



Full Length Article

Modification of coke by different additives to improve anode properties



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ABSTRACT

Aluminum is produced in electrolytic cells using carbon anodes, which consist of a mixture of coke, pitch, and recycled carbon material. Anodes play an important role in aluminum production. The quality of raw materials can vary based on the source and the process parameters. In spite of the variations in the raw material properties, the industry has to maintain the quality of anodes. In order to manufacture good quality anodes, coke and pitch must interact well with each other. The affinity between these two components depends on good wetting properties, which will lead to good binding of the particles. The main objective of this work is to modify the coke in order to improve its wetting properties using different additives. An FT-IR study was done to identify certain functional groups in non-modified and modified coke as well as in pitch. The wetting tests were carried out using the sessile-drop method to measure the contact angle between cokes and pitch. Based on FT-IR and wettability results, an additive was selected and used for the fabrication of anodes, which were characterized before and after baking. The modification of coke with the selected additive improved the anode properties.

1. Introduction

Aluminum is produced by the electrolytic reduction of alumina. In this process, the carbon anodes are consumed according to Eq. (1).



The carbon anodes are made of dry aggregate (calcined petroleum coke, butts and recycled anodes) and coal tar pitch. The dry aggregate and pitch are mixed to form the anode paste at around 170 °C. The anode paste is compacted in a press or vibro-compactor to produce the green anode. The green anode is baked in a furnace to produce the baked anode. Calcined coke constitutes around 65–70% of the anode raw materials. Carbon anode cost is one of the major elements of the aluminum production cost, which could exceed 20% [1].

In recent years, the demand for anode-quality raw materials has increased due to the increase in aluminum production. The calcined petroleum coke and coal tar pitch are the main raw materials required for the production of carbon anodes. Properties of calcined coke are important since it is present in anodes in large quantity and directly affect the quality of baked anode. It is a solid by-product from oil refineries, representing some 2% of their overall revenues [2]. Thus, the quality of coke is not a primary concern for the refineries. Its quality depends on the crude oil, processes within the refineries, and calcination conditions. Thus, the quality of calcined coke can change. Pitch is also a by-product of the coal tar industry, and its quality can also

change. A good quality baked anode has high density, low electrical resistivity, low air and CO₂ reactivities, and good mechanical properties [3]. In spite of the variation in the raw material quality, the industry has to maintain the anode quality.

During anode manufacturing, calcined coke and pitch interact with each other in the mixing stage. The pitch, which is used as a binder, must not only fill the void space between particles, but also penetrate into the pores of calcined coke [4]. During baking, the pitch carbonizes and binds the coke particles together. This requires good wetting properties between the two components [5]. To achieve this, the surface tension must be reduced, and the interaction between coke and pitch needs to be enhanced. In order to obtain good anode, the raw material properties should be improved.

Wettability of a solid surface by a liquid is the function of the surface and interfacial forces which are both adhesive and cohesive (physical wetting) and the chemical interactions (chemical wetting). When a liquid makes contact with a solid surface, a spontaneous interaction takes place at the interface. The resulting pattern (contact angle) is used to determine the wetting properties of solid [6]. Wettability of coke by pitch controls the interactions between these two components. Improved wettability of coke by pitch helps pitch better penetrate into the pores of the coke as well as the void between different particles. Three kinds of chemical interactions are possible between coke and pitch: hydrogen bonding, electrostatic interaction, and acid-base reactions/condensation. These interactions require aromatics,

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charged centres, and heteroatom-containing (O, N, S) functional groups [5].

The interactions between the pitch and the particles depend on their properties. Among the properties of coke, the particle size, the texture, and the chemical functional groups on the surface considerably affect the wettability of coke by pitch. In order to quantify the wettability, the contact angle between the solid and the liquid surfaces is measured. If the value of the contact angle is greater than 90°, it is considered non-wetting. If the contact angle is smaller than 90°, it is considered that the pitch wets the solid surface [7].

Coke is one of the major raw materials used in the anode recipe. The interactions between coke and pitch influence the resulting anode density. Hence, the wettability of coke is an important parameter to consider during the mixing stage. In the work of Sarkar et al. [5], the influence of some coke properties on the wettability was investigated. It was observed that porosity, O₂ content, and the amount of C-S bond control the wettability of coke by pitch. Usually electronegative heteroatoms such as O, N and S help formation of hydrogen and covalent bonds between coke and pitch enhancing the coke-pitch interaction. Sarkar et al. [5] identified the role of C-S based on linear multivariable analysis. Jiang et al. [8] studied the effect of chemical treatment of petroleum coke by perchloric acid (HClO₄) and hydrogen peroxide (H₂O₂). After the modification, the structure of coke changed, and the specific surface area increased. The oxygen containing functional groups increased due to the chemical treatment. However, they did not use the coke for anode production.

Pitch is also one of the important raw materials in the anode production. Researchers have studied the improvement of the pitch wetting behavior by the use of surfactants and additives [9–12], and different organic compounds such as aceptophenone, dimethyl-naphthalene, acenaphthene, fluorine, diphenylene-oxide, α-methyl-naphthalene, and polymeric resins [13]. However, to our knowledge, there is no published study on the improvement of coke properties, and use the modified coke in the production of anodes.

The aim of this study is to improve the wettability of coke by pitch using additives. Based on the wettability test results carried out with and without additives, anodes were fabricated and characterized in the carbon laboratory of the UQAC Research Chair on Industrial Materials (CHIMI) to see the effect of coke modification on anode properties.

2. Experimental

2.1. Materials used

In this study, a calcined petroleum coke and a coal tar pitch were used. They were obtained from the industry. The softening point of the pitch was around 120 °C. Six additives and a solvent (aliphatic alcohol) were purchased from Sigma Aldrich. Organic additives which would not leave any inorganic residues during heating at high temperatures (i.e., during anode baking) were chosen. Measured quantities of additives were dissolved in the solvent and were then used to modify the coke. The melting and boiling points and the physical states at room temperature of the six chemicals are presented in Table 1. The generic names of the chemicals are presented in Table 1 hiding some detailed structural information due to confidentiality.

2.2. Modification of the calcined coke with additives

2.2.1. For wettability experiments

Calcined coke particles of size less than 1 mm were crushed in a laboratory hammer mill (Retsch SK 100). The crushed particles were sieved using a sieve shaker (Humboldt MFG) and –125 + 100 μm particles were collected. This particle fraction was modified using the additives for the wettability tests.

Addition of solid or aqueous suspension chemicals directly into coke does not ensure homogeneous mixing and the modification of all coke

Table 1
Properties of the additives.

Additive	Physical appearance	Melting point (MP), °C	Boiling point (BP), °C	Generic class	Health risk
A1	Liquid	7.5	248	Phenyl-alkyl-aldehyde	It is a skin irritant at high concentration, it is never been reported anywhere that this compound is a carcinogen or causes a long-term health hazard
A2	Aqueous suspension	0	310	Polyethylene-glycol-alkyl-ether	Long term exposure at high concentration can affect reproductive functions.
A3	Solid	122	283.5	Dioxin	It may cause skin lesions. Long-term exposure can affect immune system, nervous system, endocrine system and reproductive functions.
A4	Solid	145–170	High	Aliphatic dicarboxylic acid	It can cause blisters. Ingestion can cause sore throat, abdominal pain, vomiting, convulsions, etc.
A5	Solid	101	149	Benzophenone	It may cause irritation when comes in contact to skin, eye etc. There is no report of carcinogenic nature.
A6*	Aqueous solution	–114.2	–85.5	Hydrochloric acid	It is corrosive to the eyes, skin, and mucous membranes. Short-term exposure may cause respiratory tract irritation and pulmonary edema.

* The properties given are for hydrogen chloride (HCl) gas. Hydrochloric acid (HCl), which is aqueous (aq), forms when hydrogen chloride gas dissolves in water. Boiling and melting points of aqueous HCl depend on the concentration of HCl gas dissolved in the solution.

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