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Electrochemical study of composite materials for coal-based direct carbon fuel cell

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ABSTRACT

The efficient conversion of solid carbon fuels into energy by reducing the emission of harmful gases is important for clean environment. In this regards, direct carbon fuel cell (DCFC) is a system that converts solid carbon directly into electrical energy with high thermodynamic efficiency (100%), system efficiency of 80% and half emission of gases compared to conventional coal power plants. This can generate electricity from any carbonaceous fuel such as charcoal, carbon black, carbon fiber, graphite, lignite, bituminous coal and waste materials. In this paper, ternary carbonate-samarium doped ceria (LNK-SDC) electrolyte has been synthesized via co-precipitation technique, while LiNiCuZnFeO (LNCZFO) electrode has been prepared using solid state reaction method. Due to significant ionic conductivity of electrolyte LNK-SDC, it is used in DCFC. Three types of solid carbon (lignite, bituminous, sub-bituminous) are used as fuel to generate power. The X-ray diffraction confirmed the cubic crystalline structure of samarium doped ceria, whereas XRD pattern of LNCZFO showed its composite structure.

The proximate and ultimate coal analysis showed that fuel (carbon) with higher carbon content and lower ash content was promising fuel for DCFC. The measured ionic conductivity of LNK-SDC is 0.0998 Scm^{-1} and electronic conductivity of LNCZFO is 10.1 Scm^{-1} at 700 °C, respectively. A maximum power density of 58 $mWcm^{-2}$ is obtained using sub-bituminous fuel.

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Introduction

Coal is considered as a basic source of energy for household and industry. It is used to generate electricity due to certain feature like abundance, high energy density, low cost, safe transportation and easy storage [1]. However, coal power plants (CPP) have low efficiency almost 30% and produce environment pollution (CO_2, NO_2, SO_2 gas), which causes the global warming. The efficient conversion of solid carbon fuels to generate power by clean way is significantly important for friendly environment. In this regard, direct carbon fuel cell (DCFC) is an alternative that convert solid carbon directly (without combustion) into electrical energy with high thermodynamic efficiency (100%), system efficiency (80%) and fewer emission of gases [2–9]. This can generate electricity from any carbonaceous fuel such as charcoal, carbon black, carbon fiber, graphite, lignite, bituminous, coal and waste materials [10–15]. However, DCFC with solid oxide fuel cell (SOFC) technology shows poor performance, whereas the hybrid DCFC system (HDCFC), in a combination of molten carbonate fuel cell (MCFC) and SOFC exhibit the better performance [16–19]. The reaction mechanisms in DCFC are;

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

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (2)$$

$$\text{Cathode reaction}: O_2 + 4e^- \rightarrow 2O^{2-} \quad (3)$$

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

$$\text{Overall reaction}: C + O_2 \rightarrow CO_2 \quad (5)$$

The efficiency of the DCFC is investigated by the overall cell reaction (Eq. (5)). The anode has small triple-phase boundary (TPB) so electrode, electrolyte and carbon has not direct contact among them, low fuel utilization which limit the performance [20]. To enhance the performance of DCFC improvement in reactivity of carbon fuel in DCFC is remarkable issue. The carbon with more crystallographic disorder shows more reactivity electrochemically and chemically [21]. Different carbon fuel medium density fiber board (MDF) [22] and corn cob biochar biomass has been analyzed to generate electricity and observed good performance in a temperature range of 650–750 °C [23]. The pretreated carbon with HNO_3, HCl and plasma has been studied and found that carbon pretreated with HNO_3 showed higher performance [24]. Hao [25] studied the waste paper (newspapers, magazines) as a carbon fuel for HDCFC and got the maximum power density of 172 mW cm^{-2} at 650 °C. Elleuch [2,26] studied the graphite fuel mixed with (Li-Na)CO_3 molten carbonate anode, olive wood charcoal and obtained maximum power density of 58 mW cm^{-2}, 105 mW cm^{-2} respectively at 700 °C.

To enhance the reactivity of HDCFC, some catalysts Fe, Ag, Ni, Ca, ceria, and alkali metal oxides are used [27,28]. Fuente-Cuesta [29] studied the electrochemical behavior of bituminous and anthracite coal and found that carbonaceous structure, carbon content and reactivity are the major properties for best performance. Vu [30] studied the oxidation behavior of ash free coal from bituminous and sub-bituminous and measured the voltage 0.74 V at a current density of 150 mA cm^{-2} at 850 °C. Lee [31] also studied the oxidation behavior of ash free coal (AFC) and observed that AFC can reduce the operational temperature than carbon fuel cell. Dudek [32] observed that charcoal is best fuel for DCFC and obtained the power densities of 50–100 mW cm^{-2}. Kacprzak [33–35] used the biochar fuel obtained from apple, sunflower husks and pine and obtained the power densities of 18.3–22.4 mW cm^{-2}. Different biomass obtained from wood, rice straw, corn strove and almond shell was tested as a fuel and obtained the power density of 34–39 mW cm^{-2} while in other study power density of 150 mW cm^{-2} was obtained at 700 °C with almond shell biochar fuel [36,37]. Ternary carbonate-doped ceria (LNK-SDC) electrolyte and LNCZO electrode are tested with hydrogen fuel and got a maximum power density of 525 mWcm^{-2} and 0.92 V OCV at 600 °C [38]. Samarium doped ceria (SDC) is a single phase material and has lower ionic conductivity than LNK-SDC; in which carbonate appear as a second phase or core shell. Multi-ion conduction mechanism intrinsic (O^{2-}, CO_3^{2-}, metal ions Li^+, K^+, Na^+) and extrinsic ions (H^+, HCO_3^-, OH^-) is observed in core shell structure due to which ionic conductivity is much improved [39].

In this work, lignite, bituminous and sub-bituminous were used as carbon fuel in DCFCs and cell performances were measured in the range of 600–700 °C using ternary carbonate-doped ceria (LNK-SDC) electrolyte and $Li_{0.12}$ $Ni_{0.32}$ $Cu_{0.32}$ $Zn_{0.12}$ $Fe_{0.12}$ O (LNCZFO) electrodes. LNK-SDC material shows good conductivity at lower temperature. Therefore, it is used in the present study to evaluate the performance of DCFC.

Experimental part

Electrolyte synthesis

Electrolyte material LNK-SDC was prepared via co-precipitation technique. 0.5 M solution was prepared by mixing samarium nitrate hexahydrate (Sm $(NO_3)_3 6H_2O$), cerium nitrate hexahydrate (Ce$(NO_3)_3 6H_2O$) (Sigma Aldrich) stirred and heated at 80 °C. The ternary carbonates (sodium carbonate (Na_2CO_3), lithium carbonate (Li_2CO_3), and potassium carbonate (K_2CO_3)) solution was used as the second phase in nitrate solution with molar ratio SDC: carbonate = 1:2. The mixed solutions were further stirred for 4 h at 80 °C till the white precipitates. The precipitates were washed with deionized water, followed by vacuum filtration, and dried in an oven for 5 h at 120 °C. Finally, the dried powder was fired in a furnace at 800 °C for 5 h to achieve a dense electrolyte powder.

Electrode preparation

The electrode powder was prepared using solid state reaction (SSR) method. Following chemicals were used to prepare the composite electrode, Li $(NO_3)_3 \cdot 6H_2O$, Ni_2 $(CO_3)_3$, Cu $(NO_3)_2$, Zn $(NO_3)_2 \cdot 6H_2O$, Fe $(NO_3)_3 \cdot 9H_2O$. The entire chemical ($Li_{0.12}$ $Ni_{0.32}$ $Cu_{0.32}$ $Zn_{0.12}$ $Fe_{0.12}$ oxide (LNCZFO)) were mixed in mortar pestle according to appropriate molar ratio and ground for 1 h to make fine powder. The ground powder was sintered in

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