature for 24 h with subsequent washing with distilled water. These acid-treated carbon fuels are designated as AC-HNO_3, AC-HCl, CB-HNO_3 and CB-HCl, respectively. Air plasma treatment for the CB samples was carried out using a microwave generator (Sairem, France) with 2.45 GHz frequency and 100 W power. The reactor was first evacuated to a pressure of about 8000 Pa (60 Torr), then the CB was treated in air plasma for 15 min, which is designated as CB-Plasma.

2.2. Characterization of carbon fuels

X-ray diffraction (XRD) characterization of the carbon samples was performed with a Rigaku Miniflex X-ray diffractometer (40 kV, 30 mA) with Cu Kα radiation at a scanning rate of $2^\circ\ min^{-1}$ in the 2θ range from 10° to 90°. The average size of the carbon crystallites was calculated from the Debye–Scherrer equation:

$$L = \frac{K\lambda}{\beta\ \cos\theta} \quad (5)$$

where λ is the wavelength of the X-rays, θ is the diffraction angle, K is the shape factor, and β is the peak width at half-maximum intensity. Values of $K = 0.89$ and 1.84 [22,35] were used for L_c and L_a, respectively. The crystallite size perpendicular to the basal plane, L_c, was obtained from the (0 0 2) reflection, while the crystallite size parallel to the basal plane, L_a, was calculated using the (1 0 0) reflection corresponding to the a-axis unit cell parameter.

Electrical conductivities were measured by a frequency response analyser (Solartron SI1260). Approximately 200 mg of carbon material was pressed into a small pellet (13 mm diameter) at the lowest pressure needed to form a compact, namely, 150 kg cm^{-2}. The sample pellet was then placed between two gold-plated blocking electrodes of area 0.5 cm^2 in a jig of known resistance and the sample impedance was measured over the frequency range 1 MHz to 1 Hz using a sinusoidal excitation amplitude of 10 mV root mean square (rms). Finally, the bulk conductivity σ (S cm^{-1}), was calculated from:

$$\sigma = l[(r - r_0)A] \quad (6)$$

where l is the sample pellet thickness (cm), r is the tested sample resistance (Ω) taken as the impedance at zero phase angle, r_0 is the rig short-circuit resistance (Ω), and A is the electrode contact area (0.5 cm^2).

Nitrogen adsorption/desorption experiments were performed with a Quadrasorb adsorption analyser (Quantachrome, USA) at −196 °C. The specific surface area (S_{BET}) of each carbon samples was calculated by the multiple point Brunauer–Emmett–Teller (BET) method in the relative pressure range $P/P_o = 0.05$–0.25. The total pore volume (V_{total}) was derived from the adsorption amount at a relative pressure of $P/P_o = 0.99$. The average pore diameters (D_{pore}) of carbons were calculated by the available software (QuadraWin V2.0), which applies the Barrett–Joyner–Hallenda (BJH) method. The micropore volume (V_{micro}) and surface area (S_{micro}) of samples were also calculated by the available software (QuadraWin V2.0), which applies the Dubinin–Radushkevich (DR) method. Prior to the N_2 adsorption measurements, all samples were degassed overnight at 200 °C.

Temperature-programmed oxidation (TPO) measurements were conducted under air-flow (80 ml min^{-1}) in a thermogravimetric analyser (Shimadzu TGA-50). Samples were loaded into a platinum pan and heated under a nitrogen atmosphere from room temperature to 200 °C, and held for 1 h to remove the adsorption water, and then the temperature was further increased to 900 °C in air (80 ml min^{-1}) with a heating rate of 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Kratos Axis Ultra XPS system incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic Al Kα X-ray (1486.6 eV) at 150 W (15 kV, 10 ma). Survey scans were taken at an analyser pass energy of 160 eV, and performed over a 1200 eV binding energy range using a 1.0 eV step and a dwell time of 100 ms.

The mass titration method of Noh and Schwarz [31] was used to estimate the point of zero charge (PZC) of the carbon surfaces, at which the net total (external and internal) surface charge of the carbon particles is zero. This is based on the fact that the pH of the solution changes in the direction of the PZC on contact with the carbon particles [32]. Three different initial pH solutions (pH 3, 6, 11) were prepared using HNO_3 (0.1 M) and NaOH (0.1 M). Sodium nitrate was used as the background electrolyte. For each initial pH, six containers were filled with 20 ml of the solution and different amounts of carbon were added (0.05, 0.10, 0.50, 1.00 and 10% by weight). The equilibrium pH was measured after 24 h. The plot of pH versus mass fraction showed a plateau and the PZC is identified as the point at which the change in pH was negligible. The PZC was then taken as the average of the three asymptotic pH values.

Temperature-programmed desorption (TPD) experiments were carried out in a vertical tube furnace using Ar (80 ml min^{-1}) as the carrier gas. A 0.5 g sample was placed in a quartz tube, heated to 110 °C and held for 60 min and then ramped at 5 °C min^{-1} to 900 °C. The gases evolved were analysed using a gas chromatograph (Shimadzu GC-17A) equipped with a thermal conductivity detector and a Carbosphere column.