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Ambient electrical conductivity of carbon cathode materials for aluminum reduction cells

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Abstract: The ambient electrical conductivity (AEC) of carbon cathode materials was investigated in respect to their open porosity, crystal structure and graphite content using hydrostatic method, four-probe technique and X-ray diffraction (XRD), respectively. The AEC is proportional to the specific conductivity (σ_0) and the exponential of $(1-\varepsilon)$ (ε is porosity) by a quasi-uniform formula based on the percolation theory. The σ_0 can reflect the intrinsic conductivity of the carbon cathodes free of pores, and it depends on the mean crystallite size parallel to the layer (002). The exponent n is dependent on the materials nature of the cathode aggregates, while an averaged value, 4.65, can practically work well with 5 types of cathode materials. The calculation of σ_0 can be extended to the graphitic cathodes containing different aggregates using the simple rule of mixture.

Key words: carbon cathode; electrical conductivity; porosity; crystal structure; aluminium reduction cell

1 Introduction

Carbon cathode materials are widely applied to electrolytic cells, arc furnaces and energy storage devices [1−4]. The ambient electrical conductivity (AEC) of the cathode materials is a key property for these applications. In modem aluminum reduction cells, especially for the super-high amperage cells up to 500−600 kA, a small improvement in the AEC may lead to significant energy savings [5]. The major methods in improving the conductivity of the carbon cathodes include the increase of graphite content (GC) in the cathode materials, for instances, semi- and full-graphitic cathodes [6,7], and the perfection of the crystal structure of the carbon cathodes, i.e., the graphitized cathodes [8]. The better AECs through these method above have been reported in the literature [1,9], but most of the results are limited to a rough treatment for the relationship of the AEC with the crystal structure and the GC in the carbon cathodes.

On the other hand, the cathodes have porous structures which may change during the heat treatment process [10] and have important influences on the cathode properties [11−13]. Open porosity is considered as one of the most universal parameters for the porous structures, which can be related to the AEC of carbon materials. WAGNER et al [14] studied the AEC of polycrystalline graphite, and put forward a linear relationship between the AEC and the porosity. RHEE [15] advanced WAGNER's model using a non-linear formula, while SUN et al [16] proposed another complex formula based on the ideal fluid mechanic for the carbon materials. However, the above formulae are still far from satisfactorily understanding the effects of the porosity on the AEC in carbon cathodes.

In this work, the relationship between AEC and open porosity was studied on the cathodes used for aluminum reduction cells. Experimental data obtained in our laboratory and from the literature were analyzed and modeled to describe their relationship among various carbon cathodes. The effects of crystal structures of the cathodes on the AEC were also discussed quantitatively. Moreover, a mathematical formula was developed to theoretically calculate the conductivity of graphitic cathodes with various GC values. The work is aimed to establish close relationships among the AEC, porosity,

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crystal structure and GC for quantitatively evaluating the electrical conductivity of carbon cathodes.

2 Experimental

There are five types of carbon cathodes investigated in this work, which are classified according to their aggregate materials and listed in Table 1. The data of AEC and porosity of the cathodes were tested in our laboratory, together with some collected from the Refs. [1,17,18] for a more systematic investigation. The tested samples were taken from the commercial products used in industrial reduction cells (H-1, H-2, S-1 and P-1 series), or prepared in our laboratory (Lab-1 and Lab-2 series). All the samples were machined to a cylindrical form (50 mm in length and 25 mm in diameter).

Table 1 Selected carbon cathode materials under investigation

Type	Carbon aggregate	Data resource
Amorphous cathode	100% electro-calcined anthracite (ECA)	Ref. [1]
Semi-graphitic cathode	~70% ECA+~30% artificial graphite (mass fraction)	Laboratory (H-1 and Lab-1 series)
Full-graphitic cathode	100% artificial graphite	Laboratory (H-2 and Lab-2 series) and Refs. [17,18]
Graphitized cathode	100% calcined petroleum coke (CPC)	Laboratory (S-1 series) and Ref. [17,18]
High-purity graphite cathode (HPG)	CPC added ~4% artificial graphite	Laboratory (P-1 series)

The porosity of the sample was measured by the hydrostatic method [19]. 1) Determine the dry mass (m_1) of the sample (accurate to 0.01 g) after being dried at 110 °C to constant mass. 2) Prepare a water saturated sample in the set-up illustrated in Fig. 1. The dried sample was immersed in distilled water under a pressure no more than 133 Pa until water saturation. 3) Suspend the saturated sample in water to obtain the suspended mass (m_2) (0.01 g). 4) After Step (3), blot the sample lightly with a moistened cotton towel to remove water drops from the surface and weigh in air to obtain the saturated mass, m_3 (0.01 g). Then, the open porosity (ε) was calculated as

$$\varepsilon=\frac{m_3-m_1}{m_3-m_2}\times 100\% \qquad (1)$$

The AEC was measured in a device based on a standard four-probe method [20], as shown in Fig. 2. A constant current (I) from DC power supplier passed through two Cu plates which were forced (F) to maintain a good contact on both sides of the sample, which was recorded by a high precision amperemeter (TAITAN VC9806A$^+$, 0.001 A). The voltage drop (U) between the two contact points (a and b) that were longitudinally centered on the top of the horizontal sample, was tested using a high precision voltmeter (Tektronix DMM4050, 0.0001 mV). The distance (L) between points a and b was kept constant. The AEC was calculated by

$$\sigma=\frac{IL}{UA} \qquad (2)$$

where A is the cross-sectional area of the sample. The test was repeated 8 times by axially rotating the sample every 45°, and the reported value was an average of these measurements.

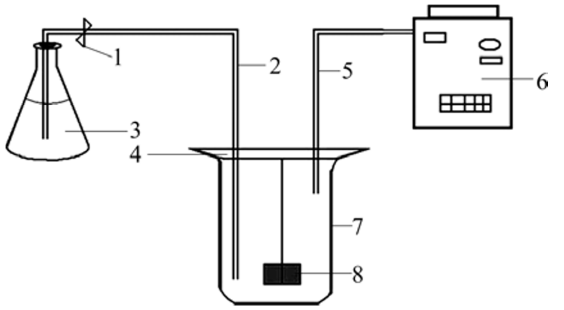

Fig. 1 Schematic drawing of set-up for preparing saturated sample: 1—Valve; 2—Glass pipe; 3—Bottle 1 (containing distilled water); 4—Rubber stopper; 5—Glass pipe; 6—Vacuum pump; 7—Drying bottle; 8—Sample

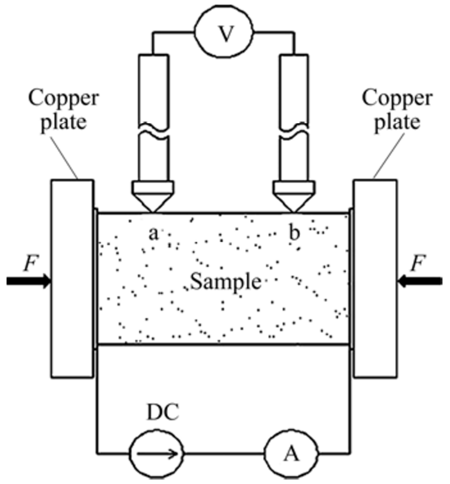

Fig. 2 Schematic drawing of four-probe method for electrical conductivity measurement

The crystal structure of the sample was examined by X-ray diffraction (XRD, Rigaku D/max-2400) using Cu K$_\alpha$ radiation within a range of 10°−90° (2θ) by step scanning of 0.020°. The XRD patterns were analyzed by