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EFFECTS OF MIXING PARAMETERS AND PORES OF COKES ON PITCH ABSORPTION IN MAKING CARBON ANODE PASTES

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Abstract

Petroleum coke, used in anode manufacture has some porosity which tends to absorb pitch into the pores during green paste mixing. This is becoming more important as the sources for higher quality petroleum coke decrease and lower quality petroleum cokes with higher porosity must be used. A theoretical formula of pitch absorption coefficient has been deduced from the formula for the density of an aggregate mixture. Variations on the absorption coefficient and porosity were studied as a function of particle size of petroleum coke, mixing temperature, mixing time and the pitch content in the paste. The pitch absorption coefficient is found to be between 0.3 and 0.8. The information obtained may be useful in optimization of the pitch level in use of cokes with various absorption coefficients.

Introduction

As an aggregate of pre-baked anodes, petroleum cokes contain a lot of pores which absorb pitch when mixed with coal tar pitch (binder) to make a carbonaceous paste. The pitch absorbed by the pores of cokes may not improve the strength of the pitch binder in anodes while it can contribute to the anode properties, such as density and electric conductivity. At the same time, the absorption level of petroleum coke has a direct relationship with the amount of pitch used in the anode formula.

With the increasing cost and deterioration in quality of the raw material, it becomes important to better understand how to best utilise raw materials to make quality anodes. Many researchers [1-3] studied the mechanisms of pitch/ coke interactions at the mixing stage using a spreading drop test, which showed pitch wetting behavior was related to both pitch surface tension and pitch viscosity. However, this method has some unsolved issues, such as the existing pitch wetting procedures, the degree of variation of test results and the sensitivity to even minor changes in experiments. Kravtzova [4] improved the method where the test procedure looks for the coefficient of pitch infiltration which was not dependent on factors such as the mass of pitch/coke, the shape or size of coke and the testing container material.

The absorption level of petroleum coke has a direct relationship with the amount of pitch used in an anode formula, but so far there is no good method to measure the pitch content absorbed into the coke pores. In the Technical Specifications for Construction of Highway Asphalt Pavements, the effective relative density of aggregate was used to calculate the asphalt absorption coefficient [5]. The aim of this work is to develop a testing method by combining the pitch absorption coefficient measurement and image analysis to determine the pitch amount absorbed into the petroleum coke during the green paste mixing.

In this paper the total porosity, open porosity and closed porosity of the petroleum coke was measured using image analysis. The particle size of petroleum coke, pitch content in the paste, mixing temperature and mixing time were studied for their effects on the absorption content of coke pores. The result will offer guidance on more accurately evaluating the amount of pitch that should be used in the anode manufacturing process with reasonable design of kneading parameters for the cokes with various porosities.

Experiment

Materials

The petroleum coke and pitch used in the experiments was provided by Sunstone Development Co. Ltd. The real density of the calcined coke was 2.05 g/cm^3. The pitch had a softening point of 103 °C and its density was 2.05 g/cm^3.

Measurements of Coke Density and Porosity

The apparent density is defined as the ratio of the mass of a particle over its external enveloped volume, which includes the internal pores. A known mass of particles was impregnated with resin under vacuum in a 2.2 cm diameter mold. The height of the impregnated samples was measured to calculate its volume. The samples were then sectioned vertically, and the marked surfaces were polished as shown in Figure 1.

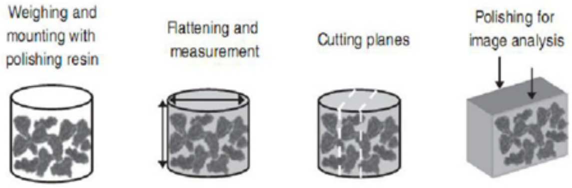

Figure 1. Schematic illustration of the procedure for measurement of apparent density of particles using image analysis.

Figure 2 illustrates a series of metallographical pictures of petroleum cokes with varying size fraction. The area fraction of particles on the polished surfaces was determined by image analysis. The average area fraction was extrapolated to volume fraction and multiplied by the sample volume to obtain the apparent volume of coke particles. With the mass and volume of coke particles, the apparent density (ρ_A) can be obtained [6, 7]. The real density (ρ_R) of coke was measured according to technical standard YS/T587.9-2006) and the pycnometer density (ρ_P) was determined with technical standard YS/T63-2006).

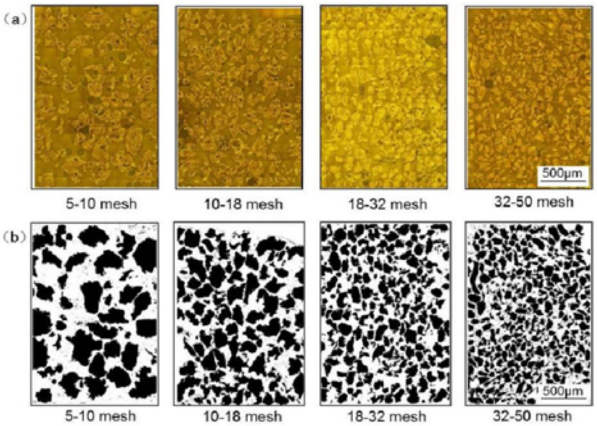

Figure 2. Metallographical pictures of petroleum cokes: (a) the original and (b) their binary images.

Volume fractions of total porosity, open porosity and closed porosity of cokes can be calculated through Equations (1) to (3):

$$\text{Total porosity}=\frac{\rho_R-\rho_A}{\rho_R}\times 100 \quad (1)$$

$$\text{Open porosity}=\frac{\rho_P-\rho_A}{\rho_P}\times 100 \quad (2)$$

Closed porosity=Total porosity-Open porosity (3)

Testing Absorption Coefficient

The absorption coefficient, C, was calculated through testing the density change before and after the coke and pitch mixing. After the mixing process, the pitch filled part of the open pores of the coke, as shown in Figure 3. The mass of the mixture had two parts, the mass of coke (M_{co}) and the mass of pitch (M_{pi}). The volume of the mixture included four parts: the volume (V_{co}) of coke aggregate, the volume (V_{cp}) of the closed pores in cokes, the volume (V'_{op}) of open pores not filled by pitch and the volume of total pitch (V_{pi}).

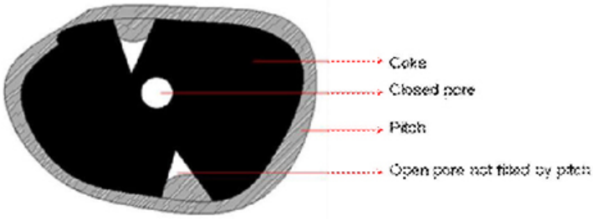

Figure 3. A schematic drawing of the mixing between petroleum coke and pitch.

The density of the pitch was known and the density of the mixture (ρ_{ag}) is measured as in [8]. After cooling, the green paste from the mixer was carefully crumbled to avoid breaking of coke particles, and the density was tested by the impregnation method (JTG E42-2005) [9]. The density of paste (ρ_{ag}) is defined by Equation (4), and the absorption coefficient, C, is calculated by Equation (5):

$$\rho_{ag}=\frac{M_{co}+M_{pi}}{V_c+V_{cp}+V'_{op}+V_{pi}} \quad (4)$$

$$C=(1-\frac{V'_{op}}{V_{op}})\times 100\% \quad (5)$$

Results and Discussion

Characterization of Coke Pores

Table I shows the density and porosity for different fractions of cokes. In Figure 4, the apparent densities of the coke particles are presented with various fractions of cokes. As expected, the pores within the particles were annihilated during size reduction and thus the apparent density increased with reducing the particle size This is confirmed by Figure 5 and Figure 6, where the fraction of total porosity, open porosity and closed porosity all decreased with decreasing the particle size of the petroleum cokes.

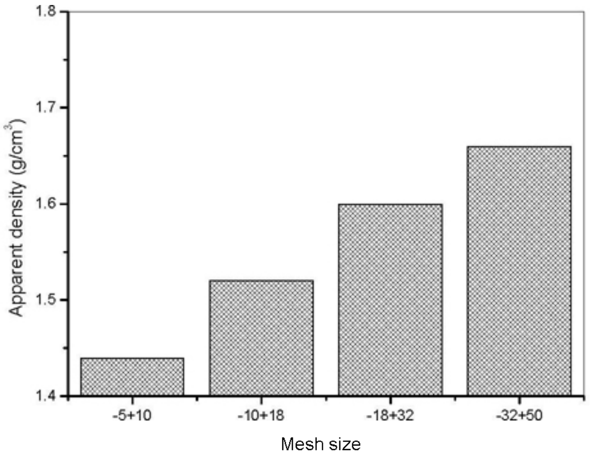

Figure 4. Apparent density vs. varying size fractions of cokes in carbon anode paste.

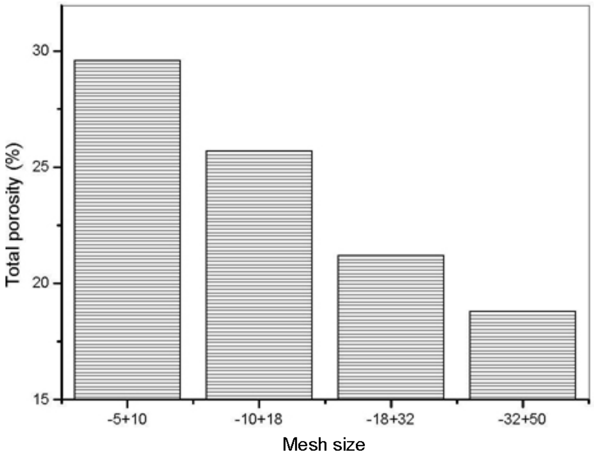

Figure 5. Total porosity vs. size fraction of cokes in carbon anodes paste.

Table I. Density and Porosity of the Anode Samples with Various Coke Fractions.

Mesh size	Real density (g/cm^3)	Pycnometer density (g/cm^3)	Apparent density (g/cm^3)	Total porosity (%)	Open porosity (%)	Closed porosity (%)
-5+10	2.05	1.85	1.44	29.6	22.2	7.4
-10+18		1.90	1.52	25.7	20.0	5.7
-18+32		1.94	1.60	21.2	17.5	3.7
-32+50		1.97	1.66	18.8	15.7	3.1

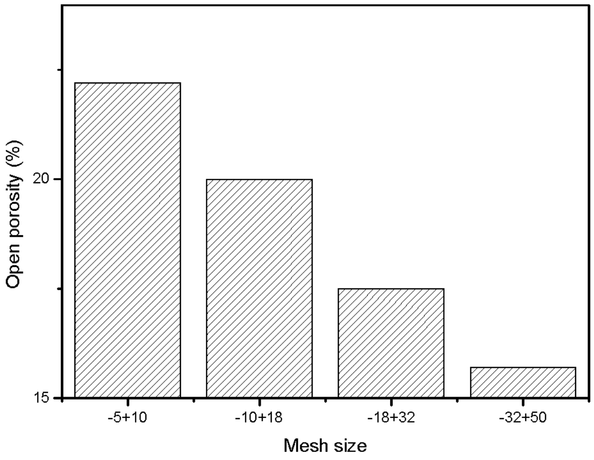

Figure 6. Open porosity vs. size fractions of cokes in carbon anode pasts.

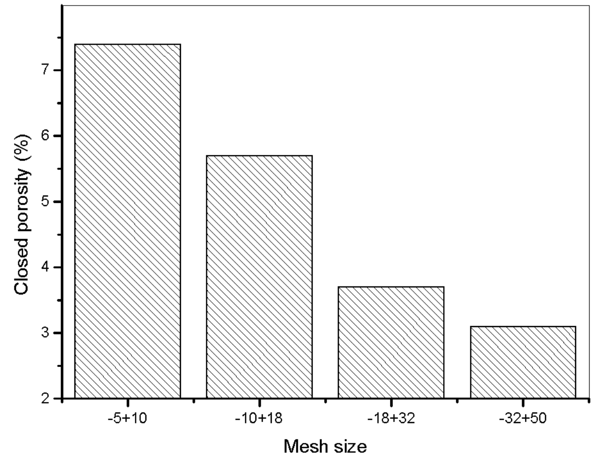

Figure 7. Closed porosity vs. size fractions of cokes in carbon anode pastes.

Absorption Coefficient

The petroleum cokes were mixed with pitch under specific conditions to form carbon anode pastes, and their density was measured to assess the state after absorbing the pitch in the open pores of coke aggregates. Then the absorption coefficient C of coke aggregates was calculated through Equation (5).

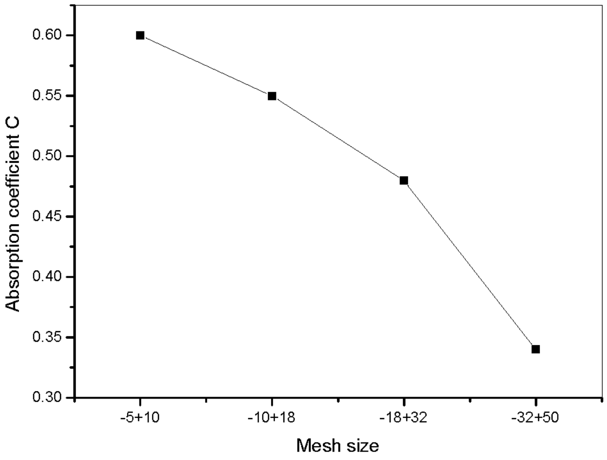

Figure 8. Absorption coefficient C vs. size fractions of cokes in carbon anode pastes

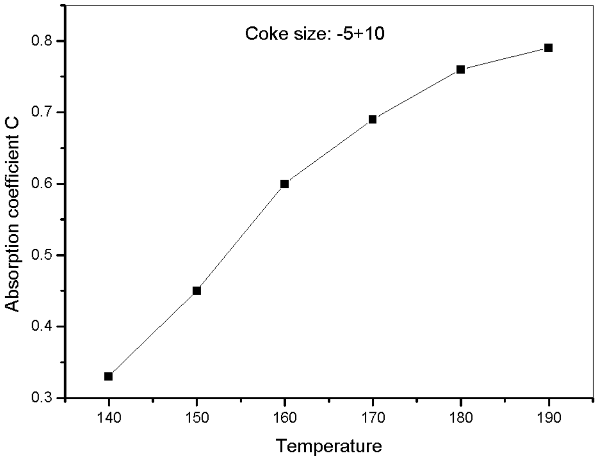

Figure 9. Absorption coefficient C vs. various mixing temperatures for carbon anode paste (mixed with 15% pitch for 5 min.)

Figure 8 shows that the absorption coefficient C changes with the size fraction of the cokes. The coke with size -5+10 had a large open porosity and a high absorption coefficient C, suggesting that the cokes with large size could absorb more pitch. This size coke was used in the later experiments for investigating other parameters.

Figure 9 shows the resulting absorption coefficient C of coke aggregates (-5+10) mixed with 15 % pitch at temperatures ranging from 140 °C to 190 °C. With increasing temperature, the absorption coefficient C increases. This is because more pitch has absorbed into the pores of the coke, as pitch viscosity lowers when the mixing temperature rises.

The absorption coefficient C can be higher, as shown in Figure 10, with increasing the pitch content in the carbon anode paste. However, this trend may not last long after the pitch content becomes higher than 15%. It seems that the pitch absorption may not increase as much as expected when larger amounts of pitch are added to the paste. This phenomenon is similar to the situation as described by Vanvoren [10], where the increased pitch content did not result in a deep penetration into the coke pores, but the filling of inter-granular voids among the coke aggregates.

Figure 11 demonstrates a trend of the absorption coefficient C increasing with prolonged mixing time. In general, a longer mixing time can achieve an even distribution of pitch and coke particles to enhance the filling of pitch into the voids among the coke particles. This should increase the density of the carbon anode paste.

The absorption of pitch into the pores of cokes is driven by capillary pressure, where the process is complicated by the non-uniformity of the pore structure and many other factors. Wade and co-workers [11, 12] had studied the absorption of various hydrocarbons and water into evacuated porous glass (Vycor). According to their work, the absorption rate on a volume basis into an evacuated porous sphere can be expressed as:

$$-\frac{1}{3}C-\frac{1}{2}[(1-C)^{\frac{2}{3}}-1]=t_r \qquad (6)$$

t_r is a reduced time given by:

$$t_r=\frac{KPt}{R^2\mu} \qquad (7)$$

where K is Darcy's Law permeability; P is capillary pressure; T is time of absorption; R is radius of sphere; and μ is fluid viscosity.

For a circular cylindrical pore of radius r:

$$P=\frac{2\sigma\cos\theta}{r} \qquad (8)$$

$$K=\frac{r^2}{8} \qquad (9)$$

Equations (6) and (9) show that the absorption process is governed by the fluid surface tension (σ), contact angle (θ), viscosity (μ), as well as the pore radius (r), and sphere size (R). Important aggregate properties are the particle size (R) and permeability (K).

Figure 12 shows absorption coefficient C changed as a function of t_r, which indicates that the mixing time required may also depend upon many other parameters relating to the properties of the pitch (see Equation 7).

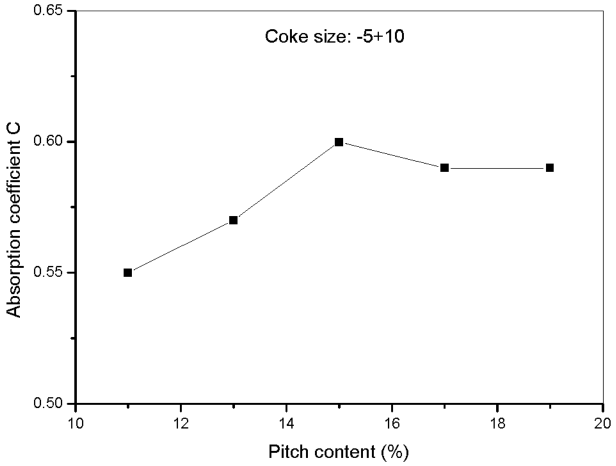

Figure 10. Absorption coefficient C vs. various pitch contents in carbon anode paste (mixed at 160 °C for 5 min.)

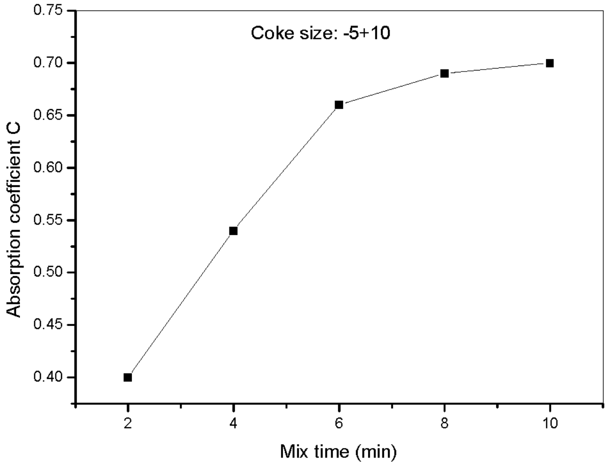

Figure 11. Absorption coefficient C vs. varying mixing time for carbon anode paste (with 15% pitch at 160 °C).

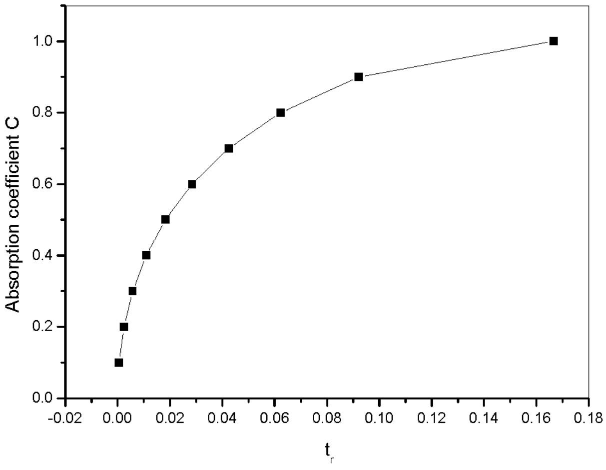

Figure 12. Absorption coefficient C changes as a function of t_r.

for carbon anode paste

The large coke particles have a big radius which can lead to a small t_r, but the large coke particles have more porosity and higher K (Darcy's Law permeability) which also produce a bigger t_r, As the mixing temperature increases, the capillary pressure increases while the pitch viscosity decreases, t_r and absorption coefficient C increase (Figure 9). When the other conditions remain unchanged, the extended time of mixing gives a higher t_r value that increases the absorption coefficient C.

The amount of pitch used in anode paste manufacture has a direct relationship with the absorption coefficient C. Higher absorption coefficient cokes require higher pitch additions. In this case, there will likely be less pitch available to fill the voids among the coke particles. The absorption coefficient C should be taken into account in optimization of pitch content, for instance, more pitch would be needed when the absorption coefficient C is higher for this coke.

Conclusions

1. The apparent density, the fraction of total porosity, the open porosity and closed porosity of the coke aggregates can be measured using image analysis, and all of them decrease with reducing particle size of petroleum cokes.

2. Coke aggregates with a higher absorption coefficient C will require more pitch addition during carbon anode paste manufacture. The pitch requirement can become higher with an increase in mixing temperature and prolonged mixing time.

Acknowledgements

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