

Production of Prebaked Anodes Using Coal-Based Co-Coking Coke

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Abstract

To address the shortage of petroleum coke resources suitable for prebaked anode production, the high energy consumption and cost associated with the high-temperature calcination required for low-ash coal to make prebaked anodes, and the difficulty of directly using low-ash coal produced by coal deashing (which is often powdery), a method was developed by blending different proportions of low-ash coal and vacuum residue for co-coking. The resulting co-coking mixed coke was then calcined at various temperatures, and the calcined mixed coke was used to produce prebaked anodes. Research results indicate that co-coking coke containing 24 % coal, calcined at 1300 °C, produces a calcined mixed coke suitable for the production of prebaked anodes, and the physico-chemical properties of the produced coal-added prebaked anodes meet industry standards.

Keywords: Prebaked anodes, Low-ash coal, Co-coking coke.

1. Background

In China, almost 100 % of the carbonaceous aggregate for aluminium electrolysis carbon anodes is petroleum coke, accounting for over 60 % of the petroleum coke consumption in the country. Due to the rapid development of the aluminium industry and the significant increase in coke demand from the new energy industry, there is a shortage of high-quality petroleum coke for the production of prebaked anodes in aluminium electrolysis. It is imperative to find alternative carbon materials to replace petroleum coke, thereby diversifying the anode coke sources. Several domestic and international research institutions have carried out experimental studies on preparing prebaked anodes by adding low-ash coal. Yingtao Luo et al. [1] used low-ash anthracite from Ningxia as raw material, calcined at temperatures of 1800–2200 °C, and replaced 20 % of petroleum coke with calcined anthracite to produce carbon anodes that met the quality requirements of the industry standard YS/T 285 for TY-2 carbon anodes. Fachuang Li et al. [2] analysed the performance of anodes prepared from different mixtures of coking coal, varying the proportion of coal added. Patent CN101255572B [3] uses calcined anthracite and calcined petroleum coke as aggregates, mixed with binders, to make aluminium carbon anodes. Patent CN101698947B [4] uses flotation deashed coal and pulverized raw petroleum coke as raw materials to prepare aluminium electrolysis carbon anodes. The preparation process involves blending the flotation deashed coal with pulverized raw petroleum coke, compressing it into lumps, drying, and calcining to produce composite calcined coke, which replaces part or all of the petroleum coke in aluminium carbon anode production. However, these studies require low-ash coal to be calcined at temperatures above 1800 °C to meet the requirements for prebaked anode coke, resulting in high energy consumption and cost. Additionally, during the deashing process, these coals are typically pulverized into very fine particles, making direct calcination difficult. They must be pressed into blocks with added binders before calcination, further increasing production costs. This experiment mixed powdered low-ash coal with vacuum residue, then co-coked them. The resulting co-coking coke can be calcined at lower temperatures to produce calcined coke suitable for use in carbon anodes. This provides an economically efficient technical

solution for replacing petroleum coke in the production of carbon anodes for aluminium electrolysis.

2. Co-coking Experiment of Low-Ash Coal and Vacuum Residue

2.1 Experimental Setup and Materials

The experiment was conducted in a temperature-controlled muffle furnace. The low-ash coal was sampled from the National Institute of Clean-and-Low-Carbon Energy, using bituminous coal from the Hongshaquan Coal Mine in Xinjiang, which underwent deashing through the sub-molten salt method to produce low-ash coal. Its physicochemical properties are shown as below.

Table 1. Physicochemical properties of low-ash coal.

Physicochemical Indices	Unit	Analysis Results
Ash Content	%	0.12
Sulphur Content	%	0.08
V	%	< 0.0005
Na	%	0.029
Ca	%	0.044
Si	%	0.0061
Fe	%	0.0071
Ni	%	0.0007
Ti	%	0.0047

Table 2. Size distribution of low-ash coal.

Particle Size	> 1 mm	1–0.5 mm	0.5–0.3 mm	0.3–0.15 mm	0.15–0.075 mm	< 0.075 mm
Weight Percent (wt%)	2.4	17.2	16.5	12.7	19.7	31.5

The vacuum residue was sourced from Chambroad Petrochemicals, and its physicochemical properties are as follows:

Table 3. Physicochemical properties of vacuum residue.

Physicochemical	Unit	Analysis Results	Notes
Carbon Residue	%	15.72	Weight Percent
Ash Content	%	0.07	Weight Percent
Salt Content	mg/L	48.98	
S	%	2.46	
Na	µg/g	12.00	
Mg	µg/g	9.63	
Al	µg/g	6.53	
Si	µg/g	14.31	
P	µg/g	1.19	
Ca	µg/g	40.69	
V	µg/g	173.54	
Fe	µg/g	54.48	
Ni	µg/g	57.34	
Asphaltenes	%	5.30	Weight Percent
Saturates	%	24.29	Weight Percent
Resins	%	24.94	Weight Percent
Aromatics	%	38.17	Weight Percent

2.2 Co-Coking Test Procedure

The co-coking test procedure was as follows: first, low-ash coal and vacuum residue were weighed according to the experimental ratios. After thoroughly blending the low-ash coal and vacuum residue, the mixture was placed into a muffle furnace and subjected to co-coking according to a preset heating curve to obtain co-coking coke. The coal contents in the co-coking coke produced from different blending ratios of low-ash coal and vacuum residue were 65.4 %, 58.7 %, 48.7 %, 38.7 %, and 24.0 %, respectively, designated GS-1 to GS-5. The obtained co-coking coke was placed in a pit-type furnace and calcined at 1250 °C. The calcined co-coking coke was analysed to determine the optimal proportion of low-ash coal addition.



Figure 1. Laboratory-scale co-coking coke produced from low-ash coal and vacuum residue.

2.3 Analysis Results and Discussion

Five types of calcined co-coking coke were analyzed, with evaluation indices including powder resistivity, ash content, and true density. The analysis results of calcined co-coking coke are shown in Figures 2–4.

The analysis results indicate that the powder resistivity of calcined co-coking coke increases with the higher coal addition. To maintain a powder resistivity below 600 $\mu\Omega\cdot\text{m}$, the coal addition in co-coking coke should not exceed 30 %. The ash content of calcined co-coking coke increases with higher coal addition, but all five samples have ash contents below 0.6 %, generally meeting the requirements for anode-grade coke. The true density of calcined co-coking coke decreases with higher coal addition, with the highest value close to 2.0 g/cm^3 , observed in the sample containing 24.0 % coal, which generally meets anode-grade coke requirements. The co-coking coke with 24.0 % coal (GJ-5) was selected for further research on the calcination process technology of co-coking coke.

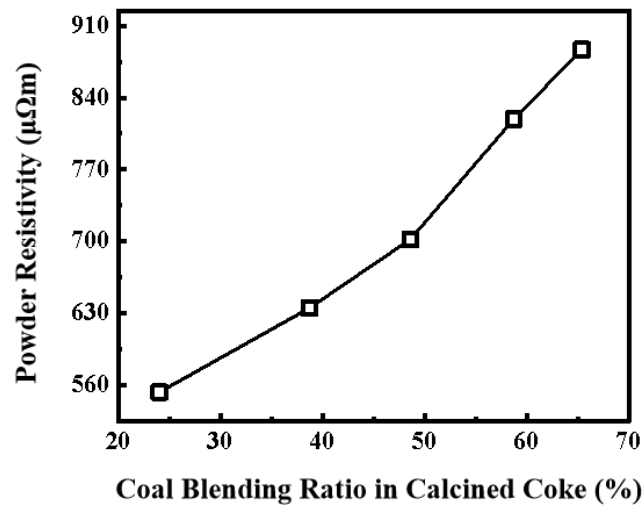


Figure 2. Effect of coal blending ratio on powder resistivity of co-coking coke.

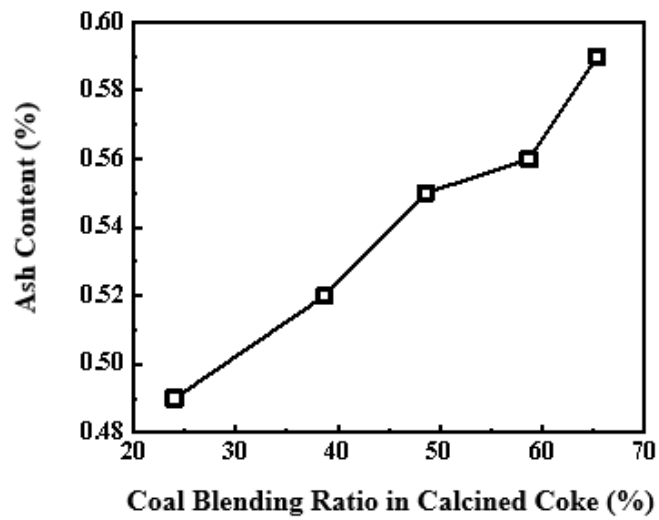


Figure 3. Effect of coal blending ratio on ash content of co-coking coke.

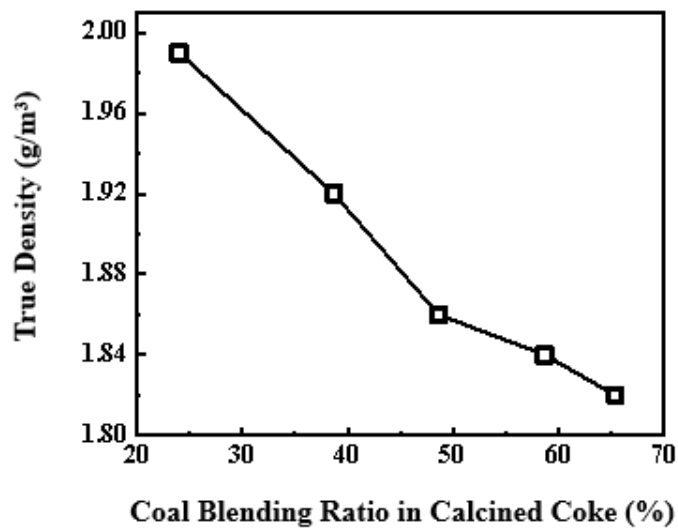


Figure 4. Effect of coal blending ratio on true density of co-coking coke.

3. Optimization Experiment of Co-coking Coke Calcination Process

3.1 Experimental Setup and Procedure

The experiment was conducted in a temperature-controlled pit-type high-temperature furnace. The co-coking coke (GJ-5) was placed into a corundum crucible, covered with its lid, and then placed inside a larger crucible. The larger crucible was filled with covering coke to prevent oxidation and then placed in the furnace chamber of the pit-type high-temperature furnace for electric heating and calcination. A total of five calcination tests were carried out, with high-temperature stages of 1150 °C, 1200 °C, 1250 °C, 1300 °C, and 1350 °C, each held for 3 hours. The resulting calcined coke was labelled DS1150, DS1200, DS1250, DS1300, and DS1350, respectively.

The calcined co-coking coke was sampled and analysed for powder resistivity, true density, air reactivity, and CO₂ reactivity.

3.2 Experimental Results and Analysis

The results of the calcination experiments are shown in Figures 5–8.

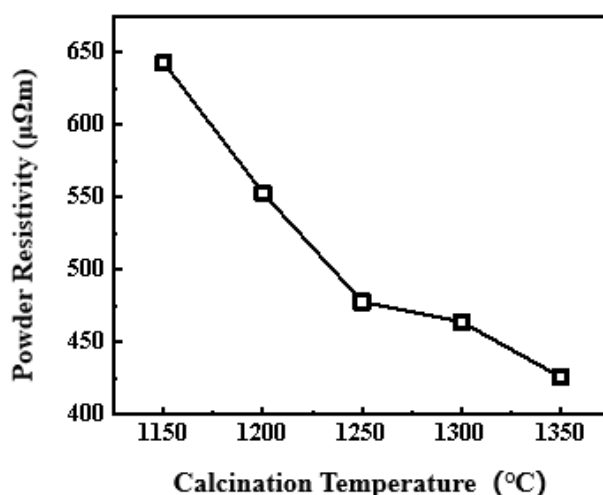


Figure 5. Effect of calcination temperature on powder resistivity of co-coking coke.

The analysis results show that the powder resistivity of calcined co-coking coke decreases with increasing calcination temperature. To maintain powder resistivity below 600 μΩ·m, the calcination temperature should not be lower than 1200 °C. The true density of calcined co-coking coke increases with rising calcination temperature at the beginning, reaching a maximum of 2.04 g/cm³ at 1300 °C, after which further temperature increases lead to a decline in true density. The air reactivity rate of calcined co-coking coke decreases with rising calcination temperature at the beginning, reaching a minimum of 0.18 %/min at 1300 °C. However, at higher temperatures, the air reactivity rate increases conversely, possibly due to significant desulfurization at high temperatures, which weakens the inhibitory effect of sulphur on the catalytic action of alkali metals in the carbon–air reaction. The CO₂ reaction residue of calcined co-coking coke increases with rising calcination temperature, peaking at 93.2 % at 1300 °C, after which a downward trend is observed. A comprehensive analysis of the variations in physicochemical properties with calcination temperature indicates that the optimal calcination temperature for co-coking coke is 1300 °C.

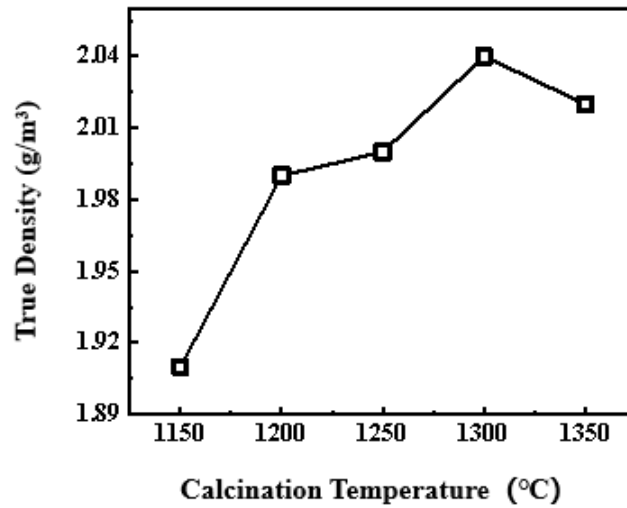


Figure 6. Effect of calcination temperature on true density of co-coking coke.

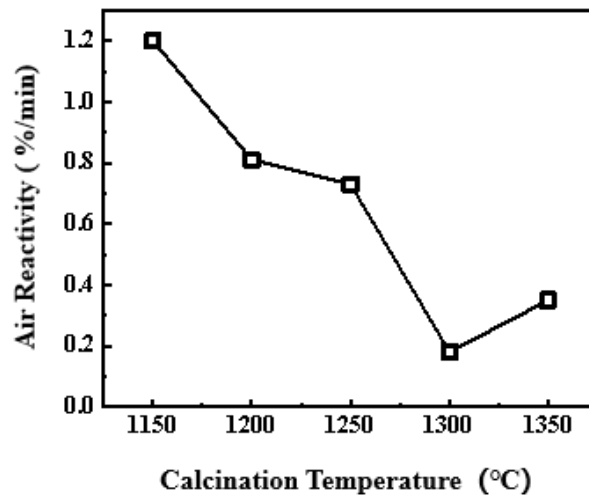


Figure 7. Effect of calcination temperature on air reactivity of co-coking coke.

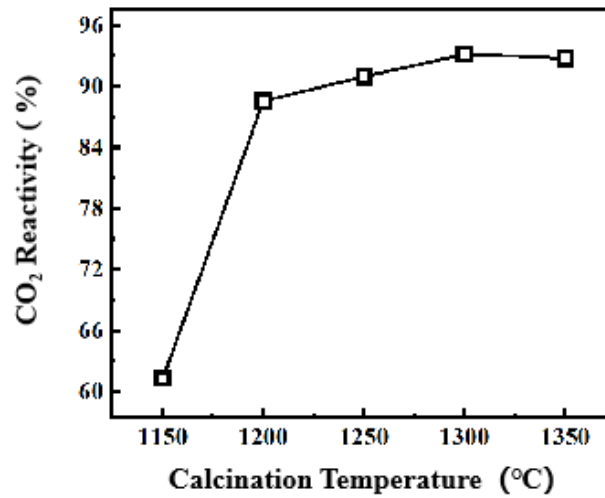


Figure 8. Effect of calcination temperature on CO₂ reactivity of co-coking coke.

4. Preparation and Performance Evaluation of Coal-Added Anodes

4.1 Preparation of Coal-Added Anodes

Prebaked anodes were prepared using co-coking coke DS1300, with the formulation shown in Table 4. The mixture was kneaded in a laboratory kneader, with a coal tar pitch content of 17.0 %. The kneaded paste was moulded into green anode samples by pressing. The green anode samples were baked in a pit-type calciner, with the baking curve shown in Table 5. The baked coal-added anodes were analysed for the physiochemical indicators, including ash content, bulk density, true density, electrical resistivity, compressive strength, CO₂ reactivity, and air reactivity.

Table 4. Formulation of coal-added anode samples.

Dry Mix Formulation	Weight Percent	Notes
4–2 mm	30 %	Weight percent refers to the proportion of material relative to the total dry weight. The purity of the powder feedstock is 57.5 %.
2–1 mm	19 %	
1–0 mm	13 %	
Powder Feedstock	38 %	

Table 5. Baking curve for coal-added anode production.

Temperature	Duration
30–250 °C	2 hours
250–650 °C	20 hours
650–950 °C	7 hours
950–1140 °C	5 hours
1140 °C	Holding for 7 hours

4.2 Analysis and Discussion of Coal-Added Anodes

The coal-added anodes were analysed for ash content, bulk density, true density, electrical resistivity, compressive strength, CO₂ reactivity, and air reactivity. The analysis results are summarised in Tables 6 and 7.

The analysis results show that the physicochemical properties of the prepared coal-added prebaked anodes all meet the requirements for Grade B products according to industry standards.

5. Conclusions

Experimental studies on the co-coking of low-ash coal and vacuum residue, as well as optimization experiments for the calcination process of co-coking coke, were carried out, and carbon anodes were produced in the laboratory using co-coking coke. The experimental results show that co-coking coke containing 24 % low-ash coal can basically meet the requirements for prebaked anode-grade coke. The suitable calcination temperature for co-coking coke is 1300 °C. The physicochemical properties of coal-added prebaked anodes produced with co-coking coke containing 24 % low-ash coal meet the requirements of industry standards.

Table 6. Conventional physicochemical properties of coal-added anodes.

Sample ID	Bulk Density /g.cm ⁻³	Electrical Resistivity /μΩm	Ash Content /%	True Density /g.cm ⁻³	Compressive Strength /MPa
1	1.477	59.1	0.51	2.04	38
2	1.482	58.5	0.46	2.03	
3	1.489	57.8	0.43	2.04	37
4	1.490	56.8	0.44	2.03	
Grade A Standard	1.56	57	0.5	2.05	35
Grade B Standard	1.53	62	0.7	2.03	32

Table 7. Air reactivity and CO₂ reactivity of coal-added anodes.

Sample ID	CO ₂ Reactivity			Air Reactivity		
	Gasification	Spalling	Residual	Gasification	Spalling	Residual
1	13.0	5.2	81.8			
2				18.2	9.4	72.4
3	12.6	5.3	82.1			
4				16.8	8.4	74.8
Grade A			85			
Grade B			80			

6. References

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