Considerations in Chemical Coke/Pitch Modification Using Additives for Anode Production

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Abstract

Energy and carbon consumption, production cost, and greenhouse gas (GHG) emissions are some of the major challenges facing the aluminum industry today. These are closely related to the anode quality which depends on the raw material (coke and pitch) quality as well as the operating conditions used in the anode paste plant (recipe preparation, kneading, and forming) and during baking.

The raw material quality has been deteriorating. However, the aluminum industry needs a supply of good quality anodes irrespective of the raw material quality. One possible avenue is to improve the coke/pitch interactions by modifying them with additives. Two studies were carried out: 1) Several types of coke were modified with one additive, and anodes were produced using the same pitch; 2) Several pitches were modified with one additive, and anodes were produced using the same coke. The modified and non-modified cokes and pitches were characterized by means of measuring coke wettability by pitch and studying the surface chemistry of the raw materials using FTIR. Then, anode quality was determined by measuring the anode properties and comparing them with those of the standard anodes, which are produced using non-modified cokes and pitches. Both studies showed that using additives can improve some anode properties such as density, electrical resistivity, reactivity, and flexural strength. Thus, both coke and pitch modifications could help produce better quality anodes. This article presents the factors that affect the anode quality if modified raw materials are used in their production. Also, the advantages and disadvantages of the modifications should be assessed in terms of its application in aluminum smelters.

Keywords: Coke/pitch interactions, Raw material modification, FTIR, Wettability, Improvement of anode properties

1. Introduction

Canada is the fifth producer (3.1 million tonnes in 2021) and the second exporter of aluminum in the world. Three major aluminum producers (Rio Tinto, Alcoa, Alouette) are currently operating nine smelters (eight in Quebec and one in British Columbia) in Canada. Thus, 90 % of aluminum is produced in Quebec. Also, aluminum constitutes 2 % of Canadian exports. Due to the utilization of hydroelectric power and know-how, Canadian aluminum industry is producing the greenest aluminum in the world with the lowest global carbon footprint of 2 tonnes CO_2 equivalent per tonne of Al [1].

Primary aluminum is produced via the Hall-Hérault process, and the overall reaction can be written as shown in Equation 1.

$$2Al_2O_3 \text{ (bath)} + 3C \text{ (anode)} = 4Al + 3CO_2 \quad (1)$$

Carbon anodes are made from two major raw materials, which are coke and pitch. The anode recipe contains 85 % dry aggregate (calcined petroleum coke, butts, and recycled green and baked anodes). Dry aggregate, which has a predetermined particle size distribution, is mixed with 15 % coal tar pitch to produce anode paste. Pitch penetrates between dry aggregate particles and into their pores. Pitch has to wet these particles in order to bind them efficiently. The paste is transferred to a mold and compacted in a vibro-compactor or in a press to form a block, called green anode, prior to baking. During the baking process, the pitch carbonizes (pitch-coke) and forms a solid matrix binding the dry aggregate particles. If dry aggregate (mostly coke) and pitch are compatible (meaning that pitch wets well the coke and penetrates between the particles as well as into the particle pores), good quality anodes are produced (high density, low electrical resistivity, good mechanical properties, and low air and CO_2 reactivities). Good anode quality reduces the energy and carbon consumptions, production cost, and GHG emissions.

Wettability of coke by pitch is an indicator of the coke-pitch compatibility. The better the wettability is, the higher the possibility of producing good quality anodes is. Several researchers studied the wettability of coke by pitch, which depends on their physical and chemical properties [2-8]. Depending on the affinity of the liquid pitch drop with the coke surface, the drop takes a characteristic shape. The degree of a liquid spreading on the surface of a solid is defined as wettability, which is measured by the contact angle (for details see [9]). The wetting behavior of a pitch drop on the surface of the coke depends on the functional groups present on coke and pitch surfaces. In literature, it is reported that hydrogen bonds, electrostatic interactions, dispersion forces, acid-base interactions, and covalent bonds are the principal interactions responsible for the cohesion between coke and pitch [10-13]. Due to these interactions, the solid surface is altered which in turn changes the contact angle with time (dynamic contact angle).

The decrease in the quality of anode raw materials (coke and pitch) affects their compatibility. Coal tar pitch and petroleum coke are by-products of coke production from coal and crude oil refining processes, respectively. Improvements of these processes are leading to a decrease in the quality of their by-products, thus coke and pitch quality. Therefore, the enhancements of raw material properties in order to improve the compatibility of coke by pitch might be one of the avenues to possibly improve anode properties.

Chemical modification of the raw material surfaces using different additives and surfactants was studied by some researchers [14-17]. Only a few researchers worked on pitch modification with the objective of improving the anode properties, especially those of the anodes used in aluminum production.

Malyi et al. [18] worked on the modification of coal tar pitch using carbolic acid for electrodes used in the electrosmelting of steel. The results showed that carbolic acid positively affected the rheological properties of pitch, and thus improved the penetration of pitch and wettability of coke by pitch. They also studied the modification of coal tar pitch with phenolic fraction of slightly pyrolyzed coal tar [19, 20]. The results showed that utilization of 15-20 % additive improved the plasticity of the pitch. It also modified the β fraction of pitch which enhanced the sorption capacity of thermoantracite (solid carbon) used in electrode production, and improved the wettability of thermoantracite by pitch.

The European Commission published a report where three additives were studied for coal tar pitch modification (sodium carboxymethylcellulose, Mobilsol 40, and polystyrene). The modifications didn't affect the anode properties [21].

The researchers of the Research Chair on Industrial Materials (CHIMI) at the University of Quebec at Chicoutimi studied the effect of both coke [22-24] and pitch [25-27] modification on properties of anodes used in aluminum production. Coke modifications were carried out using six different additives among which only one additive improved the wettability of coke by pitch. This additive was then used to modify four different cokes, which resulted in the improvement of some anode properties. Four different pitches were modified with three different additives. Two of the additives improved anode properties. The additives were selected based on their surface functional groups (chemical composition of the surface), physical properties, low cost, and non-toxicity. These studies showed that additives can increase the number of bonds available on coke and pitch surfaces and promote their interactions. This paper presents the results of coke and pitch modifications by the same additive and its effect on anode properties in order to identify the factors to be considered in the modification of raw materials destined for making anodes used in aluminum production.

2. Materials and Methods

2.1 Materials

Calcined petroleum coke, coal tar pitch, recycled anodes, and butts were obtained from an aluminum smelter. The same raw materials were used in the production of all anodes. Coke and pitch were modified using the same additive purchased from Alfa Aesar. The additive selected is a non-carcinogenic organic compound (phenyl-alkyl-aldehyde with a melting point of 7.5 °C, a boiling point of 248 °C), and it contaminates neither anode, nor aluminum. The solvent used to dissolve the additive was purchased from Alfa Aesar. Three different mass fractions (concentration in % g/g) of the additive were used, i.e. 0.5 % < c1 < c2 < c3 ≤ 5 %. Then, anodes were produced using either pitch modified with c3 % additive and non-modified coke or coke modified with c1 % and c3 % additive and non-modified pitch. The actual amounts of the additive used to modify pitch with c3 % additive and coke with c1 % additive are the same since the pitch content of anodes is much less than their coke content. Due to confidentiality, the name and concentration of the additive and the solvent are not disclosed.

2.2 Wettability

The wetting behavior of non-modified and modified cokes as well as non-modified and modified pitches were measured using the sessile-drop method. A graphite chamber containing solid pitch was placed above a packed bed of coke particles in a furnace. Coke particles were grounded, and particle size of -125 µm was used for this test in order to have a smooth coke surface. The experiments were carried out under the nitrogen atmosphere to prevent oxidation. At the desired temperature (~170 °C), a drop of liquid pitch was allowed to fall directly onto the coke surface. The change in the shape of the pitch drop was followed with a camera by capturing images at known intervals. The FTA-32 software was used to measure the angle at the triple point where a pitch-nitrogen interface meets the coke surface. Each experiment was repeated twice. The contact angles decreased (wetting increased) with time. The smaller the angle is, the better the wettability of coke by pitch is. Details of the experimental system are given elsewhere [8].

2.3 FTIR

The surface functional groups of cokes and pitches (non-modified and modified) were studied by first making potassium bromide pellets containing the sample (1 % g/g analyte/KBr) followed by

FTIR analysis using a Nicolet 6700 FTIR spectrometer. The experiments were performed at room temperature in a wavenumber range of 399 to 4000 cm^{-1}. Samples were scanned 26 times during each experiment. The recording resolution was set to 4 cm^{-1}. Each experiment was repeated three times and the average result is reported. Details of the experimental procedures are presented elsewhere for cokes [24] and for pitches [26, 27].

To interpret the spectra, two ratios (OH and H) were calculated. To do this, four areas were defined as shown below:

Area 1: Total area of the peaks of alcohol/secondary alcohol/ether functional groups in the wavenumber range of 1000 to 1300 cm^{-1}

Area 2: Total area of the peaks of inter/intra molecular hydrogen bonding region in the wavenumber range of 3300 to 3600 cm^{-1}

Area 3: Area of the specific additive peak at the wavenumber 1700 cm^{-1}

Area 4: Total area of carbon containing peaks in the wavenumber range of 2700 to 3100 cm^{-1}

The OH ratio represents the ratio of the total absorbance of alcohol/secondary alcohol/ether functional groups of the sample in Area1 to the sum of the total absorbance of Area 1 and the total absorbance of inter/intra molecular hydrogen bonding region in Area2 (Equation 2). The value of this ratio gives an idea of the availability of hydrogen-bonded species free to bind with pitch or coke. An increase in this ratio means an increase in the number of hydrogen or heteroatoms which are possibly available to enhance coke/pitch interaction.

The H Ratio was calculated based on the aldehyde functional group (containing a C=O bond) present in additive. On FTIR spectra, C=O can be observed in wavenumber range of 1600 to 1850 cm-1 corresponding to strong peaks from acids, esters, aldehydes, ketone, anhydrides, C-O or C=O bonds [28]. Therefore, the Ratio H is the ratio of absorbance of the specific additive peak around the wavenumber of 1700 cm-1 (Area 3) to sum of the total absorbance of Area 3 and the total absorbance of most of the carbon containing surface functional groups in Area 4 (Equation 3). The increase in Ratio H represents an increase in C=O acid-base interactions or hydrogen bond (when reacting with free hydrogen) [29].

$$\text{Ratio OH} \quad (\text{Area1} / (\text{Area1} + \text{Area 2})) \times 100 \tag{2}$$
$$\text{Ratio H} \quad (\text{Area3} / (\text{Area3} + \text{Area 4})) \times 100 \tag{3}$$

2.4 Laboratory Anode Production and Characterization

Coke Modifications

In this study, coke was modified using two different concentrations (c1 % and c3 %) of additive. To modify the coke, additive was dissolved in a solvent using a beaker and a magnetic stirrer (Cole-Palmer stirrer). Then, coke was added to the solution. It should be noted that this procedure is for the characterization of coke only. During anode manufacturing, the whole dry aggregate (all solid particles) was modified with the additive. For details, see [22].

Pitch Modifications

For characterization, small quantities of pitch were modified in a test tube. First, a measured quantity of additive is placed in the test tube and enough pitch was added to obtain the desired additive concentration (c1 % and c3 %). The mixture was placed in a furnace under nitrogen atmosphere, and the pitch temperature was monitored continuously. When the maximum temperature of ~170 °C was reached, the mixture was mixed manually for one minute. Once the mixing was completed, the test tube was taken out of the furnace and cooled down to room temperature. Then, the modified pitch was recovered. A similar procedure was followed to modify the pitch to be used to produce anodes in large quantities using a large container where additive was added to pitch at the desired temperature. Details can be found in [26].

Laboratory Anode Production and Core Characterizations

The pilot anodes were made in the state-of-the-art anode production laboratory of the Chair CHIMI using either pitch modified with c3 % additive and non-modified coke or coke modified with c1 % and c3 % additive and non-modified pitch. First, the dry aggregate particles were sieved to obtain different particle size fractions. Then, measured fractions were mixed in a predetermined proportion to obtain the desired particle size distribution. After, dry aggregate and pitch were preheated separately. Then, they were mixed in an intensive mixer for a specific period of time. The obtained anode paste was placed in a mold and vibro-compacted at 170 °C (green anode). Four cores were taken from each green anode. The cores were characterized by measuring the green anode apparent density and electrical resistivity according to ASTM D5502 00 and ASTM D6120-97, respectively. The results given represent the average of the properties of four green cores. Then, two cores of each anode were baked in the baking furnace (Pyradia, Model-B07D02029021SVCCH). All green anode cores were baked together under the same conditions (representative of the industrial practice) since the baking conditions can significantly affect the anode properties. The apparent density, air and CO_2 reactivities as well as dusting and flexural strength were measured according to ASTM-D5502 00, ASTM-D6559-00a, ASTM-D6558-00a, and ISO N 848, respectively. Details are given elsewhere [22, 27].

3. Results and Discussion

In this section, the results are given in dimensionless form, which is the ratio of the actual value to the maximum value obtained for that property.

3.1 Wettability

The wettability results of the present study are presented in Figure 1.Wettability of non-modified and modified coke by non-modified pitch was measured to study the effect of coke modification on the wettability; and the wettability of non-modified coke by modified and non-modified pitch was measured to study the effect of pitch modification on the wettability.

The results of the coke modification showed that the contact angle decreased (wettability increased) with increasing additive concentration. This result shows that the increase in additive concentration does contribute to the enhancement of coke/pitch interactions. As for the pitch modification, the contact angle decreased (wettability increased) with increasing additive content. As it can be seen from Figure 1, the modification of both coke and pitch improved the wettability of coke by pitch regardless of the raw material modified. However, the modification of pitch resulted in lower contact angles (better wetting) compared to those of the modified coke.

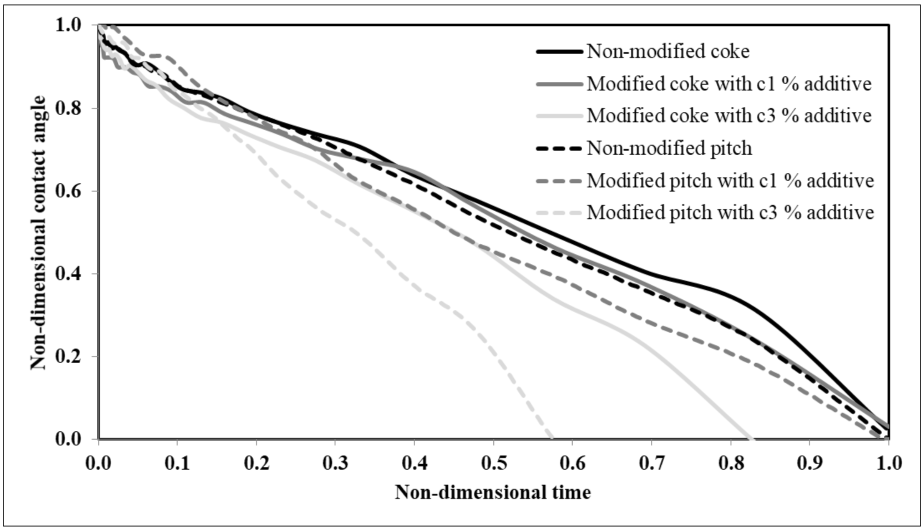

Figure 1. Comparison of wettability of non-modified and modified coke with non-modified pitch, and non-modified and modified pitch with non-modified coke.

3.2 FTIR

In order to understand the interaction between coke and pitch, their surface chemistries were studied using the FTIR analysis. The spectra obtained and possible functional groups found in literature are presented in Figure 2 and Table 1, respectively. In coke spectra, the absorbances are smaller compared to those of the pitches. To observe peaks on the FTIR spectra, the motion of the bond activated by IR light must cause a change in the dipole moment of the molecule. Thus, the symmetrical carbon bonds do not create a vibrational motion. Since coke structure contains mostly carbon bonds, absorbances are lower compared to those of the pitch. In all spectra, each functional group identified in literature (Table 1) is observed. However, the peak absorbances appearing before 3100 cm^{-1} and after 3600 cm^{-1} (which is free moisture) are greater in pitches compared to those in coke. The peaks of particular band 3300-3600 cm^{-1}, which can represent N-H group and/or secondary amine-, and/or OH stretching (mostly hydrogen bonded), are mostly absent in pitch. The bump observed is mostly due to the automatic baseline correction used to compare coke and pitch spectra.

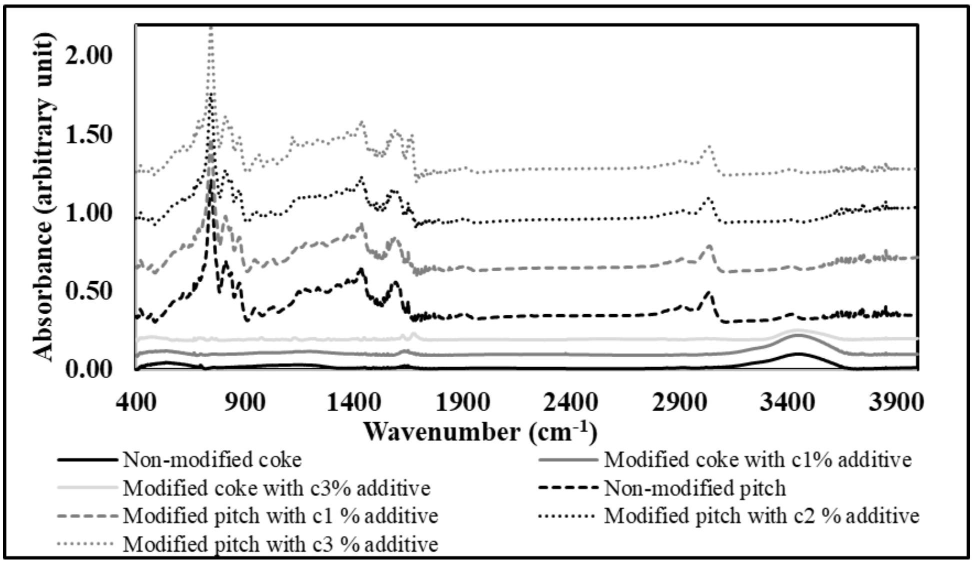

Figure 2. Comparison of spectra of non-modified coke, coke modified with c1 and c3 % additive, non-modified pitch, and pitch modified with c1, c2 and c3 % additive.

Table 1. List of functional groups at the surface of non-modified and modified calcined petroleum coke, and non-modified and modified coal tar pitch from FT-IR analysis.

Wavenumber (cm^{-1})	Functional group identified in literature	Comment
700-900	Substituted (ortho, meta, and para) aromatic ring [30]	Low in cokes and high in pitches (both for modified and non-modified pitch and coke)
1000-1300	C-O, -O- [30, 31]	
1400-1600	C=C stretching vibrations [30, 32-34]	
1700-1800	C=O or CO_2 [35]	
2700-2950	Aliphatic (C≡C, C=C, and C-C) [32, 33]	
3000-3100	Aromatic C=C [33]	
3300-3600	N-H group- secondary amine-, OH stretching (mostly hydrogen bonded) [31, 33]	
3600-3800	Free moisture, phenol or carboxylic acid [32, 36]	

From the work of Bureau et al. and Öztürk et al. [22, 26], it was determined that the modifications of pitch and coke chemically altered their surfaces, and thus increased the functional groups available. This possibly enhances the coke/pitch interactions. In order to compare the effect of the coke and pitch modifications, two ratios were calculated: OH Ratio and H Ratio (Table 2). It can be seen from this table that modifying coke with c1 % additive did not change OH Ratio, but this ratio decreased for coke modified with c3 % additive. Thus, when reacting with coke, the additive has possibly formed alcohol/secondary alcohol/ether functional groups, decreasing the free hydrogen content available to interact with pitch by forming hydrogen bond. However, H Ratio increased with increasing additive concentration corresponding to an increase in C=O bonds. Since difference is greater in H Ratio compared to those of OH Ratio, the increase in wetting with additive concentration might be explained with acid-base interactions or hydrogen bond formation (newly formed) coming from C=O. For pitch spectra, only H ratio was calculated. It can be seen from Table 2 that H Ratio increased with the increase in additive concentration which is complementing the wettability results obtained.

Table 2. Calculated ratios of non-modified and modified calcined coke, and non-modified and modified coal tar pitch from FT-IR analysis.

Material	OH Ratio	H Ratio
Non-modified coke	99.1	37.4
Modified coke with c1 % additive	99.7	73.7
Modified coke with c3 % additive	93.4	90.1
Non-modified pitch	-	15.7
Modified pitch with c1 % additive	-	15.8
Modified pitch with c2 % additive	-	18.8
Modified pitch with c3 % additive	-	26.0

3.3 Anode Properties

The characterization results for the standard anode, anodes made with coke modified with c1 and c3 % additive, and pitch modified with c3 % additive are presented in Figure 3. The additive quantity in the anode made with coke modified with c1 % additive is similar to that of the anode made using pitch modified with c3 % additive. The modified coke contains a solvent used to dissolve the additive, but the solvent vaporizes during mixing. Thus, it does not affect the chemical composition of the surface. Utilization of solvent isn't necessary in pitch modification since pitch is in liquid form at the mixing temperature.

Slight improvement in anode properties compared to those of the standard anode can have a significant impact on the electrolysis process. It can be seen in Figure 3 that green and baked anode densities (GAD and BAD) of the anodes made with modified coke or modified pitch resulted in slight improvement compared to those of the standard anode. One exception was the BAD of the anode made using pitch modified with c3 % additive, which had slightly lower BAD. In the prior study [27], it was suggested that this anode might have been over pitched, but this wasn't tested. Since the cost of the selected additive is low, using less pitch might be an advantage to consider. Higher GAD and BAD were obtained using coke modified with c3 % additive which is in agreement with the wettability results. c3 % additive represents the use of a larger quantity of the chemical agent for the dry aggregate containing coke compared to using c1 % additive. Thus, this cost should be considered when assessing the gain in BAD.

The electrical resistivity of green anodes (GER) wasn't improved with coke or pitch modifications. Pitch modification with c3 % additive resulted in GER similar to that of the standard anode and coke modifications with c1 % and c3 % additive significantly increased GER. However, the baked electrical resistivity (BER) was improved through coke and pitch modification compared to that of the standard anode. The following order was found for the BER of the anode made with: standard anode > modified coke with c3 % additive > modified pitch with c3 % additive > modified coke with c1 % additive. The BER results did not follow the trend obtained for BAD. BAD results for modified anodes were not that different compared to that of the standard anode. The modification of pitch with c3 % additive and the modification of coke with c1 % additive resulted in the largest improvements in BER where coke modification giving slightly better result. But, coke modification might require new equipment whereas pitch modification can be realized in the storage silos used presently. Thus, it is recommended to investigate if the cost of using a solvent and cost of the equipment required for coke modification worth the economy provided by the improvement of BER compared to the BER improvement obtained by modifying the pitch.

The flexural strength of the anode produced using coke modified with c3 % additive had the lowest flexural strength. But, both using coke modified with c1 % additive and pitch modified with c3 % additive improved the flexural strength compared to that of the standard anode.

The air reactivities of modified coke or pitch were similar to that of the standard anode. The dusting due to air reactivity was the lowest for the anodes made with pitch modified with c3 % additive and coke modified with c1 % additive. CO2 reactivity and corresponding dusting of all the anodes made with modified raw materials were lower compared to those of the standard anode. But the lowest values were obtained again for the anodes made with pitch modified with c3 % additive and coke modified with c1 % additive. Since it is possible to cover the anode to reduce the impact of air reactivity, it is better to reduce CO2 reactivity to lower the carbon consumption.

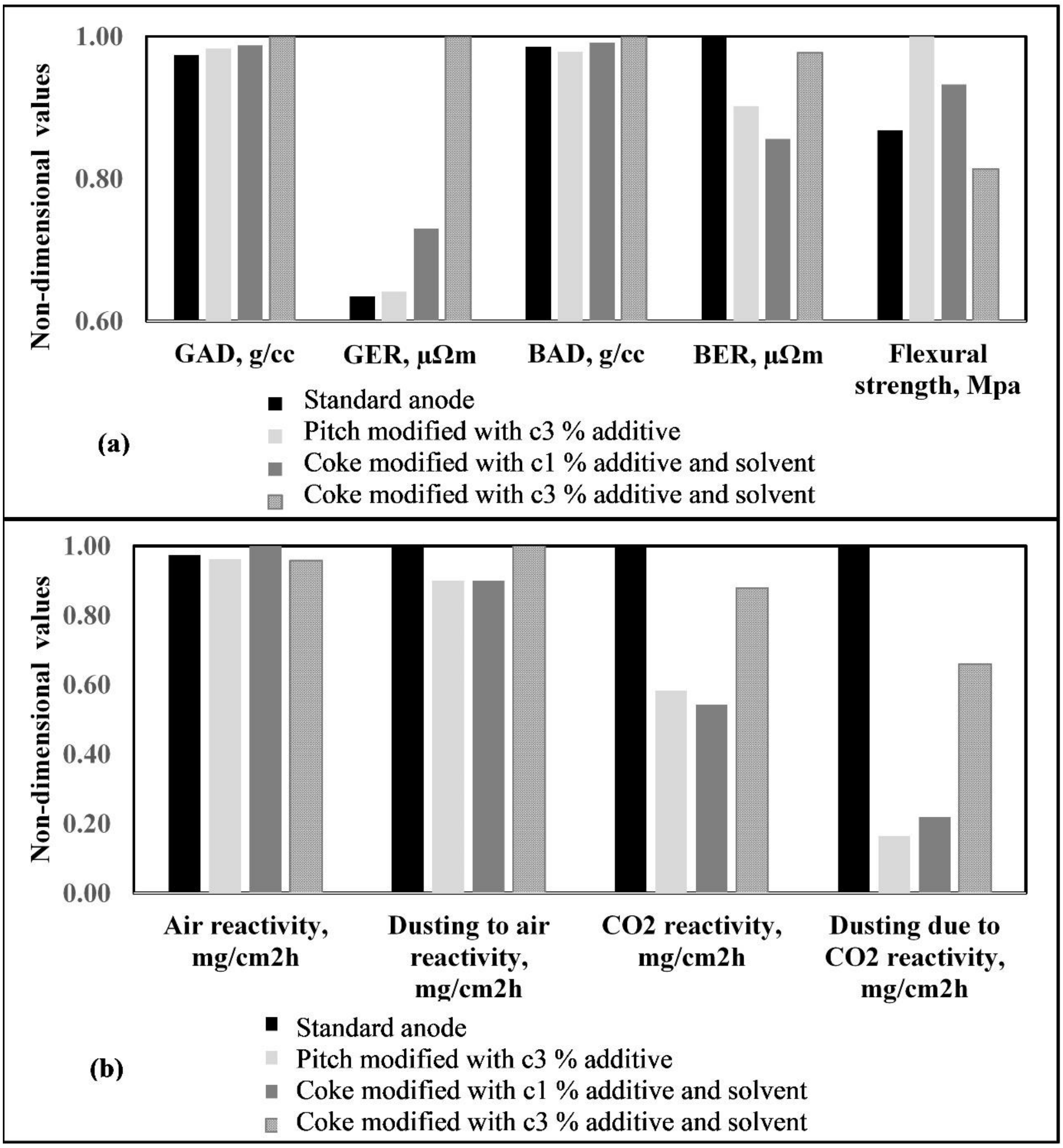

Figure 3. Comparison of anode properties standard anode and anodes made using non-modified coke with modified pitch, and modified coke with non-modified pitch: a) physical properties, b) air and CO2 reactivities.

4. Conclusions

In this paper, the effect of coke and pitch modifications on the anode properties was investigated through characterization of raw materials and laboratory anodes. It was observed that increasing the concentration of additive decreased the contact angle thus increased the wettability of coke by pitch.

The FTIR analysis revealed that the additive binds differently with coke and pitch used in this study. When modifying the coke, the additive seems to increase the number of -OH bond on the coke surface, which can form hydrogen bond with pitch. For pitch modification, the additive is possibly changing the pitch surface by increasing the presence of C=O group. In this case, the improvement of coke-pitch interactions can probably be explained by the increase in acid-base interactions or hydrogen bond formation. Modifying coke and pitch increased the presence of functional groups on their surfaces. This likely contributes to the enhancement of coke/pitch interactions.

The anode characterization results demonstrated that modification using an additive could improve some properties. Coke modification slightly improved the BAD compared to that of the standard anode. BAD of the anode made with modified pitch didn't improve. But, it is possible that this anode was over-pitched. The BER, CO2 reactivity (and its dusting), and flexural strength were improved by modifications of pitch with c3 % additive and coke with c1 % additive. These anodes had similar properties. This might be due to the same amount of additive used in both cases, but this was not verified. This study was carried out using the same pitch percentage for all the anodes. But, the pitch requirement for anodes made with modified raw materials might be different than those made with non-modified raw materials. Optimizing the pitch content might further improve the properties of anodes.

The results show that both coke and pitch modifications with additive seem beneficial for anode fabrication. One of the major differences for the application of coke and pitch modifications is the required equipment. It might be possible to realize the pitch modification in the storage silos used presently. On the other hand, coke modification not only requires an additional material (solvent), but possibly additional equipment to dissolve the additive in the solvent and mix with the coke. It was concluded that the advantages and the disadvantages of the modification should be assessed in terms of the limitations for the application of the raw material modification in the plant.

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