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Effect of sulfur and its compounds on the performance of graphite electrooxidation in molten carbonate

Jia Liu, Ke Ye, Mengmeng Du, Jinling Yin*, Dianxue Cao*, Guiling Wang

Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, PR China

HIGHLIGHTS

- Addition of sulfur and its inorganic compounds in molten carbonate was investigated for graphite electrooxidation.
- Improved performance of graphite electrooxidation was observed with addition of $CaSO_4$.
- Other sulfur compounds exhibited no effect on graphite electrooxidation in molten carbonate.

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ABSTRACT

Direct carbon fuel cells are promising power sources with their performance significantly depending on the electrooxidation activity of carbon fuel. The impurities in the carbon fuel may affect the anode reactions. Sulfur and some of its inorganic compounds ($CaSO_4$, K_2SO_3, K_2S, FeS_2) were added in molten carbonate and their effect on graphite electrooxidation was investigated. Cyclic voltammograms of gold electrode with addition of these sulfur compounds showed $CaSO_4$ was stable and other compounds were electrochemically oxidized to high valence state sulfur compounds at operating voltage range. Linear sweep voltammetry of graphite with addition of sulfur compounds exhibited enhanced current density compared to pure graphite electrooxidation. Chronoamperometry was carried out to examine steady-state test of graphite electrooxidation in presence of sulfur compounds and the results indicated the enhanced current densities were caused by improved Boudouard reaction for $CaSO_4$ and sulfur electrooxidation for other compounds, respectively. These inorganic sulfur compounds had no impact on electrooxidation process of graphite.

1. Introduction

Electric power as a most widely used and convenient secondary energy has become an indispensable element for the development of mankind society. Electricity production is heavily depended on supply of the conventional coal-fired plants and this condition will be remained for some time in the future. The current issue of utilizing coal for power generation in coal-fired plants is the low efficiency (below 40%) determined by the thermal engines. Therefore, it becomes very important to meet needs for sustainable energy supply by seeking new technologies for the conversion of coal to electricity efficiently. The direct carbon fuel cell (DCFC) allows the direct conversion of the chemical energy stored in solid carbon materials into electrical energy via an electrochemical route instead of combustion. It provides a promising means for the coal power generation in an efficient and clean way [1–4]. In the anode, carbon is electrochemically oxidized to CO_2 releasing 4 electrons; in the cathode, oxygen from air combines with these electrons and is electrochemically reduced. The electrical power is generated based on the overall cell reaction, as follows:

$$C + O_2 = CO_2, \quad E^o = 1.02\ V \tag{1}$$

Coal is continually used in direct carbon fuel cell in an attempt to generate electricity [5–11]. However, since coal is a mixture, when the electrooxidation behavior of coal is studied, effect of impurity in coal has to be taken into account. Apart from carbon, raw coal contains moisture, volatile matter, and ash [7]. With elevating temperature, moisture and volatile matter are released, while carbon and ash are remained. The ash is composed of various mineral matter, such as alkali metal oxides, alkali earth metal oxides, transition metal oxides, nonmetallic compounds, etc [12–14]. At high temperature, chemical and electrochemical reactions will be

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* Corresponding authors. Tel./fax: +86 451 82589036.
E-mail addresses: yinjinling@hrbeu.edu.cn (J. Yin), caodianxue@hrbeu.edu.cn (D. Cao).

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facilitated and reactions between carbon and ash cannot be ignored in fuel cell. An enhancement on performance of carbon electrooxidation was observed after addition of some metal oxides into molten carbonate, while an inhibition was appeared with other oxides, such as Al_2O_3 and SiO_2 [7,15]. However, effect of nonmetallic compounds involving in elements of phosphorus, sulfur, arsenic, etc., on carbon electrooxidation are scarcely studied [13].

Elemental sulfur widely exists in various coals and its content in the coal is generally in the range of 0.2–10 wt.% [16]. The sulfur compounds in the coal were partly originated from sulfur rich proteins in the plant and some fraction of these will be retained as organic sulfur in the carbonaceous phase during maturation to coal [17]. Traditionally, the sulfur compounds have been classified into two groups, inorganic and organic [18]. The forms of inorganic sulfur in the coal are mainly in two types, as disulfides and sulfate. The representing materials are pyrite (FeS_2) and $CaSO_4$, respectively [16]. Sulfur chemically bound to the hydrocarbon structure of coal is the existence formation of organic sulfur. That includes aromatic rings and aliphatic functional groups, usually categorized as mercaptans, aliphatic and aryl sulfides, disulfides and thiophenes [19]. Literature reported that sulfur in the fuel would poison the Ni-based anode in solid oxide fuel cell and leaded to loss of activity, which adversely affected the durability and stable operation of the fuel cell [20,21]. Cooper examined the thermodynamics of carbon, carbon dioxide, sodium carbonate with additions of sulfur in various oxidation states at 750 °C [22]. The carbonyl sulfide (COS) is found in gas products. However, the influence of the sulfur and its compounds on the carbon electrooxidation is still limited. To better understand that, sulfur and some of its compounds in inorganic form were introduced into the molten carbonate electrolyte and their effects on graphite electrooxidation were investigated in this work.

2. Experimental

$CaSO_4$, K_2SO_3, K_2S, S, and FeS_2 were selected as the sulfur-containing substances. 5 mmol of above substance was added in 1 mol binary carbonate mixture of 62% Li_2CO_3-38% K_2CO_3 (mole fraction), respectively. Their effects on the carbon electrooxidation were examined with graphite rod (1 cm in length and 0.6 cm in diameter) as the model carbon fuel described in previous work [23]. Electrochemical measurements were carried out with VMP3/Z potentiostat (Biologic) controlled by the EC-lab software. The reference electrode was an Au/CO_3^{2+}/O_2,2CO_2 electrode constructed from a closed-bottom alumina tube containing a gold wire. A hole of 2 mm in diameter was made at bottom of alumina tube to allow the bulk electrolyte infiltrating the gold wire. An overflow mixture gas of 33% O_2/67% CO_2 (by volume) was passed to the three-phrase interface via a tube inside of alumina tube [23]. A graphite electrode was selected as the counter electrode because carbon from counter electrode dissolved into molten would not affect the reactions on working electrode [24]. The gold plate (1×1 cm^2) was served as the working electrode when electrochemical properties of sulfur and its compounds in molten carbonate were investigated. The cell was kept air-free by purging N_2 gas continuously during measurements. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) at a potential scan rate of 2 mV s^{-1}, and chronoamperometry at −0.4 V were performed in molten carbonate electrolyte.

3. Results and discussion

3.1. Addition of $CaSO_4$

Fig. 1(a) shows cyclic voltammograms (CVs) of gold electrode in carbonate with and without $CaSO_4$. The almost overlapped curves indicate $CaSO_4$ keeps inert at 700 °C and the hexavalent sulfur in sulfate cannot be electroreduced to low valence state within operating voltage range. The influence of $CaSO_4$ on the graphite electrooxidation at 600 °C and 700 °C is examined by LSV and chronoamperometry, respectively, and the results are shown in Fig. 1(b) and (c). The current density is increased with addition of $CaSO_4$ in molten carbonate at 700 °C, while invariant at 600 °C. The same results were also obtained in the steady-state tests, which

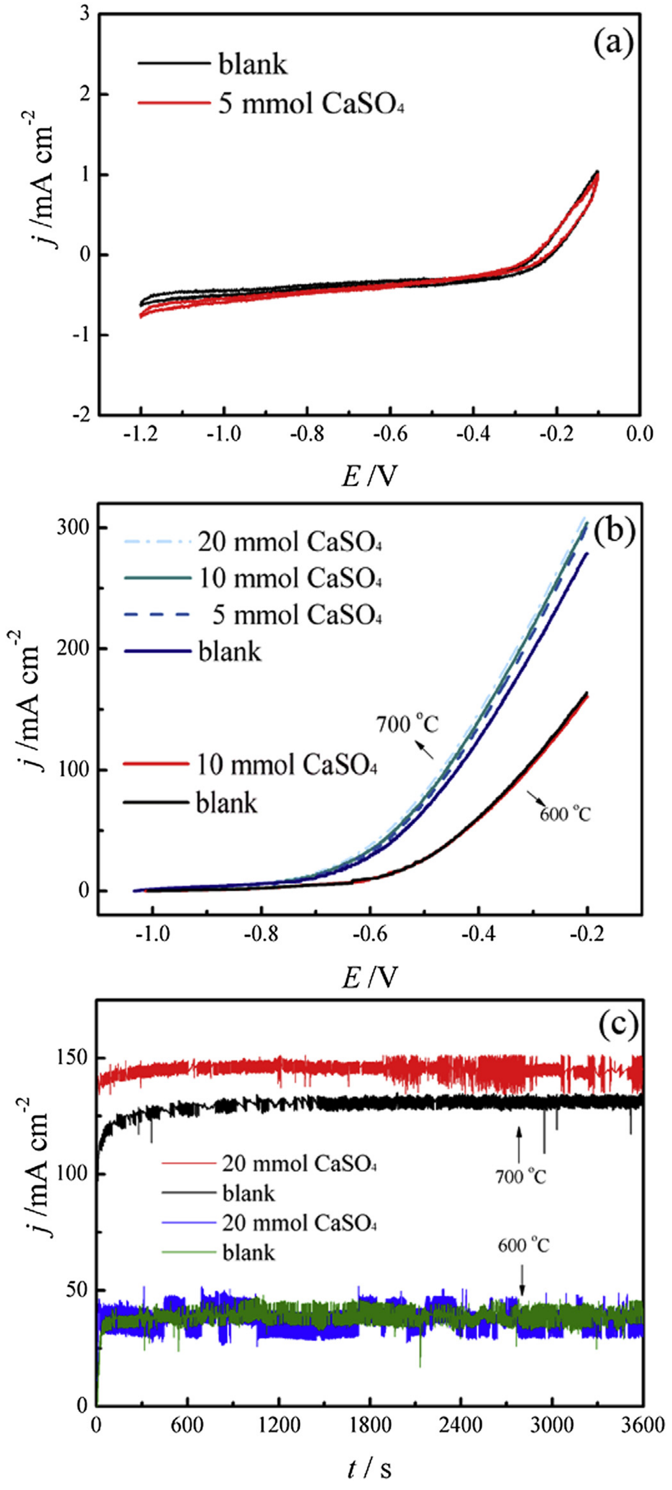

Fig. 1. (a) The CVs of gold electrode in the absence and presence of 5 mmol $CaSO_4$ at 700 °C. The LSV curves (b) and the chronoamperometric curves at −0.4 V (c) of graphite electrode in the absence and presence of $CaSO_4$ at 600 and 700 °C.