

Towards Utilization of Bio-binders in Carbon Anodes for Aluminum Industry

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Abstract

Carbon anodes are made of calcined petroleum coke and coal-tar-pitch as a binder. The fact that the classical binder is fossil, nonrenewable and mainly composed of carcinogenic polycyclic aromatic hydrocarbons, encourages researchers to develop a renewable and environmentally friendly binder to produce anodes. In this article, efforts to produce a green binder starting from a biomass-driven oil (bio-oil) and using this material to produce lab-scale anodes with acceptable properties are discussed. The bio-oil can be transformed into a thermoplastic material (bio-pitch) *via* heat treatment, under atmospheric pressure, to different temperatures using different heating rates. The ideal pitching conditions were selected based on the bio-pitch quality. In general, the bio-pitch showed better coke wetting but lower coking value comparing to the coal-tar-pitch. Laboratory-scale anodes were produced by mixing the bio-pitch with calcined coke. Reference anodes made of coal-tar-pitch, were fabricated using the same production conditions. Despite its low coking value, anodes made of bio-pitch showed similar density, electrical conductivity, and mechanical strength, comparing to reference samples. It was hypothesized that the good bio-pitch/coke adhesion resulted in a uniform volume shrinkage during the anode baking, which means shorter distances between the coke aggregates. The electrochemical performance of bio-pitch anodes was tested in a laboratory electrolysis cell. Compared to reference samples, bio-pitch anodes showed slightly lower reaction overpotential and higher electrochemical capacitance (good wettability by the molten electrolyte). So far, the lab-scale results are very encouraging, however more technical-economic studies will be needed to prove the feasibility of this approach in industrial practice. i.e., optimization of pitch demand, effect of bio-pitch in the presence of anode butts, anode performance in the industrial electrolysis cell, availability and cost of bio-pitch, and in-depth analysis of CO₂ reduction if such a technology is implemented.

Keywords: Carbon anode, Bio-pitch, Coal-tar-pitch, Anode quality, Electrochemical performance.

1. Introduction

In aluminum smelting, carbon anode acts as an electrical conductor and as a reducing agent in the electrochemical process. These anodes are made of fossil-based calcined petroleum coke and coal-tar-pitch (CTP) as a binder [1]. CO₂ produced during electrolysis is thus considered as a greenhouse gas. The production of one ton of aluminum gives rise to approximately 1.5 tons of fossil CO₂ [2]. In 2018 the annual production of primary aluminum reached about 64.3 million tons [3]. As an essential material in modern engineering designs, the annual output is predicted to rise as the global demand for aluminum is anticipated to double in the next ten years [4]. With the continuous increment in the aluminum production capacity, a massive release of CO₂ over the coming years will constitute a serious hurdle.

Coal-tar-pitch binder contains high concentrations of polycyclic aromatic hydrocarbons (PAH). These compounds are toxic to aquatic species even at low concentrations and some are carcinogenic [5]. Coal-tar-pitch is used primarily as a binder in the production of carbon anodes for aluminum smelters. However, this material is considered as an interesting candidate to produce high-value carbons such as synthetic graphite. The latter is a preferred material for electrodes in lithium-ion battery electric vehicles and in electric arc furnace for steel production. The environmental concerns and the limited supply of the coal-tar-pitch in addition to the growing demand in other sectors, represent challenges for aluminum industry to secure a high-quality binder for a reasonable price [6]. This situation attracted the research efforts toward generating an environmentally friendly binder using renewable and sustainable resources.

2. Bio-pitch Production and Properties

Bio-oil is one of the bio-mass pyrolysis products [7]. The pyrolysis-derived bio-oil is an acidic viscous liquid with a typical pH of around 2.5. It contains high oxygen and elevated moisture contents [8]. Heating the bio-oil to temperatures higher than 100 °C results in removal of water and light molecular weight fractions. The larger molecules react forming a tarry black residue, when cooled down to the ambient temperature, hardened into a solid with glassy characteristics (bio-pitch) [9].

The high oxygen content makes the bio-oil sensitive to the heat treatment process, as the crosslinking polymerization reaction could be triggered at relatively low temperatures [9]. Therefore, the final temperature, heating rate and pressure significantly affect the physical properties of the produced bio-pitch [10].

To identify the ideal heat treatment conditions, the bio-oil was heated to different temperatures using different heating rates (fast 1 °C.min⁻¹ and slow 0.5 °C.min⁻¹) under atmospheric pressure [11]. Figure 1 shows the effect of the final pitching temperature and heating rate on the physical properties of the produced bio-pitch. Increasing the heat treatment temperature from 160 °C to 200 °C resulted in a bio-pitch with elevated softening point (SP), higher quinoline insoluble (QI) and improved coking value (CV). This is most likely due to removal of more volatiles and condensation of larger molecules by increasing the temperature. Using slower heating rate to reach the final temperature also increased the softening point, the quinoline insoluble and the coking value of the resulting bio-pitch, as more volatile were eliminated over longer period [11].

It was found that using the slow heating rate to produce the bio-pitch, a thermoplastic binder can be produced within a small window of temperature ranges between 160 °C to 180 °C. Below this range, the bio-pitch was not solid at room temperature. At higher pitching temperatures, which could increase its coking value, the bio-pitch was a thermoset which preserves its solid nature even at high temperatures. This kind of binder is not fluid under the mixing condition and thus, an anode paste cannot be produced [11].

Table 1 compares the properties of the bio-pitch produced at 180 °C (0.5 °C.min⁻¹) and the coal-tar-pitch. Bio-pitch showed lower softening point (SP), coking value (CV) and primary quinoline insoluble (QI) than the CTP [11]. The low softening point of the bio-pitch means that an anode paste with acceptable consistency could be produced at lower mixing temperature. However, the low CV implies removal of more volatiles from the binder phase during the anode baking. It is expected that more volatiles result in higher porosity and gas permeability of the baked anode, therefore deteriorating its final properties. Presence of the QI fraction in the coal-tar-pitch is critical for the mechanical strength of the baked anode. These particles prevent the coalescence and alignment of the mesophase spheres, formed during the anode baking, in a larger lamellar structure. Due to the different carbonization mechanism of the bio-pitch, during the anode baking, the impact of the QI on the mechanical properties of the produced anodes could be insignificant.

5. Conclusions

In this work, a CO₂-neutral alternative binder was proposed to replace the fossil coal-tar-pitch binder in carbon anodes. The bio-pitch was produced *via* heat-treatment of the bio-oil at different temperatures and heating rates. The ideal heat treatment conditions were selected based on the balance between viscosity, softening point and coking value. The bio-pitch showed good interaction with calcined coke under the mixing conditions. The bio-pitch exhibited lower coking value and lower quinoline insoluble content than the coal-tar-pitch. Thus, it was expected that using the bio-pitch as a binder may negatively affect the density, electrical resistivity, and mechanical strength of anodes after baking. Therefore, laboratory scale anodes were produced using the bio-pitch as a binder.

The bio-binder was able to cover the outer surface of coke particles and penetrate to their open pores playing the same role of the coal-tar-pitch. Accordingly, an anode paste with acceptable characteristics was produced. Surprisingly, the density, electrical resistivity and the mechanical strength of the bio-pitch anodes were comparable to those of reference samples. The good adhesion between the coke particles and the bio-pitch resulted in a considerable volume shrinkage in the baked anodes. This uniform volume shrinkage was able of healing the probable anode's imperfections and mitigating the negative effect of the removal of high amounts of volatiles. The air and CO₂ reactivity of the bio-pitch anodes were slightly higher than that of the reference samples. This was attributed to the disordered carbon structure of the carbonized bio-pitch.

The electrochemical performance of carbon anodes made of bio-pitch as a binder was tested under electrolysis conditions. Compared to reference samples, bio-pitch anodes showed slightly lower reaction overpotential and higher capacitance. The low reaction over potential reduces the overall cell voltage, while high capacitance means good contact between the electrode and the electrolyte. Although the interesting lab-scale results, more work should be done to improve the properties of the bio-binder. For example, the coking value and the carbon structure of the baked binder can be enhanced by reducing the oxygen content in bio-oil during the biomass pyrolysis. Furthermore, the reactivity of the bio-binder against air and CO₂ must be reduced to avoid the excessive carbon consumption during electrolysis. This could be achieved by improving its carbon structure and by the addition of carbon-oxygen reaction inhibitors to the pyrolysis oil.

6. References

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