Effects of Charcoal Addition on the Final Properties of Carbon Anodes

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Abstract

Wood Charcoal is an attractive alternative to petroleum coke in production of carbon anodes for the aluminum smelting process. Calcined petroleum coke is the major component in the anode recipe and its consumption results in a direct greenhouse gases (GHG) footprint for the industry. Charcoal, on the other hand, is considered as a green and abundant source of sulfur-free carbon with a massive worldwide production of more than 50 Mt per annum. Pre-treated charcoal was used to substitute up to 10 % of coke in the anode recipe in an attempt to investigate the effect of this substitution on final anode properties. The results showed deterioration in the anode properties by increasing the charcoal content. However, by adjusting the anode recipe this negative effect can be considerably mitigated, e.g. increasing the pitch content was found to be helpful to improve the physical properties of the anodes containing charcoal.

Keywords: Anodes; charcoal; petroleum coke; specific electrical resistivity; mechanical properties.

1. Introduction

All modern smelters use the Hall–Héroult process to electrolytically reduce the alumina dissolved in molten cryolite. In this process, carbon anodes are used to conduct high amperage direct electrical current necessary for smelting from the busbar to the electrolyte. Oxygen from alumina is discharged electrolytically and reacts immediately with the carbon anodes, producing gaseous carbon dioxide (CO_2) [1]. Calcined petroleum coke (CPC) is the major component in the anode recipe. Due to the changes in the oil refining industry [2], most coke supplies do not comply with anode specifications, which are essentially based on the upper limit of sulfur and heavy metal content, the density, the molecular structure, as well as the mechanical properties.

Being an abundant source of sulfur-free carbon [3], wood charcoal seems, at first glance, to be an attractive alternative for petroleum coke. Substitution of petroleum coke by charcoal in the anode recipe would reduce the fossil CO_2 emissions. Furthermore, the very low content of vanadium (V) and sulfur (S) in charcoal could allow the use of petroleum coke with higher S and V, thus decreasing the raw material cost. However, charcoal is characterized by its amorphous carbon structure and high concentration of inorganic minerals (Ca, Na). These undesirable properties result in a material with high reactivity to air and CO_2 in addition to low real and bulk density. Charcoal was investigated as raw material for anode production [4], the results showed significant deterioration in mechanical, electrical and reactivity of the anodes containing charcoal.

Hussein *et al.* [5] tried to improve the properties of raw charcoal via acid washing and heat treatment techniques. Heat treatment at elevated temperatures (1300 °C or higher) converted its carbon structure into a more ordered one. The calcined charcoal was found to have higher real density and lower specific surface area. In addition, performing an acid washing resulted in a significant depletion in its inorganic mineral content. A combination between acid leaching and calcination reduced both air and CO_2 reactivities of charcoal. Its air and CO_2 reaction profiles became comparable to those of the calcined petroleum coke. Substituting a portion up to 10 % of coke with pre-treated charcoal in the anode recipe did not show any negative effect on air and CO_2 reactivities of the baked anodes [5].

This work attempts to explore the effects of using the pre-treated charcoal as a raw material on the final anode properties. To fulfill the objective, wood charcoal was washed using 1 mol L^{-1} of hydrochloric acid (HCl) then calcined at the same temperature as the green petroleum coke is calcined, e.g. 1300 °C. Anode samples were made by substituting portion of coke fine fraction by the pre-treated charcoal. Mechanical and electrical properties of these anodes were measured and compared to those of reference anode entirely made of calcined coke and coal tar pitch. As the composition of the anode recipe was changed the by charcoal addition, the new anode recipe should be optimized. This can be done by changing the particle size distribution and/ or by changing pitch/coke mass ratio. During mixing process, pitch must coat the dry aggregate surface and be able to fill the pores. In this context, the effect of increasing the pitch content in the anode recipe on the electrical and mechanical properties was studied.

2. Materials and methods

2.1. Materials

Industrial calcined petroleum coke provided by Alcoa Inc. was crushed and classified into different size fraction as in Table 1. Commercially available maple wood charcoal was used as the charcoal source. The charcoal was first ball milled and sieved. Particle size of -400 mesh (-0.037mm) was selected for acid washing pre-treatment. The milled charcoal powder was soaked in 1 mol L^{-1} HCl (1 g charcoal per 100 ml HCl) in a round bottom flask, kept in an electrically heated sand bath. The process was performed at 65 °C for 3 h under continuous stirring. The mixture was then filtered and washed with hot distilled water. The recovered charcoal was then dried overnight at 100 °C. The acid-washed sample was calcined at 1300 °C in a tubular furnace under continuous argon flow. Chemical composition of the pre-treated charcoal and coke is presented in Table 2.

Table 1. Size distribution of coke particles

Particle size (US No)	-4 +8	-8 +14	-14 +30	-30 +50	-50 +100	-100 +200	-200 +400	-400
Particle size (mm)	-4.75 +2.36	-2.36 +1.40	-1.40 +0.600	-0.600 +0.300	-0.300 +0.150	-0.150 +0.075	-0.075 +0.038	-0.038
Wt.%	21.8	10	11.5	12.6	9	10.6	14.5	10

Table 2. Inorganic concentration and ash content of pre-treated charcoal and industrial petroleum coke

	Na (ppm)	Ca (ppm)	Si (ppm)	V (ppm)	Fe (ppm)	Ni (ppm)	S (%)	Ash (%)
Pre-treated charcoal	29	1685	312	0	58	2	0	0.55
Pet. Coke	100	130	120	360	460	250	2.13	0.35

Only one type of coal tar pitch was used as a binder for all the experiments in this work. Table 3 shows the physical properties and chemical composition of the pitch.

Table 3. Physical properties and chemical composition of the applied pitch

Mettler softening point (°C)	Quinoline insoluble (%)	Coking value (%)	Chemical Composition (ppm)					
			Pb	Fe	Ca	Na	S%	Si
109.5	16.5	58.8	93	209	71	48	0.55	254

2.2. Laboratory pilot scale anode preparation

Laboratory scale anodes were prepared using petroleum coke aggregates with specific size fractions as listed in Table 1 and coal tar pitch. The reference anodes were made completely of petroleum coke. A pitch/coke mass ratio of 16.2/116.2 was used to produce the samples. The preheating, mixing, pressing and baking parameters were selected based on the previous works [6, 7].

To produce anodes containing charcoal, the finest fraction of coke (-400 mesh) was substituted with pre-treated charcoal with the same particle size. Two sets of samples were prepared, having an overall content of 5 and 10% of charcoal. Hereafter, the reference anode and anodes containing 5% and 10% pre-treated charcoal are named as Ref A, AC-5% and AC-10% respectively. Two other sets of anodes were prepared using 10% charcoal, but with different pitch/coke mass ratios of 18, 20 and 22/100.

2.3. Characterization techniques

2.3.1. Green and baked anode apparent density

The apparent density of the green and baked anodes was measured according to ASTM D5502 – 00 (2010) [8] standard method. The height and diameter of the sample was measured at four different points with 90° apart, and then the mean value of these measurements was determined. The apparent density of the specimen was calculated by dividing its mass by its volume.

2.3.2. Specific electrical resistivity

This property was measured according to ISO 11713 standard method [9]. The specific electrical resistivity is defined as:

$$\rho = \frac{U \,.\, A}{I \,.\, L} \qquad (1)$$

Where: ρ = specific electrical resistivity, $\mu\Omega$m
U = voltage drop over the sample, V
A = cross section of the sample, m^2
L = distance between potential contacts, m
I = electrical current through the sample, A

The test was performed eight times for each sample, four times around the sample periphery with 90° rotation between each test. For the other four tests, the sample was rotated axially and the measurements were performed in the same way. The average of these eight values was reported as the specific electrical resistivity of the sample.

2.3.3. Compressive strength and Young’s modulus

Compressive strength was measured according to ISO 18515 [10]. A MTS Servo-hydraulic press was used to perform this test. A linearly increasing compressive force was applied until the sample was crushed. The deformation of the sample (strain) was calculated and the stress-strain curve was plotted. The maximum applied stress on this curve was reported as the compressive strength. Young’s modulus was determined from the slope of the stress-strain curve.

3. Results and discussion

Figure 1 shows the apparent density of the green and baked anode samples containing different amounts of charcoal. Both green and baked apparent density decreased as the percentage of charcoal increased. This behavior could be due to the relatively low bulk density of charcoal. In addition, as the charcoal has a relatively large surface area, the amount of pitch was probably not optimum to wet all the fine particles, affecting the viscosity of the binder matrix and its compaction behavior.

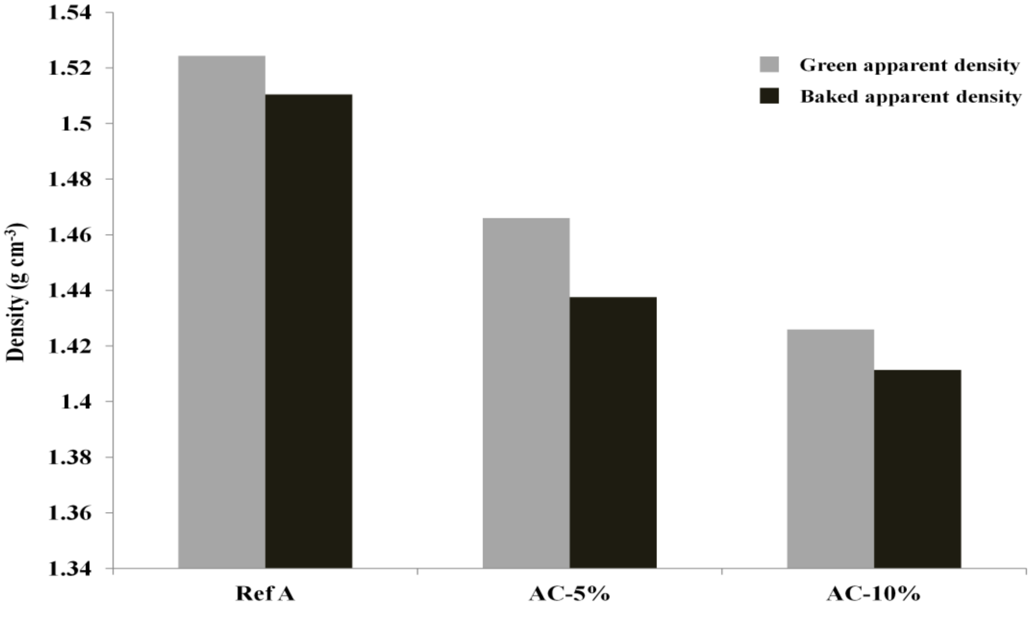

Figure 1. Apparent density for green and baked of anodes with different charcoal contents

Figure 2 shows the effect of charcoal substitution on the specific electrical resistivity and the compressive strength of the anode. Increasing the charcoal in the anode recipe resulted in remarkable deterioration in both electrical and mechanical properties of the baked anodes. This behavior was expected from the baked density results since the baked density directly affects both parameters.

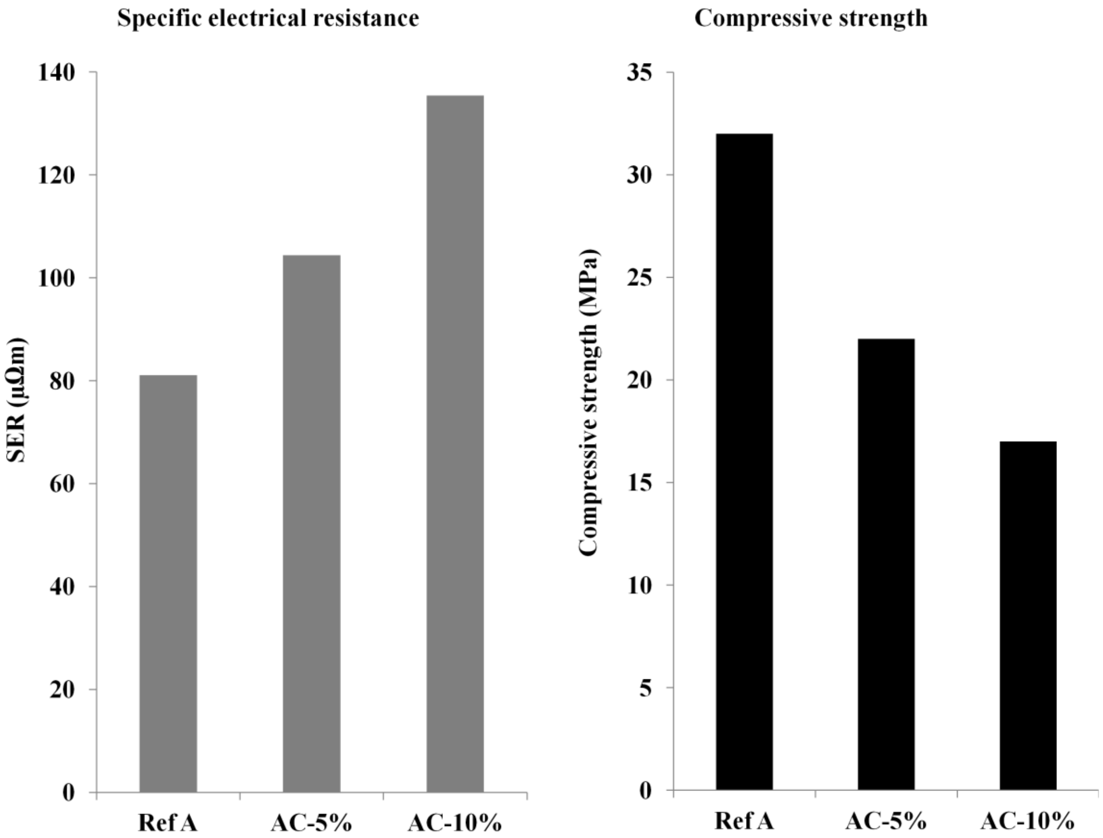

Figure 2. Specific electrical resistivity and compressive strength of anodes with different charcoal contents

3.1. Optimization of the anode recipe

One of the important parameters determining the anode paste compaction behavior and the anode density is the pitch/coke ratio. This ratio is usually determined empirically in the anode plants. The rational for the choice of optimum pitch content is the fact that pitch should wet the fine coke, providing a binder matrix with sufficient viscosity to enhance the compactability of the anode paste. Thus, the pitch content would depend on the amount of the fine fraction, as well as its specific surface area. Blain number of the fine coke is usually used as an indication of its specific surface area, and the pitch content is adjusted as a function of the Blain number.

By substituting charcoal in anode recipe, the Blain number is changed, so should be the pitch content. In order to reveal the effect of pitch content on the anode properties, four samples with 10% charcoal and different pitch/coke mass ratios of 16, 18, 20 and 22% were prepared. The same coke particle size, as presented in Table 1, was used to prepare these samples. The desired amount of pitch was added to the dry aggregate, then mixed and pressed using the same previously described conditions to produce green anodes with different pitch/coke mass ratio. The green apparent density for each sample was measured, and then all the samples were baked at the same time. After baking, the baked apparent density, specific electrical conductivity, Young's modulus and compressive strength were measured.

Figure 3 shows green and baked apparent densities of anodes containing 10% charcoal but different pitch/coke mass ratio. For comparison, the density of a reference anode is presented in the same figure. By increasing the pitch content by 2% (i.e. from 16 to 18%), a pronounced increase in the anode density was achieved. Gradual improvement in apparent density was noticed by further increasing in the pitch content. The same trend was observed for both green and baked apparent densities. As expected, this behavior can be attributed to the availability of more pitch for better wetting the fine particles and providing a suitable binder matrix for compaction. Although the negative effect of charcoal on the green and baked density is greatly mitigated by increasing the pitch content, the apparent densities of the anodes containing charcoal are still lower than that of the reference anode. In the best case (22% pitch) the density of the baked sample is 3% lower than that of the reference sample. This could be attributed to the low density (high porosity) of charcoal itself compared to that of calcined coke. The pore size of the charcoal is most likely too small to be totally filled with pitch during mixing.

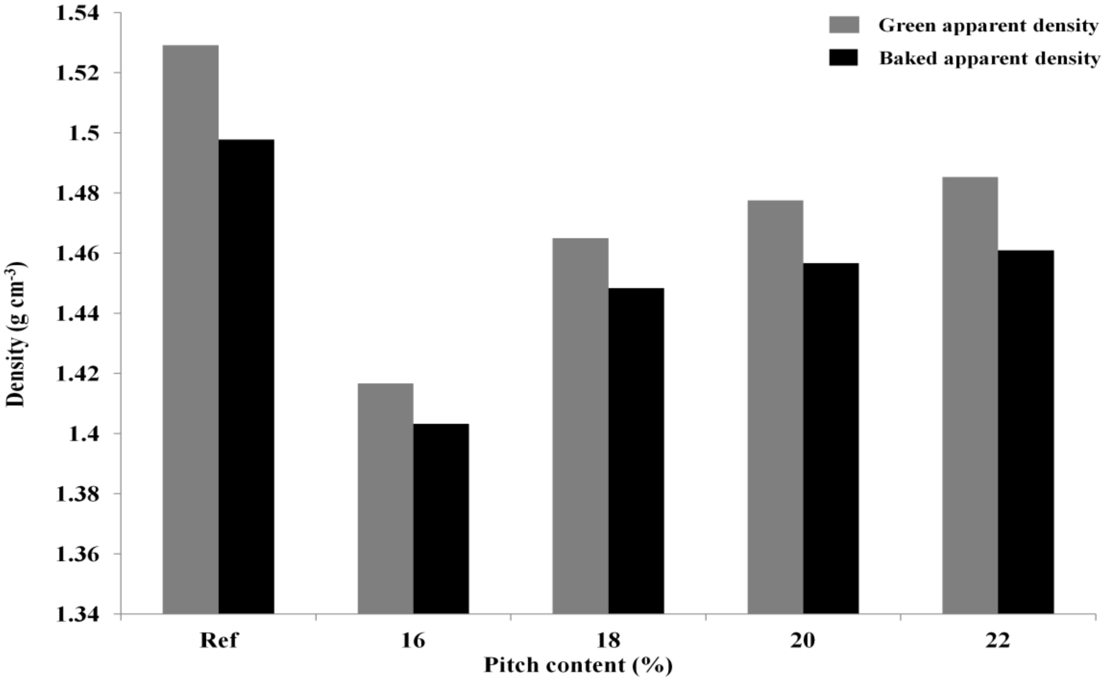

Figure 3. Influence of pitch mass ratio on green and baked apparent density of anodes contain 10% of charcoal compared to reference anode (Ref)

Figure 4 shows the effect of pitch content on the specific electrical resistivity (SER) of the anodes containing 10% of charcoal. These results suggested a direct relationship between SER and the anode density. As the density of the anode was improved by increasing the percentage of pitch, the specific electrical resistivity also had the same trend. SER of the anodes experienced reduction by 26.1 μΩm as the pitch percentage was increased from 16 to 18 %. Further pitch addition up to 22% led to slight reduction in SER.

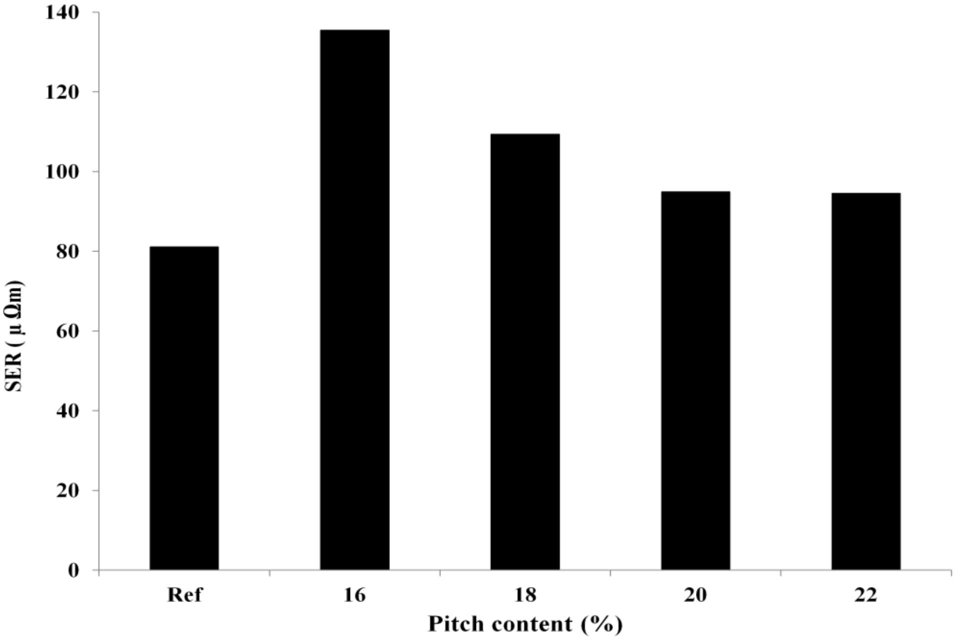

Figure 4. Influence of pitch percentage on specific electrical resistivity of anodes containing 10% of charcoal compared to reference anode (Ref).

Figure 5 shows the effect of pitch content on the mechanical properties of anodes. A significant improvement in both compressive strength and Young's modulus was achieved by increasing the pitch content. It is interesting to note that the compressive strength and Young's modulus of the baked samples with 22% pitch are the same as that of the reference samples, even though if its density is about 3% lower. These results suggest that the very negative effect of charcoal substitution on the mechanical properties of the anode can be fully neutralized by adjusting the pitch content.

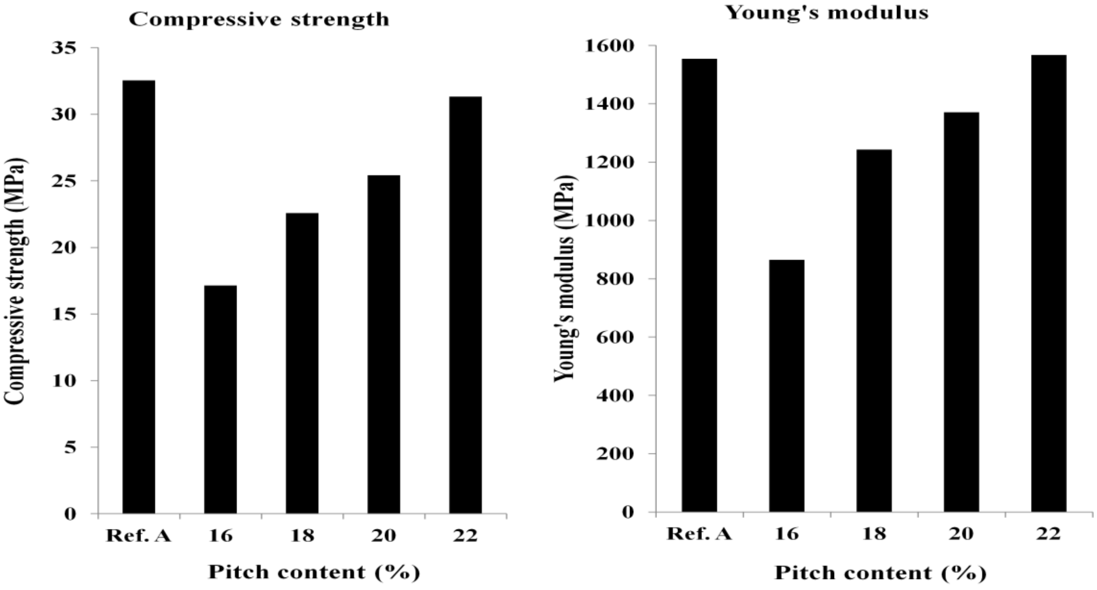

Figure 5. Effect of pitch percentage on compressive strength and Young's modulus of anodes containing 10% charcoal compared to reference anode (Ref).

4. Conclusions

Using pre-treated charcoal in the anode recipe resulted in a general deterioration in the anode properties. Increasing the charcoal content led to decrease in density, conductivity and strength of the produced anode. This behavior was attributed to the relatively large surface area and low density of the charcoal particles. However, increasing the pitch content was found to be helpful to improve the wetting of charcoal resulting in a significant improvement in the physical properties of the anodes containing 10% charcoal. The best baked anode in this study (22% pitch and 10% charcoal) showed a density of 3% lower than that of the reference anode, an electrical resistivity of 18% higher, and similar mechanical properties.

5. References

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