Effect of Calcined Coke Size on Pitch Pyrolysis Behavior
Nianbing Zhang,* Yahong Yu, Zhiying Li, Zhen Yao, and Wei Liu

ABSTRACT: Pitch coking determines the quality of pitch coke, which ultimately affects the quality of a carbon anode. In this work, green carbon anodes were studied by scanning electron microscopy (SEM), and the pitch pyrolysis process was tested using a custom-built pyrolysis device. The influence of the coke size on pitch pyrolysis was examined and the action law was analyzed. The results show that the outermost layer of the large size coke has a certain pitch thickness, the subouter layer is filled with a “mixture of fine particles and the pitch,” and the internal area is not soaked by the pitch. Meanwhile, the small particles are soaked and wrapped by the pitch. The pyrolysis dynamics analysis shows that with the increase in particle size, the activation energy gradually increases to 70.00 kJ/mol for 1−2 mm, then rapidly decreases to 31.88 kJ/mol for 3−4 mm, and finally slowly increases to 50.56 kJ/mol for 6−9 mm. When the particle size increases, the coke size <0.5 mm area is dominated by a specific surface area, the 0.5−2 mm area is mainly regulated by a combination of a specific surface area and a porous structure, and the >2−3 mm area is dominated by the porous structure.

1. INTRODUCTION
The carbon anodes used in the production of aluminum are manufactured by carbonizing the petroleum coke blended with a small proportion of coal tar binder pitch. As a carbon anode binder, pitch preheating melts the coal pitch and soaks the coke particles, thus providing the anode paste with good plasticity to ensure green carbon anode formation. Meanwhile, the high temperature during roasting allows pitch coking, fills the pores, and closely combines these materials with the coke. Thus, the carbon anode gains a certain mechanical strength to prevent breakage during electrolysis. However, the selective oxidation of the pitch coke during electrolysis causes the coking particles to fall off. Hence, the quality of the pitch coke is important in improving the carbon anode performance, and the process determines the quality of the pitch coke. The factors affecting the properties of the pitch coke are pitch quality, trace elements, additives, sulfur content in coke, heating process, and coke particles. To date, the effects of coke particles on pitch pyrolysis have never been reported. In this work, scanning electron microscopy (SEM) analysis was conducted for green carbon anodes with different coke sizes soaked by pitch. The pitch pyrolysis of different coke sizes after pitch immersion and green carbon anodes were tested using a custom-built pyrolysis device. The influence of coke size on pitch pyrolysis was examined and the action law was analyzed. These results can serve as a basis for carbon anode preparation.

2. MATERIALS AND METHODS

2.1. Materials. The chemical composition of the coal tar pitch obtained from the carbon factory of Chalco Guizhou Branch is shown in Table 1. The coke was also obtained from the same factory, and its composition is shown in Table 2. Coke particles of different sizes were obtained through screening.

2.2. Methods. 2.2.1. Soaking the Coke Particles with Pitch. Coke particles of different sizes were sieved and selected. Fifty grams of coke was placed on the screen in a blow-air drying box for heating at 170 °C for 5 min. The heated coke particles were...
placed in a powdered pitch to ensure that the surface of the coke particles had adhered to and wrapped a certain amount of pitch. The excess powdered pitch was sieved. The coke particles were placed in a powdered pitch to ensure that the surface of the coke particles had adhered to and wrapped a certain amount of pitch. The excess powdered pitch was sieved. The coke particles were placed in a powdered pitch to ensure that the surface of the coke particles had adhered to and wrapped a certain amount of pitch. The excess powdered pitch was sieved. The coke particles were placed in a powdered pitch to ensure that the surface of the coke particles had adhered to and wrapped a certain amount of pitch. The excess powdered pitch was sieved. The coke particles were placed in a powdered pitch to ensure that the surface of the coke particles had adhered to and wrapped a certain amount of pitch. The excess powdered pitch was sieved. 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particles has a certain pitch layer thickness (Figure 2a in region 2). The subouter shape of large particles can be seen in Figure 2a in area “4” amplification. Area “5” in Figure 2b,c shows that the large particles of the pores are filled by “the mixture of fine particles and the pitch.” Irregular closed holes are found inside the large particle coke, as shown in area “6” in Figure 2c. This finding indicates that pitch fails to penetrate during immersion, and this part of the pores is retained in the carbon anode product.

After different particles are charred by the pitch, the distribution of the pitch in the green carbon anode has the following characteristics: for the large particles, the outermost layer has a certain thickness of the pitch layer, the subouter layer is filled by the mixture of fine particles and pitch, and the internal area is not soaked by the pitch (Figure 2e). Meanwhile, the small particles are soaked and wrapped by pitch, as shown in Figure 2d.

3.2. Thermal Dynamics Analysis of the Pitch. Under the heating rate of 10 °C/min, 10 g of the pitch was placed into the crucible and heated to 1050 °C (Figure 1). Pitch quality was measured with the change of temperature during heating, and the test results are shown in Figure 3. The pyrolysis temperature...
of the pitch is between 500 and 700 °C, and the temperature interval was calculated using formula 8. The best linear relationship was obtained with assumed values of different reaction orders. The fitting linear correlation coefficient (R²) of the pitch is 0.99, indicating that the pyrolysis model is in good agreement with the actual process. On the basis of pyrolysis data for the best linear relationship, the apparent activation energy can be calculated using the line slope of the b-value, as shown in Table 3. According to the actual carbon anode preparation conditions, the coke value (CV) at 1050 °C can be directly read using the test results, as shown in Table 3. Pitch pyrolysis results show that the apparent activation energy is 82.31 kJ/mol and CV is 58.70%.

3.3. Effect of Different Coke Sizes on the Pitch Pyrolysis Process. The coke particles soaked in pitch are shown in Section 2.2. Under the heating rate of 10 °C/min, 50 g of coke with different sizes after immersion in pitch were placed in the crucible and heated at 1050 °C. Pitch quality after immersion in the coke particle was measured with the change of temperature during heating, and the results are shown in Figure 4. The pyrolysis temperature of pitch is also between 500 and 700 °C, and the temperature interval was also calculated using formula 8.

![Figure 4. Thermogravimetric (TG) curves of different coke sizes after pitch soaking under 10 °C/min.](https://dx.doi.org/10.1021/acsomega.0c03183)

On the basis of the pyrolysis data of the best linear relationship, the apparent activation energy can be calculated by the line slope of the b-value, as shown in Table 4. According to the actual carbon anode preparation conditions, the CV of different coke sizes at 1050 °C can be directly read through the test results, as shown in Table 4. The pyrolysis pitch mass (PPM) shown in Table 4 can be calculated by the difference between the mass after pyrolysis and the initial coke mass.

3.4. Pitch Pyrolysis of the Green Carbon Anodes. The method of determining the pitch pyrolysis of green carbon anodes is discussed in Section 2.2. The experimental green anode mass was 344.6 g, the heating rate was 10 °C/min, and the temperature was up to 1050 °C. Changes in pitch pyrolysis quality were measured, and the results are shown in Figure 5. The quality of the carbon anode after pyrolysis was 322.2 g, the pyrolysis temperature of pitch was between 550 and 750 °C, and the temperature interval was also calculated using formula 8. On the basis of the pyrolysis data of the best linear relationship, the apparent activation energy can be calculated by the line slope of the b-value, and the CV at 1050 °C can be directly read through the test results. The pitch pyrolysis in the green carbon anode results shows that the apparent activation energy is 116.40 kJ/mol and the CV is 56.20% (Table 3).

3.5. Effect of Different Coke Sizes on Pitch Pyrolysis. BET was applied to determine the specific surface areas of different coke sizes, and the results are shown in Figure 6. When the particle size increases, the specific surface area gradually decreases from 3.3521 m²/g (less than 0.15 mm) to 1.4775 m²/g (0.25–0.5 mm) and continuously decreases to 1.3897 m²/g (2–3 mm).

As stated in Section 2.2.1, different grain sizes were soaked with pitch, and SPM was obtained. The results are shown in Table 4 and Figure 6. When the particle size increases, the SPM decreases from 14.25 g (less than 0.15 mm) to 17.00 g (0.25–0.5 mm), then decreases to 4.60 g (2–3 mm), and finally slowly increases to 8.60 g (6–9 mm).

The pitch pyrolysis of different coke sizes was detected using the pitch pyrolysis device, and the test results are shown in Figure 6. The apparent activation energy of pitch is shown in Table 4 and Figure 6. When the granularity increases, the activation energy gradually increases to 70.00 kJ/mol (1–2 mm), then rapidly decreases to 31.88 kJ/mol (3–4 mm), and finally slowly increases to 50.56 kJ/mol (6–9 mm).

Under the roasted temperature condition of the green carbon anode, the quality after pitch pyrolysis was selected at 1050 °C for CV; the CV is shown in Table 4 and Figure 2. When the particle size increases, the CV increases to 57.99% (0.25–0.5 mm), then decreases to 53.72% (1–2 mm), and rapidly increases to 58.45% (2–3 mm). The final CV shows a decreasing and subsequent increasing trend. PPM was calculated according to the accumulation of SPM and CV. Numerical changes are not evident because CV is within the

**Table 4. Linear Fit of Different Coke Sizes by Pitch Infiltrated, Activation Energy, and CV**

| sample          | a   | b    | R²  | N  | Eₐ/(kJ mol) | CV/(%) | SPM/(g) | PPM/(g) |
|-----------------|-----|------|-----|----|-------------|--------|---------|---------|
| <0.15 mm + pitch| −9.291 | −5902.96 | 0.96 | 0  | 49.08       | 56.21  | 14.25   | 8.01    |
| 0.15–0.25 mm + pitch | −9.435 | −5779.58 | 0.93 | 0  | 48.05       | 56.88  | 14.1    | 8.02    |
| 0.25–0.5 mm + pitch | −9.242 | −5894.77 | 0.96 | 0  | 49.01       | 57.99  | 17.00   | 9.86    |
| 0.5–1.0 mm + pitch | −7.809 | −7247.58 | 0.96 | 0  | 60.26       | 57.94  | 12.30   | 7.13    |
| 1.0–2.0 mm + pitch | −6.490 | −8419.74 | 0.97 | 0  | 70.00       | 53.72  | 12.10   | 6.50    |
| 2.0–3.0 mm + pitch | −9.314 | −5372.84 | 0.99 | 0  | 44.67       | 58.45  | 4.6     | 2.69    |
| 3.0–4.0 mm + pitch | −11.095 | −3835.01 | 0.99 | 0  | 31.88       | 54.23  | 5.55    | 3.01    |
| 4.0–5.0 mm + pitch | −10.449 | −4518.90 | 0.99 | 0  | 37.57       | 52.41  | 5.40    | 2.83    |
| 5.0–6.0 mm + pitch | −9.961 | −4767.50 | 0.99 | 0  | 39.64       | 52.41  | 5.80    | 3.04    |
| 6.0–9.0 mm + pitch | −8.790 | −6081.66 | 0.99 | 0  | 50.56       | 54.07  | 8.60    | 4.65    |
range of $53.72$–$58.45\%$. These results show that PPM follows the same law as SPM.

When the particle size increases, the coke particle size <0.5 mm area can provide a coking interface for pitch coking, i.e., "A area," which is dominated by the specific surface area. The coke particle size >2–3 mm area is dominated by the porous structure area, i.e., "C area," where the effect is related to the pore size, porosity, and pore distribution. The coke particle size of 0.5–2 mm area, i.e., "B area" is mainly controlled by a combination of the specific surface area and the porous structure.

According to SEM micromorphology results, the pitch pyrolysis of the green carbon anode involves the following: the pitch pyrolysis in Figure 2a, region "2," of the outermost layer of the pitch immersion layer; the pitch pyrolysis of "small particles and pitch mixture," as shown in Figure 2d; the pitch pyrolysis in Figure 2a, region "4," of the subouter small particles and pitch mixture layer; and the interaction between different particles. Therefore, the pitch pyrolysis of the green carbon anode is the result of the combination of many factors. This observation can be supported by the following experimental results. The pitch CV of the green carbon anode is $56.2\%$, which is within the $53.72$–$58.45\%$ range for coke with different particle sizes. The apparent activation energy of the pitch pyrolysis of the green carbon anode is $116.40$ kJ/mol, which is larger than the $31.88$–$70.00$ kJ/mol range for coke with different particle sizes and the $82.31$ kJ/mol for large-mass pitch.

4. CONCLUSIONS

(1) Different coke sizes are charred by the pitch. The outermost layer of large coke size has a certain thickness of the pitch layer, the subouter layer is filled by the mixture of fine particles and the pitch, and the internal area is not soaked by the pitch. Meanwhile, the small particles are soaked and wrapped by the pitch.

(2) Pitch pyrolysis data conformed to the dynamic model of formula 7. Pyrolysis dynamics analysis shows that when the particle size increases, the activation energy gradually increases to $70.00$ kJ/mol for 1–2 mm, then rapidly decreases to $31.88$ kJ/mol for 3–4 mm, and finally slowly increases to $50.56$ kJ/mol for 6–9 mm.

(3) When the particle size increases, the coke particle size <0.5 mm is dominated by the specific surface, 0.5–2 mm is mainly controlled by the mixing control of the specific surface and the porous structure, and >2–3 mm is dominated by the porous structure.

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Notes
The authors declare no competing financial interest.

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