



## Effect of high-temperature pyrolysis on the structure and properties of coal and petroleum coke



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### ABSTRACT

In this study, for the purpose of substituting part of petroleum coke with low ash anthracite to prepare carbon anode used in aluminum electrolysis, the effects of high-temperature pyrolysis on the structure and properties of coal char and petroleum coke were studied at the temperature range of 1000 °C–1600 °C. Results showed that the carbon crystallite structure of coal char and petroleum coke became more ordered with the increase of the temperature. However, the graphitization degree of coal char was lower than that of petroleum coke at the same pyrolysis temperature. The Brunauer-Emmett-Teller (BET) surface area of coal char decreased with the increase of temperature, whereas the BET surface area of petroleum coke decreased first and then increased. The increase of pyrolysis temperature generally inhibited the gasification reactivity of coal char, whereas the gasification reactivity of petroleum coke was inhibited first and then promoted. Moreover, the increase of pyrolysis temperature led to the rapid decrease of powder resistivity of coal char and petroleum coke. In particular, the powder resistivity of coal char was significantly higher than that of petroleum coke at the same pyrolysis temperature. Additionally, the real density of coal char and petroleum coke showed a different trend with the increase of temperature. Specifically, the real density of the former decreased, whereas that of the latter increased. The causes of the above observations were also discussed. Overall, this study provides further understanding about the differences between coal char and petroleum coke, which will facilitate the preparation of carbon anode from the mixture of coal char and petroleum coke.

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### 1. Introduction

Petroleum coke is the main raw material of carbon anode used in aluminum electrolysis. Hence, petroleum coke significantly influences the energy consumption and environmental benefits of aluminum electrolysis. The cost of carbon anode accounts for 15–20% of the total cost of aluminum electrolysis production. With the rapid development of the electrolytic aluminum industry in China, the demand for high-quality petroleum coke is also growing. However, the quality of petroleum coke is deteriorating because of the increasing proportion of imported heavy crude oil used in China, consequently leading to a tight supply of high-quality petroleum coke used for aluminum electrolysis [1,2]. Thus, expanding backup reserves of resources for carbon anode is beneficial to the sustainable development of the aluminum industry. Furthermore, finding

low-cost raw materials to replace petroleum coke is necessary to reduce the cost of carbon anode.

As an important raw material for carbon products, high-metamorphic anthracite exhibits the characteristics of high carbon content, compact structure, high strength, good thermal stability, and lower cost than petroleum coke [3–6]. Hence, high-metamorphic anthracite can be an ideal raw material to replace petroleum coke for the preparation of carbon anode. To date, attempts have been made to produce carbon anode from coal extracts [7–10], which were obtained by solvent extraction technology. However, this high-cost technology is complex and the yield is low. Additionally, good physical and chemical properties of prebaked anodes have been achieved using low-ash calcined anthracite to partly substitute petroleum coke [1,11,12]. However, coal and petroleum coke presented obvious differences because of the different formation processes. Even after high-temperature treatment, the properties of coal char and petroleum coke (such as carbon crystalline structure, specific surface area, gasification reactivity, electrical resistivity and real density) remain different, and such difference will affect the properties and energy efficiency of

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carbon anode in aluminum electrolysis. Although, studies [1,11,12] have demonstrated that high-quality carbon anodes can be produced by adding an appropriate amount of coal char to petroleum coke, the effects of pyrolysis on the structure and properties of coal and petroleum coke have not been thoroughly investigated.

High-temperature pyrolysis of coal and petroleum coke is a primary process for their carbon products. Moreover, pyrolysis conditions significantly influence the performance of calcined coke (char), thereby affecting the performance indicators of the carbon products. The current study systemically investigated the effects of high-temperature treatment on the structure and properties of coal and petroleum coke. Accordingly, the differences in pyrolysis characteristics and performances between two kinds of calcined cokes are determined. Overall, this study provides theoretical basis to prepare carbon anodes by substituting coal for petroleum coke.

## 2. Experimental

### 2.1. Raw materials

Low-ash anthracite (Shenhua Group Corp., China) and petroleum coke (Qilu Petrochemical Co., Ltd., China), which were named A and PC, respectively, were used for the investigation. Proximate analysis, ash compositions, and ash melting properties are listed in Tables 1 and 2. The ash compositions of anthracite and petroleum coke were determined by X-ray fluorescence (PANalytical Axios mAX equipment).

As shown in Table 1, the fixed carbon content of coal is slightly higher than that of petroleum coke, whereas the volatile and sulfur contents of coal are significantly lower than those of petroleum coke. These features are the major advantages of coal as raw material to prepare carbon anode for aluminum electrolysis. However, compared with petroleum coke, the disadvantage of coal is also obvious, that is, a higher ash content. The impurity elements in Table 2, such as Si and Fe, will significantly affect the quality of electrolytic aluminum, because the impurities of Si and Fe in the carbon anode will turn into the aluminum liquid. Although the content of aluminum is also high, aluminum is considered a valuable element. The allowed impurity content in raw carbonaceous materials for carbon anode is generally based on the standard of 2B grade in SH/T0527-1992 [13]; this standard states that the contents of Si and Fe should be <0.08% each. The contents of Si and Fe in coal are relatively high, whereas those in petroleum coke are low. Therefore, when adding an appropriate amount of coal, the content of impurities in the carbon anode can also meet the requirements.

### 2.2. Preparation of char samples

The pyrolysis of coal and petroleum coke was completed in a high-temperature furnace. The inert atmosphere was maintained in the furnace to prevent oxidation of coal and petroleum coke. The samples were heated to a desired pyrolysis temperature at a heating rate of 4 °C/min, and then held at this temperature for 120 min. The pyrolysis temperatures were 1000 °C, 1150 °C, 1300 °C, 1450 °C, and 1600 °C. When the heat preservation time was over, the samples kept in the furnace were cooled to room temperature. The samples were then removed from the furnace, broken, and graded in different particle sizes. Coal chars prepared under different temperatures were referred to as A1000, A1150, A1300, A1450, and A1600, whereas the petroleum cokes were referred to as PC1000, PC1150, PC1300, and PC1450. The proximate analysis and ultimate analysis of coal chars and petroleum cokes are listed in Table 3.

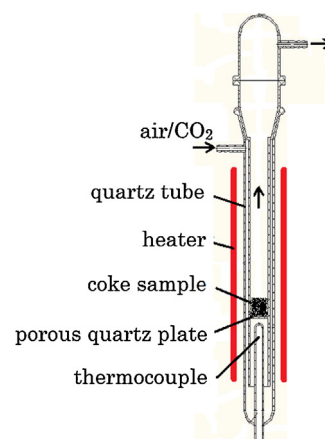


Fig. 1. The schematic diagram of the testing device for gasification reactivity.

### 2.3. Measurements of air gasification reactivity and CO<sub>2</sub> gasification reactivity

Air gasification reactivity and CO<sub>2</sub> gasification reactivity are important indicators of coke chemical activity, which significantly affect the overconsumption of carbon materials in aluminum electrolysis [14,15]. In accordance with the principle of weight loss method, the air gasification reactivity and CO<sub>2</sub> gasification reactivity of cokes were characterized in terms of residual rate after reaction with air and CO<sub>2</sub> following the test standard YS/T 587.7-2006 [16] in China.

The tests for air gasification reactivity and CO<sub>2</sub> gasification reactivity were conducted in a quartz tube reactor testing equipment; a schematic of this testing device are shown in Fig. 1. The detailed measurement procedure is as follows: 5 g of coke with particle size of 1 mm to 1.4 mm was placed in the reactor; air gasification reactivity was performed in air atmosphere at 600 °C for 60 min, whereas CO<sub>2</sub> gasification reactivity was measured in CO<sub>2</sub> atmosphere at 1000 °C for 100 min; and the flow rate of both gases was 50 L/h. At the end of the reaction, the cooled char was collected from the testing equipment and then weighed. The reactivity was indicated in terms of the ratio of the mass loss to the initial weight of the sample. The gasification percentage (*X*) is calculated as follows:

$$X = \left(1 - \frac{m_t}{m_0}\right) \quad (1)$$

where *m*<sub>0</sub> represents the initial weight of the sample, and *m*<sub>t</sub> is the residual weight of the sample.

### 2.4. Analysis of carbon crystalline structure and BET surface area of the samples

The crystallite structure of coke was characterized by X-ray diffraction (XRD) with Cu K $\alpha$  radiation in a Rigaku D/Max 2500 diffractometer at a scan speed of 4° min<sup>-1</sup>.

XRD is an effective means to analyze carbon crystallite structure. The interplanar spacing *d*<sub>002</sub> and the stacking height of the carbon crystal *L*<sub>c</sub> are the basic parameters for analyzing the carbon crystallite structure. According to Eqs. (2) and (3), the parameters *d*<sub>002</sub> and *L*<sub>c</sub> were calculated from the (002) peak as follows:

$$d_{002} = \frac{\lambda}{2\sin(\theta_{002})} \quad (2)$$

$$L_c = \frac{0.89\lambda}{\beta_{002}\cos(\theta_{002})} \quad (3)$$

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