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Modification of biocoke destined for the fabrication of anodes used in primary aluminum production

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ABSTRACT

Calcined petroleum coke, recycled anodes and the coal tar pitch are the raw materials used to manufacture carbon anodes for aluminum production. In order to reduce greenhouse (GHG) emissions from the aluminum industry and to add a value to the residue of wood industry, a small part of the calcined petroleum coke, used for the production of carbon anodes, was replaced with biocoke produced from wood by-products. Since the addition of biocoke deteriorates the properties of carbon anodes, it was modified using an additive in order to assess if the modification can render biocoke more suitable for carbon anode production by modifying the surface chemistry of the biocoke.

Three samples of biocoke, unmodified, modified using 3% additive and modified using 4% additive, were produced and studied before and after modification to identify its effect on biocoke properties. First, the chemical characterization was carried out using X-ray photoelectron spectrometry (XPS) to verify whether the functional groups were added to the biocoke surface during the modification. To study the influence of the biocoke modification on the biocoke/pitch interactions, the wettability of the unmodified and modified biocokes by the coal tar pitch, which is used as a binder in anodes, were measured using sessile-drop test. After, the laboratory scale anodes were produced and their green and baked densities, electrical resistivity, air and CO_2 reactivities, and bending strength were measured. The results showed that the biocoke modification was effective. A number of new surface chemical groups were added to the biocoke coke surface. This improved the biocoke/pitch wettability, consequently affected the anode properties.

1. Introduction

Aluminum is considered as the most commonly used metal in the world. The alumina is reduced to aluminum via the Hall-Héroult electrolytic process. The anodes supply the necessary carbon for the alumina reduction according to the reaction given below [1]:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \quad (1)$$

Carbon anodes are produced using petroleum coke, butts (part of the anodes left after the electrolysis), as well as the anodes recycled due to their poor quality (dry aggregate), and coal tar pitch. The particles are sieved to have a desired particle size distribution. First, the dry aggregate and the binder are mixed to produce the anode paste. The paste is compacted using either press or vibro-compactor to manufacture the green anodes, which are then baked in large furnaces to produce the baked anodes used in electrolysis [1].

Canada is one of the major producers and exporters of aluminum with an annual production of around three million tons [2], 90% of which is produced in Quebec. In Canada, about 2 tons of CO_2 (equivalent) is generated per ton of aluminum [3]. The aluminum industry is making considerable efforts to improve their process and reduce GHG emissions [4]. The decreasing quality of coke [5] and environmental concerns lead to the exploration of different solutions to find alternative materials to petroleum coke.

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The wood industry, one of the important industries for Quebec and Canada, produces by-products (chips, sawdust, etc.). These by-products have been used mainly for the production of pulp and paper, but their uses have decreased significantly due to progress in the electronic media and the decline continues [6]. It is therefore important to find new markets to ensure the development of these by-products in the future. This will provide flexibility to the wood industry to accommodate the variation in demand by different users. One option is the production of biocoke from the residue which can be used in anode production. Even replacing a small portion of coke with biocoke could make a significant difference in environmental emissions since an aluminum smelter produces and uses several tons of anodes annually (approximately 1.5 million tons of carbon anodes per year in Canada based on approximately 0.44 tonne of carbon utilization to produce one tonne aluminum [7] and the total Canadian aluminum production [3]). This will be beneficial for the two major Canadian industries, namely, aluminum and wood industries. In addition, petroleum coke is calcined and there is GHG emission during its calcination. Therefore, the GHG emission will also be reduced, as less calcined petroleum coke will be used due to its partial replacement by biocoke.

Biocoke is an attractive carbon source because it is renewable and contains low amounts of ash and sulfur. However, there are challenges: its density is low, and its electrical resistivity and CO_2 reactivity are high [5]. During the mixing of the biocoke with the pitch, the pores of the biocoke are not filled with the pitch due to the poor wettability [8]. It has been suggested to replace only part of the fine fraction of coke with biocoke since the effect of porosity is much less for this fraction. The structure of biocoke was also found to be similar to that of the petroleum coke and the wettability depended on the type of pitch and the petroleum coke used [8,9]. However, it was found that the anode quality deteriorated with biocoke addition, which is not acceptable to the aluminum industry [10–12]. Biocoke is produced from wood residues at high temperatures by a chemical decomposition under neutral atmosphere which is called pyrolysis [8]. Its yield is about 25% of the initial biomass [13]. The efforts continued in recent years to find a way for using biocoke in anode production. Elkasabi et al. [14] calcined biocoke (10–27%) and petroleum coke in a rotary furnace in continuous mode. The overall sulfur, vanadium, and nickel contents of the coke blend decreased while phosphorous and titanium contents increased compared to those of the calcined petroleum coke. Authors claimed that all the anode properties are related to the crystallite thickness (Lc). An optimum blending ratio gives low metallic impurity concentration and a reasonable Lc for anode production. From this information, authors proceeded to carry out a life cycle impact analysis and predict the reduction in CO_2 emissions in aluminum industry. However, anodes were not produced from this blend; thus, the impact on anode properties are not known. Senanu and Solheim [15] wrote a review article on the biocoke in aluminum industry. The results of cited articles show that the anode properties decrease with biocoke addition with the exception of the articles by Huang et al. [16] and Hussein at al. [17]. The results of Huang et al. [16] indicated that it is possible to replace up to 3% of petroleum coke with biocoke and produce anodes similar to the anodes made with only petroleum coke. However, this study was carried out with one type of coke and pitch. Hussein et al. [17] obtained anodes with biocoke addition (3% and 10% biocoke, respectively) with the properties comparable to the anodes made with petroleum coke only. But they treated the biocoke with acid (HCl) and increased the pitch content of the anode. The feasibility of using HCl and its effect on the health in an aluminum plant was not discussed. The review article states that although there is a potential for using biocoke in anode production, there are still many challenges which need to be solved before it can be used in aluminum industry.

Anodes made without biocoke (standard) and with unmodified and modified biocokes have to be characterized to measure their properties and assess how the anode quality is affected with biocoke addition. The characterization tests include the measurement of green and baked anode densities, electrical resistivity, air and CO_2 reactivities, and mechanical resistance [1–3]. High anode density means more carbon available for the aluminum production, Also, the higher the anode density is, the lower the electrical resistivity is. However, too high density might result in anode cracking during baking, which in turn will yield increased resistivity. Low electrical resistivity means less power consumption during the electrolytic process. The air can filtrate in to the electrolysis cell from the top and react with the anode (air reactivity). Also, CO_2 produced during the electrolysis can react with anode (CO_2 reactivity) as can be seen from reactions (2) and (3). These reactions are undesired since they consume a part of the carbon which can otherwise be used to produce aluminum. Therefore, low reactivity is sought. Also, the anodes must be mechanically strong [1,18].

$$C + O_2 \rightarrow CO_2 \tag{2}$$

$$C + CO_2 \rightarrow 2CO \tag{3}$$

It is reported in the literature that some researchers modified the surface properties of pitches or cokes using different additives such as sulfur, divinylbenzene (DVB), etc. to improve pitch carbonization or increase its softening point or increase pitch coking value [19–22]. Other researchers used surfactants [23] to increase the pitch viscosity. However, these modifications were not aimed for the pitch used in anode production. Recently, Bureau at al. [24,25] modified four different pitches using three different additives and produced anodes. This study was carried out at the University of Quebec at Chicoutimi (UQAC) carbon laboratory. Additives shouldn't be toxic and expensive. They should have higher boiling point than the coke/pitch mixing temperature so that they stay in the mixture and improve the wettability during mixing. In addition, they shouldn't contaminate the anodes. That is to say, the components of additive should be released in gas form during anode baking. The results showed that the utilization of additive could improve certain anode properties such as bending strength, electrical resistivity and air/CO_2 reactivities. Utilization of surfactants did not improve the anode properties.

There are not many studies reported in the literature on coke modification. Jiang at al. [26] showed that coke treated with perchloric acid and hydrogen peroxide changes the coke structure and increases functional groups containing hydrogen. However, in this study, no anode was produced using this coke. Ozturk at al. [27,28] modified petroleum coke and produced anodes. They compared the properties of the anodes made with unmodified and modified cokes. This study was also carried out at the UQAC carbon laboratory. The results showed that the green and baked anode densities increased, electrical resistivity as well as the air and CO_2 reactivities decreased when modified coke was used compared to the properties of standard anode made with unmodified coke. They also said that the additive used should have heteroatom (O, N) containing functional groups to enhance interaction between coke and pitch.

As mentioned previously, a preliminary study carried out at the carbon laboratory of UQAC [16], showed that anodes which contain 1–3% unmodified biocoke had similar properties to those of the standard anodes (without biocoke). It was concluded that biocoke has a potential to be used as raw material in anode production.). However, this study was carried out with one specific type of coke and pitch and limited number of anodes were produced. The present study aims to investigate if the percentage of biocoke added during the manufacture of anodes could be further increased without deteriorating the anode properties and if the biocoke properties can be improved with additive utilization. This will further decrease the GHG emissions.

2. Material and methods

2.1. Materials used

The raw materials used for fabrication of anodes were petroleum coke, recycled carbon materials, coal tar pitch, and wood residue. Anode raw materials obtained from Aluminerie Alouette and the wood residue is obtained from Boisaco Inc., two industrial partners of the project.

The biocoke is produced at the carbon laboratory of the UQAC Research Chair on Industrial Materials (CHIMI) by heating the wood residue under nitrogen atmosphere up to 1100 °C with a heating rate of 7 °C/h. The biocoke modification was carried out using an additive which has melting point of 7.5 °C, boiling point of 248 °C, and it belongs to the generic class of phenyl-alkyl-aldehyde [25].

Four anode samples were made and characterized. All the properties given are the average of these four measurements except for the results of XPS tests. It is not possible to repeat this test due to high cost. However, the sample was scanned 20 times during each XPS test, and the result is the average of these 20 scans.

2.2. XPS spectroscopy analysis

The samples of different biochars and petroleum coke were ground into fine particles and characterized by X-ray photoelectron spectrometry (Kratos Axis Ultra DLD). The tests were carried out at the University of Sherbrooke. The spot size (the area analyzed) was 300 × 700 μm. The survey scan was taken with Pass Energy (PE) of 160 eV and a step size of 1 eV in order to identify the percentage of contamination. The instrument energy scale and work function were calibrated internally using clean Au, Ag, and Cu standards. The high-resolution spectra were taken with PE of 20 eV and a step size of 0.05 eV to analyze C1s. The analysis was done with CasaXPS (version 2.3.23) software.

2.3. Wettability tests

The Sessile-Drop method was used to measure the contact angles. The tests were carried out using coke, unmodified and modified biocoke samples. The detail of the equipment is given elsewhere [18]. The pitch was placed in a graphite crucible, which has a small hole, and placed on top of the coke/biocoke bed made of particles smaller than 45 μm. These are placed in a furnace and heated to 170° C under nitrogen atmosphere. When the desired temperature is obtained, a drop of pitch is placed on the bed by turning the crucible so that the small hole is positioned on the bed side and applying a small pressure to the pitch crucible using nitrogen gas. The evolution of the contact angle between the pitch drop and the coke/biocoke bed was recorded using a camera connected to a computer. All the images collected were analyzed by the FTA.32 software to have the evolution of dynamic contact angle as a function of time. For each experiment, the contact angle was taken as the average of the angles measured on two sides of the drop. Each experiment was repeated a number of times.

2.4. Laboratory anode production

The anodes of 10 kg were produced at the laboratory without biocoke as well as with unmodified and modified biocoke. First the dry aggregate is sieved in order to prepare a desired particle size distribution (anode recipe) which was similar to that used in industry. Then, the dry aggregate and pitch, which were preheated separately, were mixed in known proportions in an intensive mixer to produce an anode paste. The paste was vibro-compacted to produce green anode. Four cylindrical cores of 50 mm in diameter and 130 mm in height were taken from each anode. Then, the cores were baked at 1100 °C. The green anode production and baking carried out under the conditions similar to those used in the industry.

Seven carbon anodes were prepared as shown in Table 1. In this table, the biocoke percentage is represented with "B" and the additive percentage is represented with "A". The anodes are represented as B (% biocoke) A (% additive). For example, B3A3 shows that 3% of the petroleum coke was replaced with biocoke and the biocoke was modified with the additive. The amount of the additive used was equal to 3% of the biocoke.

Table 1
The composition of anodes.

Anode	Biocoke content (%)	Additive content (%)
STD*	0	0
B3A0	3	0
B3A3	3	3
B3A4	3	4
B4A0	4	0
B4A3	4	3
B4A4	4	4

* STD: Standard anode made only with petroleum coke (no biocoke and no additive).

2.5. Characterization of anodes properties

First, he density and electrical resistivity of green cores were measured. After baking, density, electrical resistivity, air and CO_2 reactivities, and flexural strength of baked cores were measured according to the standards ASTM D5502-00 [29], ASTM D6120-97 [30], ASTMD6559-00a [31], ASTM-D6558-00a [32], and ISO 12986-1 : 2014 [33], respectively.

3. Results and discussion

3.1. XPS characterization of unmodified and modified biocokes samples

An X-ray photoelectron spectroscopy (XPS) survey scan shows the presence of carbon at 284.3 (eV) and oxygen at 532.3 (eV) for biocoke samples of UNMOD (unmodified biocoke), MOD3 (biocoke modified using 3% additive), and MOD4 (biocoke modified using 4% additive). The XPS survey spectra of those are depicted in Fig. 1 within the binding energy range of 200–1400 eV. The atomic percentages of the functional groups found for these samples are shown in Table 2. The carbon and oxygen contents of biocoke samples changed with the biocoke modification process. The percentage of carbon content of MOD3 and MOD4 was lower than that of UNMOD but the percentage of oxygen content of MOD3 and MOD4 was higher than that of UNMOD. No nitrogen is detected in biocoke. Sulfur is not desired. Oxygen content of petroleum coke and pitch are lower, and their carbon content is higher than those of biocokes. However, they contain some nitrogen. The presence of heteroatoms (O and N) increases the possibility of bond formation between coke and pitch as well as between biocoke and pitch. Modified biocoke (MOD3 and MOD4) contains more oxygen compared to that of the unmodified biocoke, which points out that the modification added oxygen containing surface groups, hence, improved the biocoke/pitch interactions. This improvement permits the better penetration of pitch into the biocoke pores which results in better anode properties such as density, electrical resistivity, etc.

The XPS analysis is used to determine the concentration of functionals groups grafted on the sample. The interest was on the resolution of the C1s peak since it was the major element found in carbon samples. To evaluate the chemical structures of the biocokes, high-resolution XPS spectra of C 1 s levels were studied for UNMOD, MOD3 and MOD4 samples.

The high-resolution spectra of C 1 s indicates the presence of five functional groups which are C = C, COO, C = O and C-O, Tables 2 and 3 show all functionals groups found in samples and their binding energies, respectively.

After modification process the concentration of heteroatom-containing functional groups found on MOD3 and MOD4 increased compared to UNMOD, contrary to that of aromatic functional groups (C = C). This shows the presence of interaction between the biocoke and the additive. This might be due to the substitution reaction of the aromatic ring, the heteroatom-containing functional groups (COO, C = O,

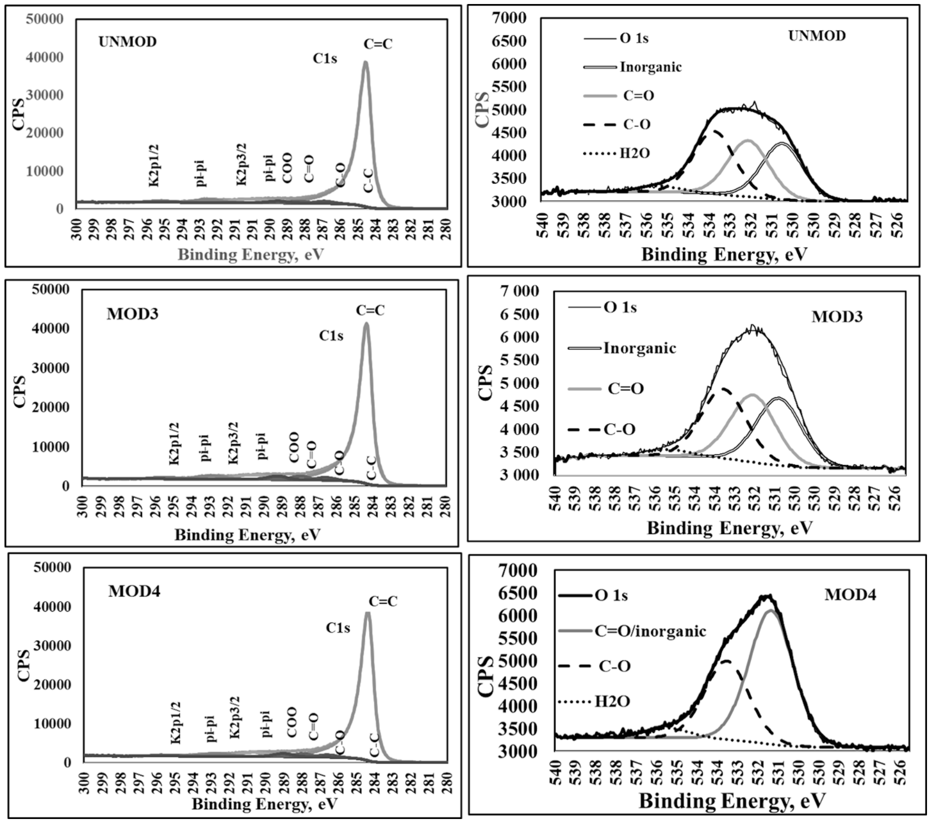


Fig. 1. Deconvoluted C1s and O1s for (a-b) UNMOD, (c-d) MOD3, and (e-f) MOD4 samples.

Table 2
Atomic percentages of different components of unmodified biocoke, modified biocokes, petroleum coke, and pitch.

Sample	Carbon C 1s components (%)					
	Aromatic C = C	Aliphatic C–C	Alcohol ether C-O	Carbonyl C = O	Carboxyl, imide, ester COO/ COON	Amine, epoxy CN
UNMOD	89.8	0	1.5	1.2	1.2	0
MOD3	88.3	0	1.7	2.2	2.2	0
MOD4	88.5	0	1.5	2	2	0
Petroleum coke	91.1	0	1.7	0.7	0.7	0
Pitch	66.1	25.8	0.9	0.4	0.4	0.5

Sample	Atomic percentage				
		Heteroatoms			
	C (%)	0 (%)	S (%)	N (%)	K (%)
UNMOD	93.8	4.9	0.1	–	1.1
MOD3	91.9	6.3	–	–	1.2
MOD4	92.9	6.4	–	–	0.6
Petroleum coke	94.8	3.6	0.9	0.7	–
Pitch	96.4	1.3	0.1	2.2	–

Table 3
List of functional groups in unmodified biocoke, modified biocokes, petroleum coke, and pitch found from XPS.

Sample	Binding Energy (eV)
C 1s C = C	[284.2 ; 284.3]
C 1s C–C	284.7
C 1s C-O	[286.2 ; 286.6]
C 1s CN/epoxy	287.2
C 1s C = O	[287.6 ; 288]
C 1s COO/imide	[288.7 ; 289.3]

C-O and COON) take place of aromatic functional groups (C = C). MOD3 shows the highest intensity of heteroatom-containing functional groups.

3.2. Wettability of UNMOD, MOD3, and MOD4 by pitch

Fig. 2 shows the results of the wettability of UNMOD, MOD3, and MOD4 biocoke samples by pitch. Wettability indicate the quality of binding between coke and pitch. The contact angle is a measure of the ability of pitch to spread on the coke surface and penetrate through the coke bed. The lower the contact angle is, the higher the wettability is. If the value of the contact angle is greater than 90°, a liquid/solid is considered non-wetting. If the contact angle is smaller than 90°, it is considered that the liquid (pitch) wets the solid (coke/biocoke) surface

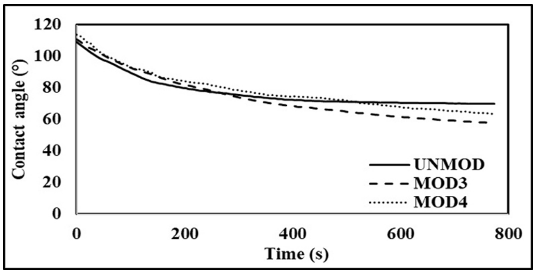


Fig. 2. Contact angle of UNMOD, MOD3, and MOD4 samples.

[34].

It was observed that the contact angles decrease with increasing time, and the pitch spreads and penetrates through all the samples. The complete wetting (zero contact angle) was not reached. The results showed that the modified biocokes (MOD3 and MOD4) have lower contact angles (better wetting) than the unmodified one (UNMOD), and MOD3 (lowest contact angle) was wetted better than the MOD4. This is in agreement with the XPS results, which showed that the amount of heteroatom-containing functional groups found in MOD3 was higher than those found in UNMOD and MOD4 as mentioned above. The wettability is related to the interaction of functional groups on the pitch surface with those on the surface of biocoke. Increase in functional groups increases the possibility of interaction between biocoke and pitch, hence the wettability increases with biocoke modification.

3.3. *Effect of modified biocoke on anode properties*

3.3.1. *Green and baked anode densities*

The biocoke and additive contents of the anodes produced during this study are presented in Table 1. The standard anode does not contain any biocarbon nor additive. This corresponds to the anodes presently used in the industry and it is used as a reference in this study. Two groups of anodes were manufactured, one containing 3% biocoke and the other containing 4% biocoke. The anodes in each group contained one anode with unmodified biocoke. The biocoke of the other two anodes were modified using 3% and 4% additive.

As can be seen from Fig. 3, the densities of both green and baked anodes decreased with biocoke addition (B3A0 and B4A0) compared to that of the standard anode (STD). This can be explained by the low density of the biocoke [8]. The densities of anodes containing 3% or 4% biocoke modified with 3% and 4% additive (B3A3, B3A4, B4A3 and B4A4) increased compared to those of the anodes containing corresponding amount of unmodified biocoke (B3A0 and B4A0). This is due to the better wettability of modified biocoke by pitch compared to the wettability of unmodified biocoke (Fig. 2). As mentioned before, the better wettability is due to the attachment of additional functional groups to the biocoke surface during its modification (Tables 2 and 3). The densities of anodes made by replacing 3% of the petroleum coke with modified biocoke (B3A3 and B3A4) were found to be similar. Replacing 4% of petroleum coke reduced the density of both green and baked anodes significantly compared to that of the standard anode without biocoke and this was not improved with the utilization of an additive. It was found that the density of the anodes did not change appreciably when 3% percent of petroleum coke was replaced with modified biocoke.

3.3.2. *Air and CO_2 reactivities*

- *Air reactivity*

During electrolysis, the air infiltrating from the top of the cell reacts with anode carbon, which results in overconsumption of carbon [35–37]. The effects of replacing part of the petroleum coke with biocoke and biocoke modification on air reactivity were investigated. The results are shown in Fig. 4a. As it can be seen from this figure, the air reactivity increases with increasing anode density for the anodes containing 4% unmodified and modified biocoke (B4A0, B4A3, and B4A4). These results are in agreement with the results of Xianai at al. [16] which claims the reactivity is reaction controlled. As the density increases (the porosity decreases), the amount of carbon in contact with air increases. For the anodes containing 3% of modified and unmodified biocoke, the reverse trend was observed (B3A0, B3A3, and B3A4). The air reactivity of these anodes decreased with increasing density. Increasing density decreases the porosity. In that case the gas can't diffuse through the anode and reacts less with the carbon. This is a characteristic of a diffusion-controlled reaction. It is not clear why the mechanism might change with the increase of additive content by 1%. The non-homogeneity of the anodes might also have played a role. Air reactivity of all the anodes were lower than that of the standard anode with the exception of B4A4. Therefore, replacing 3% of the petroleum coke with modified biocoke is feasible in terms of air reactivity.

- *CO_2 reactivity*

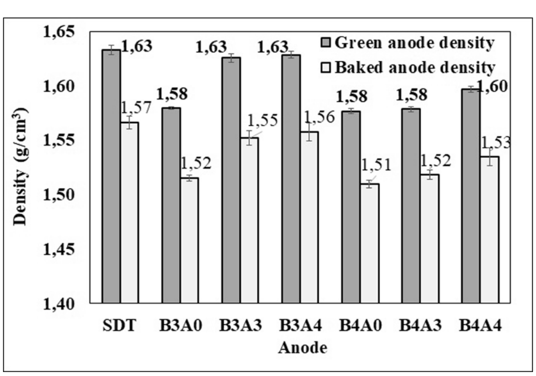


Fig. 3. Green and baked anode densities for all the anodes (error bars indicate standard deviation).

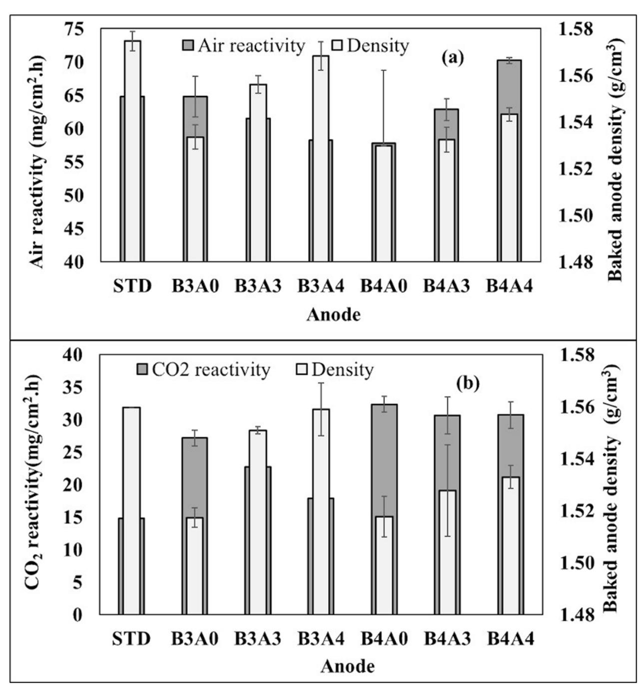


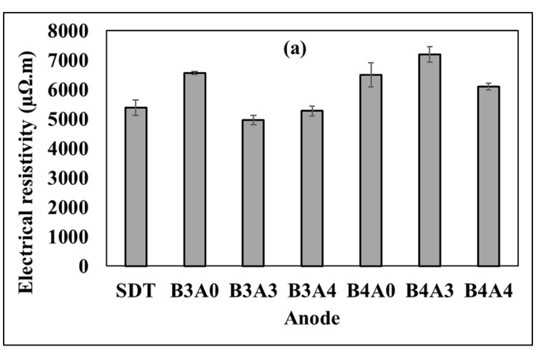
Fig. 4. Density and (a) Air (b) CO_2 reactivity of all the anodes (error bars indicate standard deviation).

A reaction takes place between the CO_2 produced during the electrolysis and anode as shown in Equation (1) and anode. CO_2 infiltrates through pores of the anodes and reacts with carbon [35–37]. This reaction also results in carbon overconsumption. The results of these tests are illustrated in Fig. 4b. The CO_2 reactivity of anodes made with 3% and 4% of unmodified biocoke (B3A0 and B4A0) was higher compared to that of standard anode. However, the modification of biocoke with additive decreased the CO_2 reactivity of anodes (the CO_2 reactivity of B3A3 and B3A4 compared to B3A0 as well as the CO_2 reactivity of B4A3 and B4A4 compared to that of B4A0). Increasing additive content decreased the reactivity. It was also observed that the CO_2 reactivity decreased with increasing density. This is due to the decrease in porosity with increasing anode density. The CO_2 reactivity is diffusion controlled. The diffusion of the gas, hence its contact with anode carbon decreases as the porosity decreases. Similar trend was observed for standard anodes by Lu at al. [38]. The CO_2 reactivity was higher for all cases compared to that of the standard anode. However, this increase was less severe when only 3% of the petroleum coke was replaced with biocoke. In this case, the utilization of 4% additive gave the lowest CO_2 reactivity.

The slight differences in densities shown in Figs. 3 and 4 are due to the differences in the densities of the samples used to carry out the tests. However, these differences are within the range of the standard error.

3.3.3. Electrical resistivity

Electrical resistivity affects the power consumption, consequently, the cost of the production. There are several parameters that can affect electrical resistivity such as porosity, anode cracking, non-homogeneity of anodes and raw materials, and interaction between dry aggregate particles and pitch [39]. The results, which are presented in Fig. 5, indicates that the resistivity of the anodes containing 3% and 4% unmodified biocoke (B3A0 and B4A0) is higher than that of the standard anode both for green and baked anodes. The modification of biocoke reduced the electrical resistivity of the anodes except for B4A3 green anode compared to those of the anodes containing unmodified biocoke. This is due to the functional groups grafted on the surface of biocoke during modification, which increase the wettability of biocoke. This was shown by the XPS and the wettability test results as mentioned previously. Pitch can diffuse better into the biocoke decreasing the porosity, thus the electrical resistivity of the anode decreases. The results clearly show that replacing 3% or 4% of petroleum coke with modified biocoke does not increase the electrical resistivity both for green and baked anodes, therefore, the electrical energy and the cost of production will not be affected.



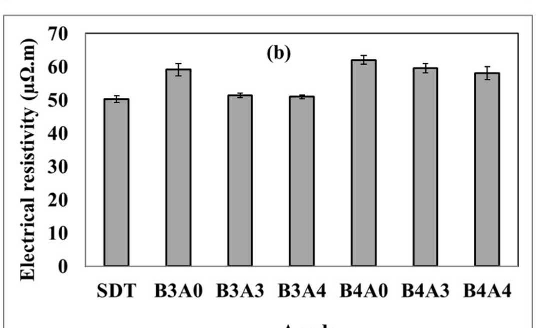


Fig. 5. Electrical resistivity of (a) green and (b) baked anodes (error bars indicate standard deviation).

3.3.4. Bending strength

The three-point bending tests were carried out to measure the bending strength of the anodes. The results are presented in Fig. 6. It can be seen from this figure that the addition of unmodified biocoke (B3A0 and B4A0) decreased the bending strength of resultant anodes. It is also shown that the bending strength of the anodes made with modified biocoke is higher than that made with unmodified one. These results can be explained with the improvement of biocoke wettability with modification. It can be seen from the results that the replacing 3% of petroleum coke with biocoke modified with 3% additive (B3A3) has slightly higher bending strength than even that of the standard anode. Increasing the percentage of biocoke decreased the bending strength, Therefore, 3% biocoke seem to be a good choice.

4. Conclusions

The aim of the study was to reduce the GHG emissions of aluminum industry and add value to the wood industry by-products by replacing a small part of the petroleum coke used in anode production with biocoke without deteriorating the anode properties. Since the properties of biocoke are different than those of the calcined petroleum coke, the addition of biocoke deteriorates the anode properties.

In a previous study, the UQAC carbon group found that by replacing part of the small particle fraction of the petroleum coke with 3% biocoke, it was possible to maintain the anode properties similar to those without petroleum coke. In the current study, similar trials with another petroleum coke did not prevent the deterioration of anode properties. A biocoke modification method was developed to improve biocoke properties. The modification of biocoke with an additive successfully increased its wettability by increasing the surface functional groups of biocoke as shown by XPS and wettability results. Then, using 3% modified biocarbon with 3% additive, it was possible to produce anodes with similar properties (with some slight differences) compared to the ones made with unmodified biocoke. The above findings suggest that the coke type is likely an important parameter, and testing with other cokes should be carried out.

Utilization of nontoxic and low-cost additive might make the utilization of biocoke in anode production possible for any type of petroleum coke. The financial and environmental effects of this replacement such as reduction in carbon tax (if exists locally), utilization of cheaper raw material, decrease in the amount of calcined coke (decreasing the energy requirement) etc. have to be considered.

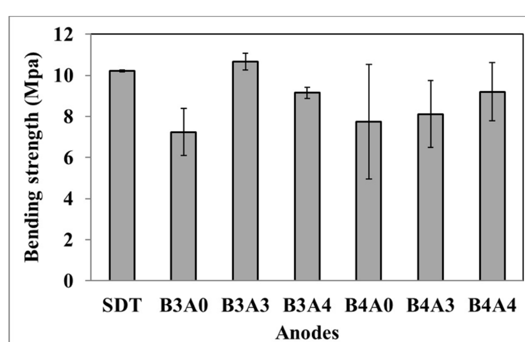


Fig. 6. Bending strength of all the anodes.

CRediT authorship contribution statement

Belkacem Amara: Investigation, Formal analysis. **Fatima-Ezzahra Faouzi:** Formal analysis. **Duygu Kocaefe:** Supervision, Project administration, Funding acquisition, Conceptualization, Methodology, Validation, Writing - review & editing. **Yasar Kocaefe:** Supervision, Conceptualization, Methodology, Writing - review & editing. **Dipankar Bhattacharyay:** Supervision, Formal analysis, Software. **Jules Côté:** Resources. **André Gilbert:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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