





# **Improvement of Anode Quality Through Pitch Modification**

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## Résumé

Les anodes en carbone sont utilisées dans le processus d'électrolyse pour produire de l'aluminium primaire. Une anode en carbone est composée de coke de pétrole, de brai de houille et de matériaux carbonés recyclés. La qualité de l'anode a un impact direct sur la consommation d'énergie et de carbone, le coût de production et les émissions de gaz à effet de serre. De nombreuses études ont été consacrées à l'amélioration des propriétés de l'anode. La modification des propriétés du brai peut améliorer les propriétés de l'anode.

Dans cette étude, deux types d'additif (additif 1 et additif 2) ont été utilisés à différentes proportions pour modifier les brais. De plus, les effets du type de brai (HQI et LQI)\* et de la proportion du brai sur les propriétés de l'anode ont été étudiés en servant de la modification du brai.

Les résultats ont montré que le brai HQI modifié avec 1 % d'additif 1 à une proportion de brai de 16 % présentait de meilleures propriétés d'anode grâce à une densité d'anode plus élevée, une résistivité électrique plus faible et une perméabilité à l'air plus faible. Cela est également en accord avec les résultats de mouillabilité car l'additif 1 a amélioré la mouillabilité du coke par les brais HQI. En général, le brai HQI modifié avec l'additif 1 permet d'obtenir des anodes de haute qualité avec une teneur en brai plus faible par rapport à son équivalent non modifié, ce qui peut entraîner des avantages économiques.

L'additif 2 a amélioré la densité (densité plus élevée) de l'anode produite avec le brai LQI. Cela est en accord avec l'amélioration observée de la mouillabilité du coke par le brai LQI modifié avec l'additif 2.

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\* Voir la page suivante

## Abstract

Carbon anodes are used in the electrolysis process to produce primary aluminum. A carbon anode consists of petroleum coke, coal tar pitch, and recycled carbon materials. The anode quality has a direct impact on the energy and carbon consumptions, production costs, and the greenhouse gas emissions. Numerous studies were dedicated to improving the anode properties. Modification of pitch properties may enhance the anode properties.

In this study, two types of additive (additive 1 and additive 2) were used at different percentages to modify pitches. In addition, the effect of the pitch type (HQI<sup>1</sup> and LQI<sup>2</sup>) and the pitch percentage on the anode properties were studied using the pitch modification.

The results showed that the HQI pitch modified with 1 % additive 1 at 16 % pitch percentage exhibited better anode properties owing to the higher anode density, lower electrical resistivity, and lower air permeability. This is also in good agreement with the wettability results because the additive 1 improved the wettability of coke by the HQI pitches. In general, the HQI pitch modified using the additive 1 led to the high-quality anodes at a lower pitch content compared to its unmodified counterpart, and this could lead to economic benefits.

The additive 2 improved the density (higher density) of the anode produced with the LQI pitch. This is in a good agreement with the observed improvement in the wettability of coke by the LQI pitch modified using the additive 2.

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<sup>1</sup> High quinoline insoluble

<sup>2</sup> Low quinoline insoluble

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## **Acknowledgements**

First of all, I appreciate my research director, Professor Duygu Kocaefe, who supervised me throughout my work. I am delighted to work with her, because in addition to her scientific support, she has always been there to support and advise me during the development of this project and has always made sure that everything is done to ensure that my work progresses continuously. Thank you very much for your support.

I would also like to express my deep appreciation to my co-director, Prof. Yasar Kocaefe for his continued assistance.

I would also like to express my gratitude to the organizations that contribute to this work, Rio Tinto for the technical and financial support and the Natural Sciences and Engineering Research Council of Canada (NSERC) for the financial support.

I would like to thank my family, especially my spouse Siamak Nikzad Khangholi, for their support. My master's degree could not have been completed without their support.

# Chapter 1

## Introduction

### 1.1. Production of aluminum by Hall- Héroult process

Aluminum<sup>1</sup>, as the third most abundant element in the earth's crust, is a light, malleable, and silvery-white metallic element, always found in an oxidized form and in tight combination with other elements, principally in bauxite. Aluminum is used in aerospace industry, transportation and building industries, etc. Its ability to be recycled indefinitely without losing its properties, its light weight, high resistance to atmospheric corrosion, etc. make aluminum a choice of metal in many applications. Aluminum alloys are available to meet the almost any strength requirement. Its electrical conductivity led to the aluminum to be used in the transmission high voltage lines. Bauxite<sup>2</sup>, a natural mineral consisting of hydrated form of aluminum oxide<sup>3</sup> with small amounts of iron oxides<sup>4</sup>, silicon oxide<sup>5</sup>, and titanium dioxide<sup>6</sup> is the mineral resource of alumina which is electrolyzed by Hall-Héroult process to manufacture aluminum metal [1-4].

Aluminum is produced by the electrolysis of alumina dissolved in cryolite<sup>7</sup>. The molten aluminum is produced at temperatures around 955-960 °C using the Hall-Héroult process, according to the reaction given by Eq. 1.1. This equation shows that carbon anodes reacts with oxygen coming from the electrochemical dissociation of alumina [5]. This process was developed simultaneously by Charles Martin Hall and Paul Louis Toussain Héroult, in 1886.

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<sup>1</sup> Al

<sup>2</sup> Al<sub>2</sub>H<sub>2</sub>O<sub>4</sub>

<sup>3</sup> Al<sub>2</sub>O<sub>3</sub>

<sup>4</sup> Fe<sub>2</sub>O<sub>3</sub>

<sup>5</sup> SiO<sub>2</sub>

<sup>6</sup> TiO<sub>2</sub>

<sup>7</sup> Na<sub>3</sub>AlF<sub>6</sub>



Due to different secondary reactions and the electrolytic cells' current efficiency, more carbon than that theoretically required is used throughout the electrolytic process as follows:

- If the anodes are not protected, oxygen from the air oxidizes the upper section of the anodes.
- As the anodes are immersed in a liquid bath, carbon oxidation reaction with  $CO_2$  takes place within the immersed part of the anode in the electrolyte.
- Selective oxidation of pitch-coke which is formed during baking by the carbonization of pitch occurs during the electrolysis (dusting) [6].

Due to the carbon consumption taking place during electrolysis, prebaked anodes need to be replaced every 2 to 4 weeks depending on the anode size and the current density, which has an impact on cost and environment. At the time of anode changing, about three quarters of the anode is consumed. The remaining part is called 'butt' [7].

Carbon anodes need to have:

- Low impurity levels to avoid the contamination of the aluminum metal and to prevent the excess anode consumption;
- High electrical conductivity (low resistivity) to reduce the power consumption;
- High thermal shock resistance to avoid cell disruptions;
- High density and low permeability to minimize anode (carbon) consumption and dusting as well as longer anode life;
- High resistance to oxidation to minimize excess carbon consumption;
- High mechanical strength and homogeneity for structural integrity and handling;

- Low carbon dioxide (CO<sub>2</sub>) and air reactivities [2].

Anode quality is significantly affected by the anode properties given above and the properties of raw materials, which are obtained from crude oil residues and tars in the coal and petroleum industries. Furthermore, the aggregate formulation, processing parameters, and equipment used to manufacture and bake carbon anodes influence the anode quality. A typical range of the industrial values is given in Table 1.1.

Table 1.1. Typical industrial anode properties [8]

<b>Anode property</b>	<b>Unit</b>	<b>Typical Range</b>
Green Apparent Density	kg/dm <sup>3</sup>	1.55-1.65
Baked Apparent Density	kg/dm <sup>3</sup>	1.50-1.60
Baking Loss	%	4.5-6.0
Specific Electrical Resistance	μΩm	50-60
Air Permeability	nPm	0.5-2.0
Compressive Strength	MPa	40-55
Flexural Strength	MPa	8-14
Static Elasticity Modulus	GPa	3.5-5.5
Dynamic Elasticity Modulus	GPa	6-10
Coefficient of Thermal Expansion	10 <sup>-6</sup> /K	3.7-4.5
Fracture Energy	J/m <sup>2</sup>	250-350
Thermal Conductivity	W/mK	3.0-4.5
Air Reactivity Residue	%	65-90
Air Reactivity Dust	%	2-10
Air Reactivity Loss	%	8-30
CO <sub>2</sub> Reactivity Residue	%	84-95
CO <sub>2</sub> Reactivity Dust	%	1-10
CO <sub>2</sub> Reactivity Loss	%	4-10

## **1.2. Carbon anode fabrication**

Anode production consists of the following steps: raw material preparation, mixing, compaction, green anode cooling, and anode baking. Dry aggregate (calcined petroleum coke, butts, and recycled green and baked anodes) is mixed with coal tar pitch (binder) in a kneader to prepare the anode paste. The composition of this mixture is called anode recipe, and this recipe plays an important role in defining anode properties [2, 7, 9]. To produce pre-baked anodes, approximately 65 % coke, 15 % pitch, and 20 % recycled anodes and butts are used. A good interaction between the coke and the pitch is important to provide a good wettability of coke since pitch has to fill the coke pores and the space between the particles. The determination of the optimum pitch amount (percentage) used in anode production has a crucial role in defining the anode quality. If the pitch amount is less than the optimum value, the anode paste becomes too dry and anode becomes under-pitched, causing poor binding between pitch and coke particles. If the pitch amount is too high, the anode paste is too wet resulting in over-pitched anode, causing weak binding between coke particles and pitch. Besides, particles are separated by a thick pitch layer. Thus, the physical and mechanical properties deteriorate, pores and cracks form, power consumption and GHG emissions increase. In addition, the amount of volatiles released increases and overloads the volatile burning system causing fire risk and safety hazard [9-12].

The stages and principle of anode fabrication are presented in Figure 1.1.

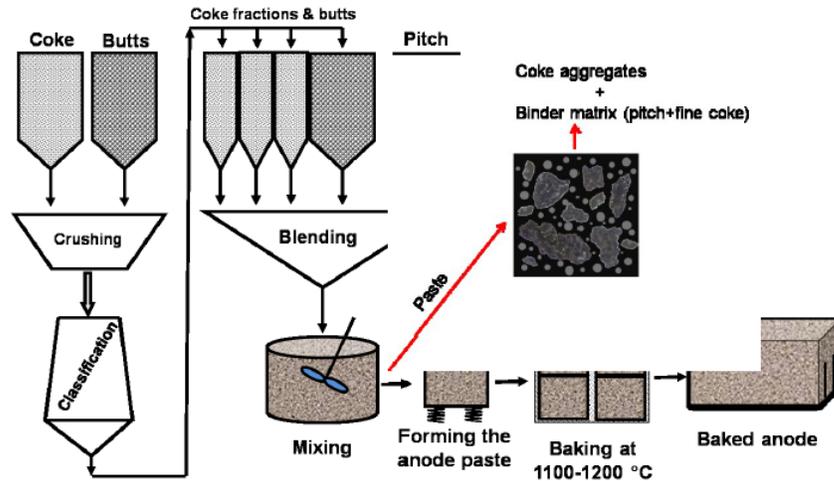


Figure 1.1. A schematic of anode manufacturing process [10]

### 1.3. Interaction between pitch and coke

Good quality anodes decrease the energy consumption, greenhouse gas emissions (GHG), and cost and increase anode life and production. A good interaction between pitch and coke in the kneader or mixer during the paste production is one of the requirements to obtain the desired final properties of the baked anodes. Therefore, choosing a suitable coke-pitch pair that tends to form bonds is an important step for having a good quality anode [4, 11, 13].

Pitch should coat the dry aggregate particles, penetrate into the coke pores, and fill the pores and the void between coke particles. Furthermore, pitch must adhere onto the coke surface and carbonized pitch should not separate from the coke particles at the later stages of the baking process (Figure 1.2). Therefore, the amount of pitch added to the dry aggregate is important and must be as close to optimal value as possible to promote the cohesion of the granular material. In fact, during the baking process, the pitch should form strong bonds between coke particles through carbonization, which enhances strength and

electrical conductivity of anodes. The degree of their interactions is directly related to the wettability of coke by pitch, which is determined by the properties of both the filler coke (particle size, texture, chemical functional groups on the surface, porosity, etc.) and the binder pitch (softening point, chemical composition, surface tension, and viscosity). Also, the effectiveness of the kneader's mixing is important for the distribution of pitch uniformly around the dry aggregate particles [10].

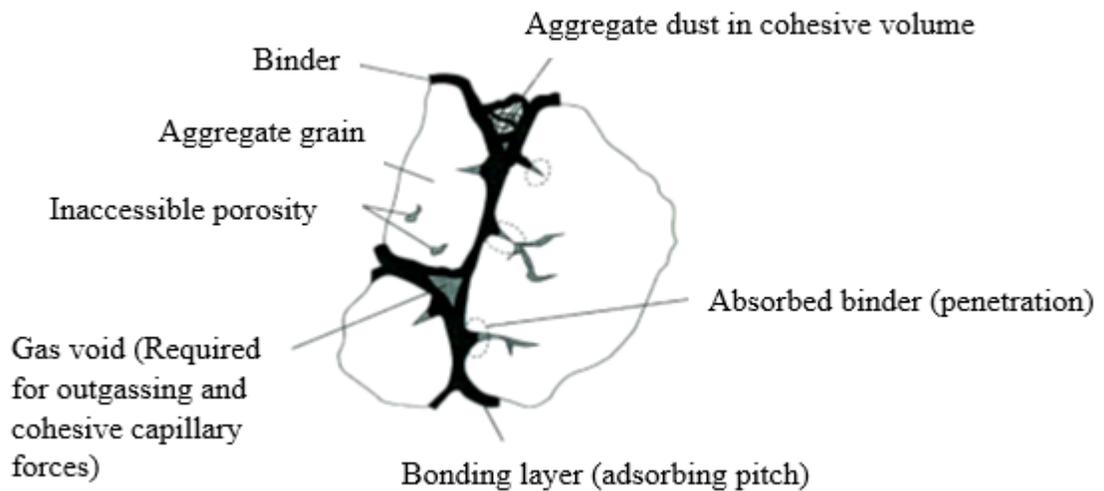


Figure 1.2. Pitch-coke aggregate system [4]

Presence of enough pitch in anode formulation is an important factor, which prevents any excessive shrinkage, expansion, as well as crack and porosity formation within the anode structure (Figure 1.3). With an insufficient amount of pitch, the bonding between pitch and coke particles is not strong enough. The under-pitched anodes have large voids between coke particles; hence they have high porosity. Figure 1.3 illustrates the pitch and dry aggregate system interactions.

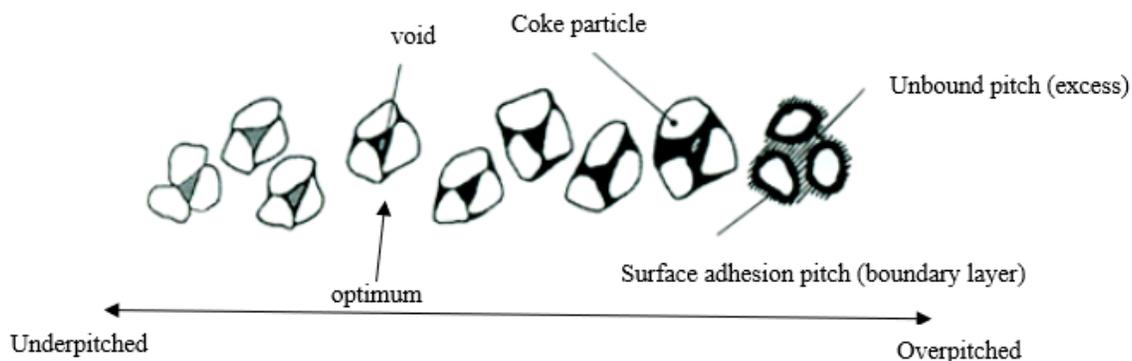


Figure 1.3. Binder-dry aggregate structure [4]

#### 1.4. Modification of the raw materials

One of the means of improving the interactions between coal tar pitch and petroleum coke is the modification of pitch properties using additives. It is reported in the literature that several researchers have worked on modifying the properties of pitch, but the studies on the utilization of modified pitch in anode production are rare. This will be explained in the next chapter in more detail. The additives used to modify the pitches should not contain toxic components. They should not contaminate the anodes and the aluminum produced. They should be inexpensive and have boiling points higher than the coke and pitch mixing temperature so that the additive does not evaporate during mixing. Since the chemical compositions of pitch and coke used in industry are variable, their compatibility can also change. Therefore, it is important to understand the underlying mechanisms between chemical additives and pitch interaction to effectively choose the appropriate additive and the amount of additive to use. However, the addition of chemical additives involves an additional expense to the industry. In order to economically justify the use of chemical

additives, it is required that its utilization results in a decrease in production cost, energy consumption, and environmental emissions as well as an increase in productivity [4].

### **1.5. Statement of the problem**

One of the big challenges for every primary aluminum producer is to produce good quality anodes. This depends on the parameters used during the anode manufacturing process and the raw material quality. Many investigations have been done to enhance the anode quality. The fabrication and the characterization of the anodes using the coke modified by additives were investigated only in our research group [7, 14, 15]. On the other hand, modifying the pitch using additives and surfactants has been recently studied by some researchers [4, 16, 17]. However, these researchers did not study the impact of the utilization of modified pitch on the quality of anodes used in aluminum production. The results of the work done by the carbon group at UQAC, the pitch modification by additives which allows the formation of the functional groups on the pitch surface, could help reduce cost and environmental emissions coming from the carbon anode production [4, 16, 17]. The modification changes the pitch surface and could enhance the pitch-coke interaction by modifying the wettability of coke by pitch. In addition, pitch is expensive and its quality has been decreasing. The modification of pitch using additives might make the utilization of low-quality pitch in anode production possible [18].

This study investigates whether the pitch modification with a given additive will lead to an improvement in anode quality or not by measuring the wettability of coke by the non-modified and modified pitches followed by the production of anodes using these pitches and their characterization.

## **1.6. Objectives**

The main objective of this study is to investigate the effect of the pitch and additive types, and the pitch percentage on the effectiveness of pitch modification in improving anode properties. Hence, better quality anodes could be produced with the available raw materials. The specific objectives are listed below:

- 1- Choose the best chemical additives according to the established criteria (chemical composition, melting and boiling points, and cost) ;
- 2- Improve the wettability of coke by pitch;
- 3- Determine if the selected additive is reliable and can prevent anode contamination;
- 4- Produce good quality anodes with available raw materials.

## **1.7. Scope**

The thesis is composed of five chapters, the introduction is given in Chapter 1. Chapter 2 presents the literature search review. Chapter 3 describes the methodology and the experimental procedure used in this study. The results of the study are presented in chapter 4. Chapter 5 gives the discussion of the results followed the conclusions and the recommendations of the study.

## Chapter 2

### Literature review

#### 2.1 Aluminum and aluminum production

Aluminum is found in the form of oxides. It is not available in metal form in nature due to its strong affinity toward oxygen. For this reason, it can be found in the earth crust. Aluminum with an atomic number 13 has a low density (only one third of that of steel), great ability to reflect light, high strength, and high resistance to corrosion. It is a good conductor of electricity and heat, ductile, nonmagnetic, nontoxic, recyclable [1, 11, 19].

Canada is the fourth producer of this metal in the world with 3.1 million tonnes of primary aluminum in 2021; thus, any improvement in energy efficiency of the aluminum production process will bring great economic and environmental advantages, especially in Quebec where 90 % of Canadian aluminum is produced [20].

The aluminum production was industrialized following the development of the Hall-Héroult process. This electrolytic process was invented by Charles Martin Hall, an American engineer, and Paul Louis Toussain Héroult, a French engineer, in 1886 independently. In this process, alumina ( $\text{Al}_2\text{O}_3$ ) dissolves in cryolite ( $\text{Na}_3\text{AlF}_6$ ) containing molten electrolytes, reduced electrochemically usually at temperatures around 955-960 °C to produce aluminum via the reaction shown in Eq. 1.1 [1, 2].

This reaction has two reactants, carbon coming from the anode and alumina, and two products, molten aluminum, the desired product, and carbon dioxide, which is a greenhouse gas (GHG) that is harmful to environment [1].

Alumina is consumed according to the stoichiometric ratio indicated in Eq. 1.1 Alumina supplied is not pure and always contains small amounts of oxides (impurities) such as  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$ . Based on Eq. 1.1, for every kg of aluminum produced, 2.22 kg of  $\text{CO}_2$  is produced. Theoretically, 1.89 kg alumina should react with 0.33 kg of carbon to produce 1 kg of aluminum. However, due to additional carbon interactions with oxygen and  $\text{CO}_2$ , between 0.40 and 0.45 kg of carbon are used for every kilogram of aluminum, which is called net anode consumption. If the mass of the butts is included, the gross carbon consumption may lay between 0.50 to 0.55 kg C/kg Al, and this makes each kilogram of aluminum to produce approximately 1.5 kg of  $\text{CO}_2$ . The theoretical consumption of the Hall-Heroult process is 334 kg C/ tonne Al (see Figure 2.1) [1, 2, 21].

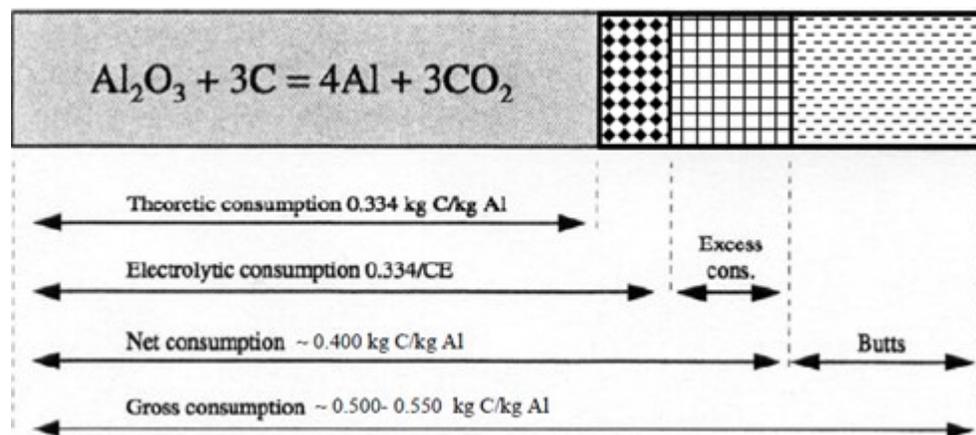


Figure 2.1. Prebaked carbon anode consumption in an electrolysis cell [4]

Excess carbon consumption occurs during the electrolysis due to the following processes:

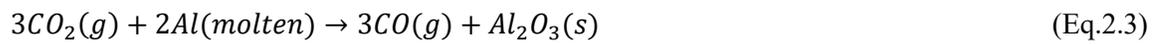
- Carboxy reaction called  $\text{CO}_2$  reactivity (Boudouard reaction, Figure 2.2):



- Dusting, which is the mechanical release of carbon particles from the anode into the bath (Figure 2.3).
- Air burn, air oxidation (air reactivity) of the parts of the anode exposed to air (Figure 2.3)



- Back reaction, the metal being re-oxidized to its oxide (Figure 2.2)



A reactivity imbalance between the various coke phases leads to selective oxidation. Dusting results from oxidation, wear, and selective burning around the anode above the electrolyte at the electrode working contact (Figures 2.2 and 2.3).

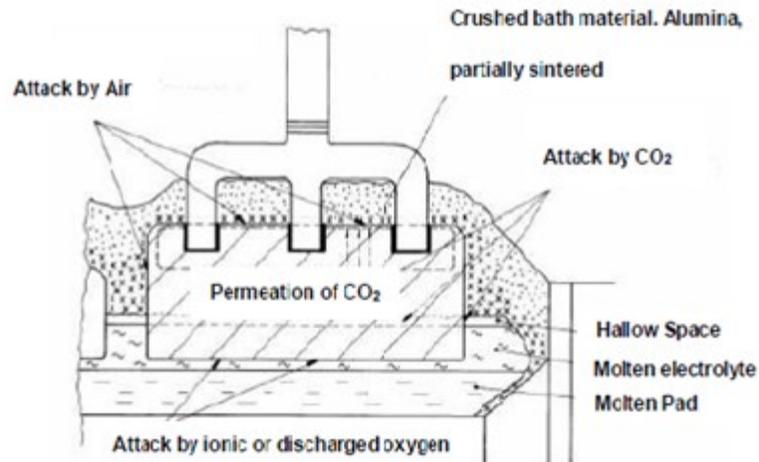


Figure 2.2. Reactions in the cell [21]

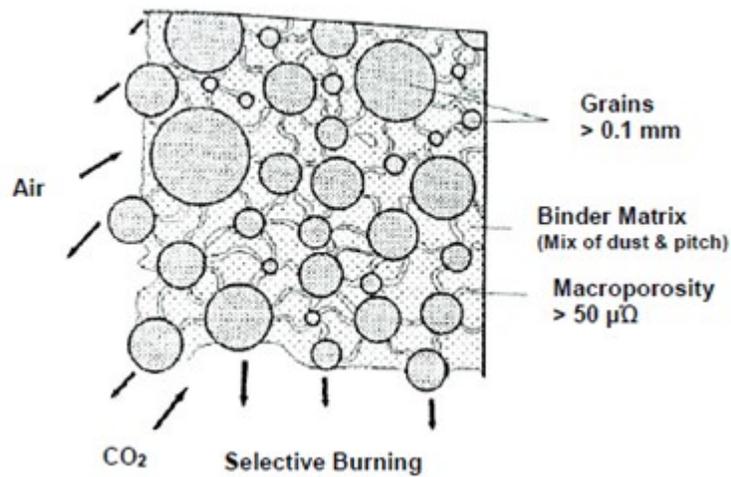


Figure 2.3. Selective oxidation of anode [21]

Two of the major goals of the aluminum industry are to decrease carbon and energy consumptions and to reduce the cost. Thus, monitoring of the anode consumption during cell operation is important.

In the Hall-Héroult process, molten cryolite ( $\text{Na}_3\text{AlF}_6$ ), which serves as a solvent, aluminum fluoride ( $\text{AlF}_3$ ), and calcium fluoride ( $\text{CaF}_2$ ) are used to create the electrolyte's

foundation. The melting point of pure cryolite is around 1010 °C. Other salts are added to decrease the melting point to 940-980 °C which is the operating temperature of the electrolysis cell [11].

## **2.2 Anode production**

The cost of anode production and related problems in cells could account for up to 25 % of the cost of aluminum production. Therefore, the anode cost is one of the major components of total production cost. The anode consumption increases due to the side reactions mentioned previously; hence they are undesirable. The anodes are changed every 3 to 4 weeks. One of the important goals in industry is to decrease anode and energy consumptions and production cost [1].

Today all aluminum smelters use carbon anodes since carbon has good electrical conductivity, good stability against the corrosive fluoride present in the electrolyte at temperatures of about 960 °C [1].

There are two different technologies in use, Søderberg and prebaked carbon anodes. In the Søderberg process, a mixture of petroleum coke and coal tar pitch is fed directly into the anode box placed above the cell. In fact, the carbon raw materials are bonded into a solid composite by the pyrolysis of pitch using the heat generated in the anode due to the Joule effect and received from the electrolytic cell. The amount of coal tar pitch used to fabricate these types of anodes is about twice the pitch amount used in the fabrication prebaked anodes. The prebaked anodes have particles consisting of petroleum coke, butts, and rejected anodes (about 85 %) and coal tar pitch used as a binder (about 15%). These materials are mixed at a temperature about 50 °C higher than the softening point of the

pitch to produce the anode paste. Then, they are formed in a vibro-compactor or a press to fabricate “green anode”. Figure 2.4 illustrates the anode fabrication process. The particles are bonded together by the pitch carbonized in the baking furnace before the anode is rodded and introduced into the electrolytic cell. The prebaked anodes have more advantages compared to the Söderberg anodes in terms of quality and pollution control. In this work, the focus is on prebaked anodes. The bonding between coke and pitch is very important to fabricate good quality anodes since pitch must coat the coke particles, penetrate and fill the coke pores and voids during the mixing of the paste and the forming of green anodes. While baking, pitch-coke bridges form between the coke particles. The green anodes are baked at temperatures up to 1050 -1200 °C to carbonize the binder which keeps the dry aggregate particles together, improves physical and mechanical properties, and reduces electrical resistance. Anodes are not consumed completely in the electrolysis cell when prebaked technology is used to prevent metal contamination from steel stubs; they are removed usually when they are reduced to about 1/3 of their original size called “butts”, which are recycled to be used in the production of new anodes. This decreases coke demand and waste material [1, 2, 6, 11, 14, 16, 22-25].

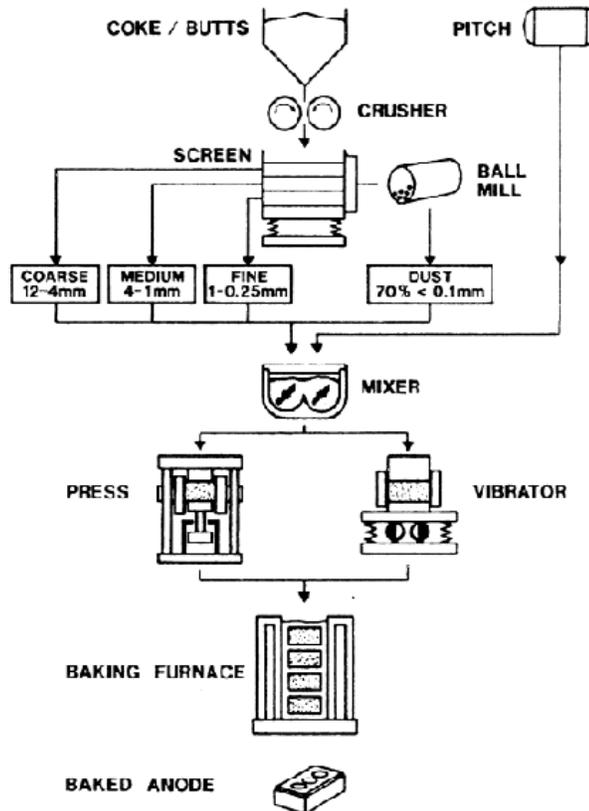


Figure 2.4. Anode manufacturing process flow sheet [6]

### 2.3 Anode properties

Good quality carbon anodes should have:

- High chemical purity to avoid the contamination of the aluminum metal and excess anode consumption,
- High electrical conductivity (low resistivity),
- High thermal shock resistance to avoid the disruption of cell operation,
- High mechanical strength and homogeneity for structural integrity and handling,
- Low carbon dioxide and air reactivities,

- High density and low permeability important to reduce anode consumption, dusting, and anode change cycle.
- High resistance to oxidation for decreasing excess carbon consumption,
- Low specific electrical resistivity for low power consumption.

The raw material characteristics, which are obtained from crude oil residues and tars of the coal and petroleum industries, significantly influence anode quality and anode behavior. The aggregate formulation, processing parameters, and equipment used to manufacture and bake the carbon electrodes are also other important parameters defining the anode quality [2, 3].

### **2.3.1 Green anode density**

Green anode density is measured from the geometrical dimensions and anode weight of green anode core after compaction. Variations in this parameter are an indication that there are process disturbances, particularly in the forming temperature and mixing conditions [2].

### **2.3.2 Baked apparent density**

Baked anode apparent density measured from the baked anode cores. High baked anode density tends to reduce anode air permeability and can extend anode life in the cells. Extremely high-density levels can lead to thermal shock problems. Baked anode density is controlled by raw material selection, aggregate granulometry, optimal pitch content, optimal processing parameters to avoid poor compaction during forming (or expansion during baking) [2].

### **2.3.3 Shrinkage**

Cracking of the anode can occur at high shrinkage values [2].

### **2.3.4 Specific electrical resistivity**

The specific electrical resistivity of the carbon anodes ideally should be as low as possible to reduce energy losses associated with resistive heating in the anodes. Resistivity depends on basic coke structure, anode density, and pore distribution. Cracks and other flaws can be the result of mixing or forming problems, excessive moisture in the paste or thermal shock during baking or cooling. The distribution of this property shows anode homogeneity. Very low values of electrical resistivity and high thermal conductivity levels may be a result of over baking and can lead to air burn problem [2].

### **2.3.5 Air permeability**

Air permeability is an index of ease with which a fluid flows through a porous solid. The permeability of an anode should be minimized to restrict the transport of oxidant gases to the reactive surfaces within the anode structure. Open porosity and channeling which creates permeability is often associated with the interface between large aggregate particles and the binder matrix. Changing the composition of the binder-fines matrix can also change the permeability. Finer formulations (particularly the dust fraction) generally result in low air permeability [2].

### **2.3.6 Carbon dioxide and air reactivities**

The reactivity values are important for determining the susceptibility of an anode to excess carbon consumption and dusting in the electrolysis cell. This is strongly influenced

by the impurities present in the raw materials forming and baking parameters such as the maximum baking temperature, heating rate, and soaking time [2].

## **2.4 Anode raw materials (coke and pitch)**

Calcined petroleum coke, recycled anode butts, and rejected anodes are used as dry aggregate to produce green anode blocks using binder pitch. There are different types of coke and pitch with varying constituents and properties. In addition to the types and properties of raw materials, factors such as granulometry of particles and proportion of materials in the paste (formulation or anode recipe) affect the final anode density, electrical resistivity, strength, and reactivity.

### **2.4.1 Coke**

Calcined petroleum coke is the principal carbonaceous anode raw material and has the highest mass fraction in anode paste with at least 65 %. Coke is in the form of particles with different size fractions as aggregates; and dust (fine) forms the binder matrix with pitch. Coke particle size varies from about 15 mm diameter to a few microns as dust. Petroleum coke is a mixture of heavy hydrocarbons and is obtained from the thermal decomposition and polymerization of residuals of raw petroleum distillation [11, 26]. It is a relatively low-value by-product. Its quality is not the main concern for oil refinery and petroleum industry [27]. It is obtained from delayed coking process. Thus, there are significant differences in the physical properties and chemical impurities of different cokes. The green coke is calcined up to 1200 °C to remove volatile constituents (see Table 2.1), to increase coke strength and density for using it in anode production. Since the green coke quality is variable, the quality of calcined coke also varies even shipment to shipment. The calcined coke quality also depends on calcination conditions [2, 3]. To achieve optimum

porosity and maintain low air and CO<sub>2</sub> reactivities, it is important to control the calcination conditions. Closed pores are inaccessible and open pores are interconnected reaching surface. Usually, good quality coke contains more open pores (0.5 μm – 15 μm) than closed pores.

Table 2.1 shows typical coke composition. Petroleum coke is preferred to metallurgical coke (coke of coal) for use in aluminum industry due to its lower surface area, volatile content, and ash content [28].

Table 2.1 Typical composition of petroleum coke [3]

Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
88-95 %	3-4 %	1-2 %	0.6-6 %	1-7 %

The coke properties such as porosity, shape, surface characteristics affect thermal, mechanical, and physical anode properties such as density, mechanical strength, electrical resistivity, pore size distribution, air permeability, reactivity, and anode chemical composition (Table 2.2). Different particle size distributions need different pitch contents in the anode paste [6, 25]. Thus, an optimum quantity of coarse, medium, and fine particles are required to make an anode recipe which will yield good anode quality [6, 25].

Petroleum coke, which is used in anode manufacturing, has some porosity, which causes pitch to absorb into the pores during green paste mixing, resulting in a carbonaceous paste. This is becoming increasingly important as the availability of higher quality petroleum coke diminishes, necessitating the use of lower quality petroleum coke with higher porosity.

The pitch absorbed by the coke pores (Figure 2.5) may not increase the strength of the pitch binder in anodes, but it may improve anode characteristics like density and electric conductivity. The amount of pitch employed in the anode formula is directly related to the petroleum coke's absorption level. There is currently no reliable way to assess the pitch content absorbed into the coke pores.

Figure 2.5 shows schematic drawing of the mixing between petroleum coke and pitch [4].

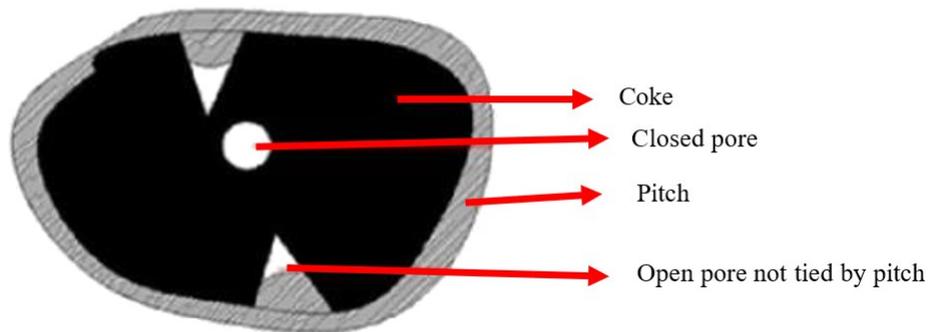


Figure 2.5. Schematic drawing of the mixing between petroleum coke and pitch [4]

Table 2.2 Typical range of properties of coke used in aluminum smelters [8]

Property	Method	Units	Range
Water content	DIN 51904	%	0.0-0.2
Oil content	ISO 8723	%	0.10-0.30
Dust forming factor	RDC 177	%	0.002-0.001
Grain size >8mm	ISO 2325	%	10-20
8-4mm	ISO 2325	%	15-25
4-2mm	ISO 2325	%	15-25
2-1mm	ISO 2325	%	10-20

1-0.5mm	ISO 2325	%	5-15
0.5-0.25mm	ISO 2325	%	5-15
<0.25mm	ISO 2325	%	2-8
Tapped Bulk Density			
8-4mm	ISO DIS 10236	kg/dm <sup>3</sup>	0.64-0.70
4-2mm	ISO DIS 10236	kg/dm <sup>3</sup>	0.73-0.79
2-1mm	ISO DIS 10236	kg/dm <sup>3</sup>	0.80-0.86
1-0.5mm	ISO DIS 10236	kg/dm <sup>3</sup>	0.86-0.92
0.5-0.25mm	ISO DIS 10236	kg/dm <sup>3</sup>	0.88-0.93
Mean Bulk Density	-	kg/dm <sup>3</sup>	0.78-0.84
Grain stability	ISO DIS10142	%	75-90
Density in Xylene	ISO 8004	kg/dm <sup>3</sup>	2.05-2.10
Specific electrical resistance	ISO DIS 10143	μΩm	460-540
CO <sub>2</sub> reactivity loss (1000 °C)	ISO N 802	%	3-15
Air reactivity at 525 °C	ISO N 803	%/min	0.05-0.3
Crystallite size (L <sub>c</sub> )	-	Å°	25-32
Ash content	ISO 8005	%	0.10-0.20
Elements			
S	ISO N 837	%	0.5-3.5
V	ISO N 837	%	30-350
Ni	ISO N 837	ppm	50-220
Si	ISO N 837	ppm	50-250
Fe	ISO N 837	ppm	50-400

Al	ISO N 837	ppm	50-250
Na	ISO N 837	ppm	30-120
Ca	ISO N 837	ppm	20-100
Mg	ISO N 837	ppm	10-30

#### 2.4.2 Pitch

Coal tar pitch, which is used as a binder for dry aggregates, is produced by the distillation or heat treatment of coal tar. The coal tar is produced as a by-product of the coking of bituminous coals. High temperatures (900-1100 °C) yield metallurgical coke, and low temperatures (600 °C) are used to produce domestic smokeless fuel. A small amount of tar is obtained in the low temperature processes. Pitch is the residue remaining following the removal of the heavy oil (creosote oil) and anthracene oil fractions. Mineral matter or ash is concentrated in the residual coal-tar. Prior to tar distillation, the feedstock is dosed with controlled amounts of either a sodium carbonate or sodium hydroxide solution to neutralize ammonium chloride dissolved in the tar water. This eliminates the problem of corrosion in the fractionating equipment due to chloride attack. Unfortunately, the added sodium ends up in pitch and subsequently in the anode, where it can catalyze carbon consumption reactions. Table 2.3 shows a typical coal tar pitch analysis [3].

Table 2.3 Example of coal tar pitch analysis [8]

Property	Method	Units	Range
Water content	ISO 5939	%	0.0-0.2
Distillation 0-270 °C	AKK 109	%	0.1-0.6
Distillation 0-360 °C	AKK 109	%	3-8
Softening point (Mettler)	ASTM D3104-87	°C	110-115
Viscosity at 140 °C	ASTM D4402-87	cP	3,000-12,000
Viscosity at 160 °C	ASTM D4402-87	cP	1,000-2,000
Viscosity at 180 °C	ASTM D4402-87	cP	200-500
Density in water	ISO 6999	kg/dm <sup>3</sup>	1.30-1.33
Coking value	ISO 6998	%	56-60
Quinoline insoluble	ISO 6791	%	7-15
Toluene Insoluble	ISO 6376	%	26-34
Ash content	DIN 51903	%	0.1-0.2
Elements			
S	ISO 12980	%	0.3-0.6
Na	ISO 12980	ppm	10-400
K	ISO 12980	ppm	10-50
Mg	ISO 12980	ppm	5-30
Ca	ISO 12980	ppm	20-80
Cl	ISO 12980	ppm	100-300
Al	ISO 12980	ppm	50-200
Si	ISO 12980	ppm	50-200
Fe	ISO 12980	ppm	50-300

Zn	ISO 12980	ppm	100-500
Pb	ISO 12980	ppm	100-300

Coal tar pitch is often the binding pitch used in the manufacture of prebaked anodes (although in some instances selected grades of petroleum pitch are used) and they are mostly mixtures of the chemicals found in the distillable fractions of the tar's higher homologues and are chemically similar to the tars from which they are made of. The pitch coats the dry aggregate particles during mixing. This is particularly important during the early heat-up phase of anode baking when the binder coke bridges between the aggregate particles have not yet formed [29]. Desired properties of binder pitch are related to the quantity and/or nature of their higher molecular weight aromatic constituents. Between high ranges of coal tar pitches, those which derived from high temperature tars are satisfactory as binder for manufacturing carbon anodes. A good pitch should have a high coking value, not swell too much, and have minimum shrinkage, which will result in final product with low porosity [29].

Coal tar pitch is a complex material and includes aromatic compounds with different functionalities and a broad molecular weight distribution. It is a good material to apply in carbon composites because of its high carbon content and included inorganic compounds in its composition and its capacity to graphitize. The processing of carbon materials or carbon-carbon composites with coal-tar pitch as the matrix precursor becomes not only time consuming but also expensive [30].

As discussed before, coal tar pitch is used both in Soderberg smelters and prebaked anodes as binding materials [2, 3]. Now, pitches are transported in liquid form in dedicated ships for environmental and hygiene reasons.

Pitch has an important role in anode quality. The pitch properties depend on:

- The carbonization process of the parent coal and thus crude tar, especially the tar nature and composition.
- The tar distillation method: batch or continuous.
- The lower boiling constituents retained in the pitch (distillation efficiency)
- Additional treatment of the pitch, e.g., air blowing, thermal treatment, distillation under very low residual pressure [2, 3].

Most important properties of pitch as a binder are:

- Strong adherence/ bonding to the dry aggregate particles,
- Satisfactory wetting characteristics,
- High coking value yielding a strong coke structure,
- Low relative cost and ready availability in large quantities,
- Low ash and sulfur content,
- Smooth volatile emission across the anode baking temperature range,
- Formation of an oxidation resistant binder matrix,
- Low reactivity,

- High electrical conductivity.

Therefore, pitch quality that is a combination of its physical and chemical properties affects the anode properties [2, 3]. Table 4 presents pitch properties.

## **2.5 Pitch properties**

### **2.5.1 Softening point**

It is defined as the point at which a pitch starts softening. Pitches used in anode production have a Mettler softening point between 100 and 120 °C. With increasing softening point, anode properties improve due to increase in aromaticity index, coking value, apparent density and decrease in electrical resistivity, porosity, and baking loss in the anode. The softening point-viscosity relationship is important for anode manufacturing. The softening point should not be too high, because the anode paste will not flow at the working temperature and too low softening point of pitch causes pitch to separate from the coke particles or grains [2, 31].

### **2.5.2 Coking value**

It is defined as the residual carbon retained in the form of carbonized pitch after baking. It increases with increasing pitch softening point. Volatiles are released from pitch during the baking process. The typical range for coking value is between 55-60 % for coal tar pitches. Pitch density, its QI content, and aromaticity help increase the coking value [2, 31].

### **2.5.3 Pitch density and C/H ratio**

It is connected to molecular packing and stereochemistry. The aromaticity of the pitch is indicated by pitch density. Denser pitches have higher aromaticity which results in high

density carbon anodes. Carbon to hydrogen ratio (C/H) of pitch gives an indication of the aromaticity level of pitch. The higher the C/H ratio is, the higher the aromaticity of pitch is [2, 31].

#### **2.5.4 Quinoline Insolubles (QI)**

The pitch can be categorized by its solubility in selected solvents such as quinoline, toluene, and benzene. There are two types of quinoline insolubles which are primary and secondary QI. Primary QI can be beneficial to anode properties and are formed in coke oven, and their size is about 1  $\mu\text{m}$ . Secondary QI (and mesophase) is either neutral or harmful to anode quality and formed by heat treatment of pitch (at temperatures greater than 400 °C). The secondary QI particles are larger than the primary QI particles in size. QI material has a large influence on pitch density, because they are very dense. They have effect on density, mechanical strength, and reactivity of carbon anodes [2, 31].

There is no agreement on the optimum QI level of pitch to have good anode properties. In fact, that it is not only the level of QI, but also the QI particle size as well as the coke particle size distribution affects the anode properties [2, 31].

#### **2.5.5 Toluene Insolubles (TI)**

TI influence pitch binding;  $\beta$  resins are the difference between the toluene insoluble and the quinoline insoluble (TI-QI), which contribute to the coking value and bond formation between the filler particles and pitch. Increasing  $\beta$  resin content indicates increasing aromaticity and the coking value of pitch. It also affects pitch viscosity and wetting characteristics of pitch (pitch binding ability) [2, 31].

### **2.5.6 Viscosity**

Viscosity is a measure of pitch fluidity which is measured between 150 and 260 °C. Pitch viscosity information is also used to guide liquid pitch handling. Pitch viscosity decreases with increasing temperature and affects wetting [2, 31].

## **2.6 Interaction between pitch and coke**

The coke-pitch interaction could be physical, chemical or a combination of the two together. Coke-pitch interaction could be studied by using different techniques such as wettability test (sessile-drop test), FTIR (Fourier Transform Infrared Spectroscopy), etc. [10, 11, 13, 22, 32].

Between coke and pitch, there are typically three different types of chemical interactions [33]. A hydrogen atom linked to an electronegative atom (O, N) and another electronegative atom forms a hydrogen bond as the first type of interaction. The hydrogen of the O-H group and the functional groups containing oxygen can form a hydrogen bond with other molecules (such as the hydroxyl, ether, carboxylic, and nitrogen atoms). The second way that basic and acidic functional groups might interact is through the acid-base interaction. As a result, nitrogen atoms or functional groups with oxygen atoms (such hydroxyl, ether, or carboxylic groups) can form a hydrogen bond with the hydrogen of the O-H group. The second way that acidic functional groups (such as carboxylic and phenolic) can interact with basic functional groups is through the acid-base interaction (amine). Electrostatic interactions are the third type. In this case, carboxylic and phenolic functional groups can interact with basic functional groups [34].

### 2.6.1 Wettability

Wettability of coke by molten pitch drop can be defined in terms of the contact angle between coke and pitch, and Young proposed Eq. 2.5 in 1805:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (\text{Eq. 2.5})$$

where  $\gamma_{sv}$  is the interfacial tension of solid- vapor interface,  $\gamma_{sl}$  is the interfacial tension between solid and liquid interface,  $\gamma_{lv}$  is the interfacial tension of liquid- vapor interface, and  $\theta$  is the contact angle. The smaller the angle is, the better the wetting is (see Figure 2.6) [35].

The Young equation provides a mathematical formula for the relationship between the interfacial tensions of solid, liquid, and gas when a drop is created on an ideal flat, smooth, homogeneous surface, and there is no reaction between the phases. A liquid is referred to as non-wetting if it contacts a surface at an angle greater than  $90^\circ$ . A liquid is considered to be wetting if the contact angle is smaller than  $90^\circ$  [35].

In the wettability test, an inert atmosphere is used inside the sessile-drop equipment. The image of the liquid (pitch) drop, which is placed on the coke bed, is taken, and the contact angle is determined from this image. The wettability of different coke-pitch pairs can be compared when the experiments are carried out under the similar conditions as a function of time and temperature [33, 34, 36].

During the test, a pitch droplet's observed contact angle with a bed of fine coke particles is recorded as a function of time at a constant temperature. The wetting test may be useful to identify pitch and coke combinations that are likely to produce baked anodes of acceptable

quality under standard paste preparation conditions. It does not, however, provide a measure of the actual contact angle since the coke bed surface is not ideal smooth surface. The wettability experiments demonstrate that the observed contact angle of a pitch on a coke bed changes continuously from  $>90^\circ$  to  $<90^\circ$  at a constant temperature [37]. This is due to the surface change during coke-pitch interactions as well as the penetration of pitch into the coke bed.

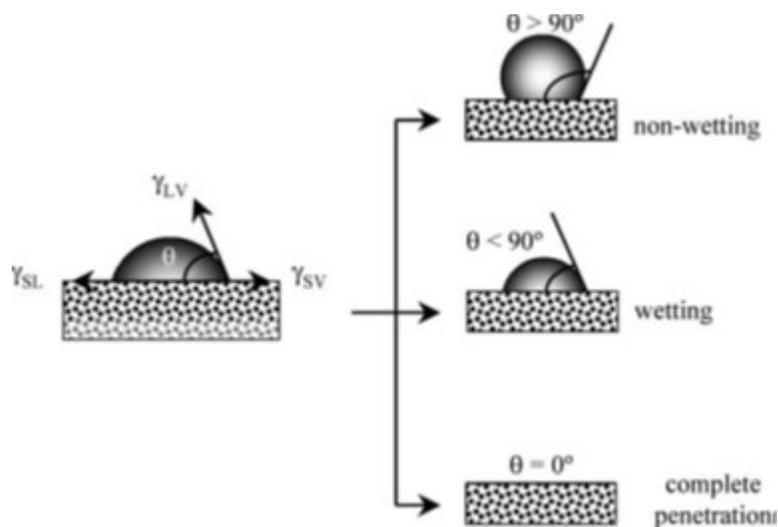


Figure 2.6. Schematic illustration of the liquid-solid wetting principle [38]

Functional groups on the coke and pitch surfaces can improve the wettability of coke by pitch [4]. Research on coke's wettability by pitch is quite important. The wettability test can be carried out under isothermal or non-isothermal condition. Several investigations have been carried out on the wettability of petroleum coke by pitch at various temperatures. Various techniques were employed to estimate a molten pitch's ability to penetrate the coke bed [3]. Numerous authors discovered that the wettability behavior of pitch and coke is affected by their properties. [39-42].

Rocha et al. [40, 41] studied the influence of the chemical composition and structural order of the substrate (petroleum coke as the substrate, with a number of substrates made by thermally processing petroleum pitch) on the pitch/substrate wetting behavior. Rocha et al. [40] also indicated that the wettability is influenced by surface tension and viscosity of pitch.

Sarkar et al. [13] investigated on the wettability of cokes by pitches. They reported that the surface functional groups on the coke and pitch surfaces might form chemical interactions which enhance the wetting behavior of coke by pitch. The contact angles decrease with increasing time and temperature. Decreasing the pitch viscosity with increasing temperature is one of the factors that improve pitch spreading and penetration into the coke bed.

Huang et al. [33] investigated the wettability of bio-coke by pitch and found that because the surfaces of bio-cokes differ chemically from those of petroleum coke, they are more wettable by pitch than petroleum coke.

Mirchi et al. [43] also observed that increase in temperature can increase wetting.

The qualities of the anodes are influenced by the wettability of the coke by pitch employed as the anode's binder. Therefore, by choosing the best coke-pitch pair, it is possible to have good final baked anode properties such as high density, good mechanical properties, and low electrical resistivity.

## **2.7 Pitch modification by using chemical additives**

The raw material quality (both coke and pitch) is decreasing [44]. The aluminum industry is looking for alternative solutions. One solution can be the improvement of pitch quality with additives since pitch production requires considerable time and it is costly.

Additives can be used to improve coke-pitch interactions in order to form a bridge between coke and pitch that is explained in more detail below.

As mentioned before, it was considered that the chemical composition of raw material does not always provide sufficient cohesion between coke and pitch. Depending on the nature of the materials, certain chemical functions do not allow pitch to bond with coke. As shown in Figure 2.7, there are several functional groups between these two materials. For example,  $F_1$  does not have enough chemical affinity to bond with  $F_4$  of pitch. Since addition of additive may provide the sufficient bonding ( $F_2$  and  $F_3$ ) between  $F_1$  and  $F_4$  of pitch. In fact, by forming bonds, a link between coke-pitch particles will be established. Increasing in number of these interactions will increase the bonding between raw materials and will lead to good quality anodes [4, 16].

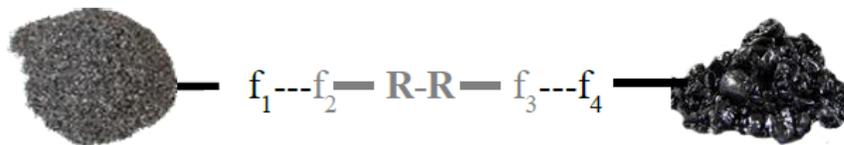


Figure 2.7. Representation of chemical forces ( $F_i$ ) between the different components (R: organic groups) [4]

Several studies investigated the pitch modification using additives, but there are not many studies where the modified pitch was used in anode fabrication. The modification was carried out to change the pitch properties.

Oh and Park [45] have investigated the use of the addition of elemental sulfur as a chemical additive to modify the pitch. Sulfur can have a positive or negative effect on anode production depending on its concentration. One part of the sulfur neutralizes some of the

impurities which affect anode reactivity. If the sulfur content of coke is too high, the sulfur gases are emitted to the atmosphere during baking which is harmful to the environment. Pitch modification by sulfur leads to better pitch carbonization compared to unmodified pitch. It increased the softening point by increasing quinoline (QI) and high thermal stability.

Ren et al.[46] investigated pitch modification with three different additives, consisting of activated glyceride (GA), aluminum sulfate with polyethylene oxides (SA-OPE), and divinylbenzene with p-toluene sulfonic acid (DVB-APTS). They found that the addition of GA increased the pitch viscosity and improved the permeability.

Lin et al.[30] have investigated pitch modification with divinylbenzene. Their results showed that modified coal tar pitches have many methyl and methylene functional groups. The modified pitches also have higher QI content and lower TS content compared to the non-modified pitches. Pitch modified by divinylbenzene included polymer chains which have good linearity when shear stress and temperature are present. Thus, they have better thermo stability than the coal tar pitch.

Hu et al.[30] investigated the effect of oligomer addition to petroleum pitch on the coking behavior. The results showed that the modified pitch contains many microfibers made of polymer chains which are mostly responsible for the improvement of optical textures of semi-cokes.

Rocha et al. [39] developed methods to modify petroleum pitch and study their interaction with coke particles of 100-125  $\mu\text{m}$  in diameter. One method uses a surfactant (fatty acid) from the paper manufacturing industry. The addition of an active surface agent improves

the wettability properties of a non-wetting pitch. However, based on the results obtained, it is impossible to determine the minimum value of surface tension and viscosity required that will ensure improved wettability.

Rocha et al. [41] also carried out other tests with other types of surfactants following the method proposed in their previous articles [47, 48]. The additive used in this work contains alkyl and sulfur groups, added to the petroleum pitch. The addition of the surfactant used reduces the surface tension and maintains the viscosity at similar values initially without changing the other properties. Nevertheless, the initial temperature of the impregnation is higher, which is less effective. However, the impregnation time is faster, probably thanks to the presence of primary QI according to the authors. This implies that the modified petroleum pitch requires higher temperatures in order to overcome the forces of cohesion. Once this barrier has been crossed, the diffusion of this pitch through petroleum coke is thermodynamically possible.

There are few investigations on pitch modification and utilization of modified pitch in anode fabrication.

Bureau et al.[4, 17] have investigated pitch modification with three different additives. Among the three additives, two additives improved the pitch properties, since they contained more aliphatic and heteroatoms compared to the third additive used. They fabricated laboratory anodes based on these modifications and found that the anode properties were improved. This was carried out by the carbon group of UQAC.

The European commission [49] reported that they studied making anodes by modifying paste with water of sodium carboxymethylcellulose (CMCNa), Mobilsol 40 (M40), and

polystyrene granules (PS). By addition of CMCNa and Mobilsol did not significantly improve the anode properties since they encapsulated pitch which prevented coke wetting.

Lu et al. [50] investigated on modification of bio-pitch by adding bio-char particles to increase the insoluble particles in the pitch. The results showed that QI content of modified bio-pitch increases linearly with bio-char addition, coking value, density, viscosity, C/H and C/O molar ratios of the resulting modified pitches also increased with higher quantities of bio-char. This suggests that the modified bio-pitch has most likely more suitable characteristics than non-modified bio-pitch.

Amara et al.[51] studied on modification of 3% bio-coke using 3% of three different additives in order to improving biocoke-pitch interactions. The XPS results showed that the modification of bio-coke using additives A(1) and A(3) improved the biocoke-pitch interactions. The laboratory anodes were produced using modified and non-modified bio-cokes. The properties of the anodes made with modified bio-coke using additives A1 and A3 were similar to or often significantly superior than those of normal anodes.

Amara et al.[52] investigated on modification of bio-coke by 3% and 4% of an additive to increase the surface chemical groups in the bio-coke. The XPS and wettability results showed that surface functional groups were increased by modification. They produced laboratory anodes using non-modified and modified bio-cokes. It was considered that anode properties improved using modified bio-coke in anode production.

Based on the literature search, only a few researchers modified the pitch in order to manufacture anodes. In the present study, that is in collaboration with Aluminum industry, the sessile-drop tests were carried out to study the coke wettability by pitches which have

different QI content (non-modified and modified with different additives). The analysis of the results makes it possible to see the effect of pitch modification on the wettability of coke by pitch. In general, better wettability leads to good quality anodes.

## Chapter 3

### Methodology

A general diagram of the methodology is presented in Figure 3.1. Anodes consist of two parts: the dispersed phase and the binding phase. The dispersed phase contains petroleum coke, butts, and rejected anodes. The binder phase consists of coal tar pitch and coke fines. Two types of pitch were used in this study: Pitch 1 (P<sub>1</sub>) and Pitch 2 (P<sub>2</sub>). Coke with different particle sizes was obtained from the aluminum industry.

Chemical additives were selected and characterized with the objective of modifying the surface functional groups of pitches in order to improve the compatibility between pitch and coke. Pitches were modified with the selected additives. The non-modified and modified pitches as well as the coke were characterized in order to evaluate their interactions. Selection criteria for the additives were: they should be non-toxic and inexpensive, do not contaminate the aluminum, and shouldn't have a boiling point below the anode paste mixing temperature (~180 °C) so that they would not vaporize during mixing.

In order to modify the pitches, two additives were used. Additive 1 (Add1) and Additive 2 (Add2) were obtained from Alfa Aesar. The pitches were modified using different additive concentrations ( $0.5 < c_1 < c_2 \leq 5 \%$  g/g). After, the laboratory anodes were manufactured using these pitches.

The wettability tests were carried out with coke and pitches in order to determine their interactions. Then, the effect of pitch modification with additives on anode properties was studied by characterizing the baked anodes produced. Their apparent density, electrical resistivity, air, and CO<sub>2</sub> reactivities, air permeability, thermal expansion coefficient, and

compressive strength were measured. The properties of the anodes made with modified pitches were compared with those of the corresponding standard anodes.

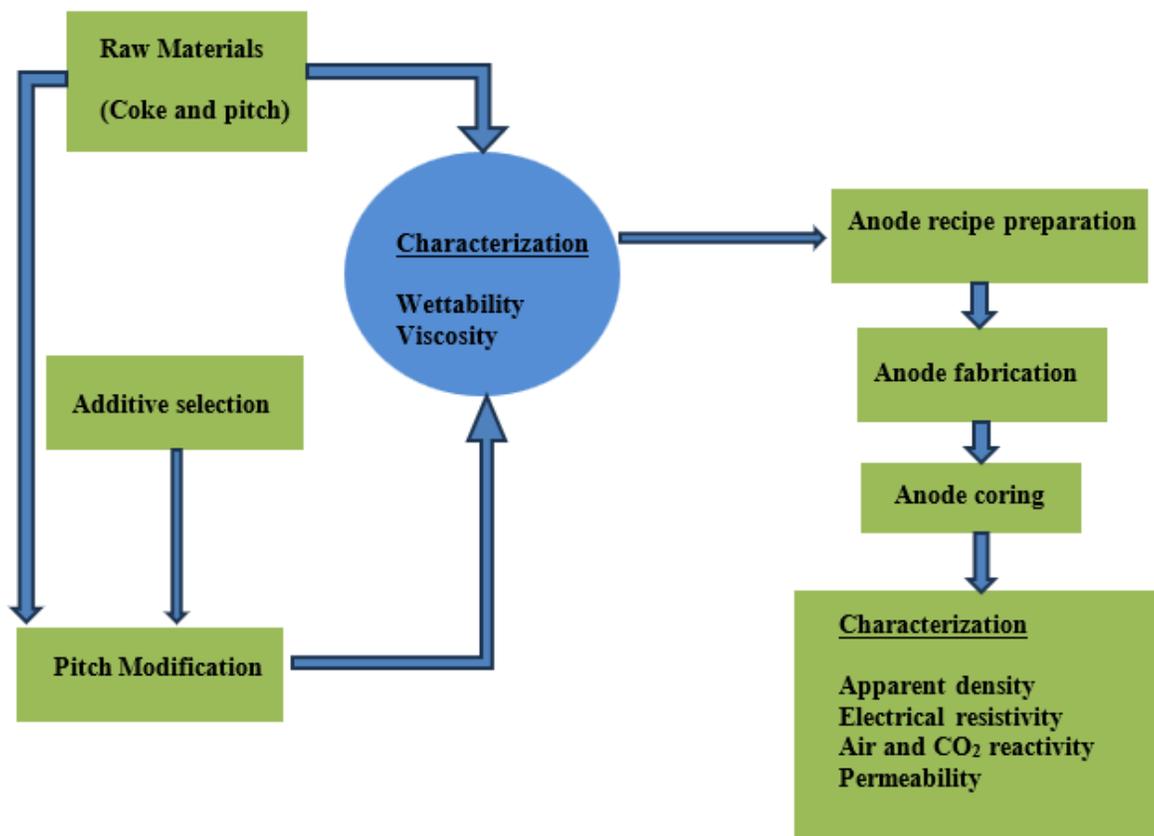


Figure 3.1. Methodology

### 3.1 Raw material properties

The properties of both pitches are given in Tables 3.1 and 3.2. The coke properties are given in Table 3.3. The butt properties used in this study are given in Table 3.4.

Table 3.1. Properties of Pitch 1

<b>Pitch 1</b>					
<b>Property</b>	<b>Units</b>	<b>Range</b>	<b>Elements</b>	<b>Units</b>	<b>Range</b>
Density (20°)	g/ml	1.310	Ca	ppm	96
Softening point, Metler	°C	120.3	Fe	ppm	140
Quinoline Insoluble	% m/m	7.5	Si	ppm	155
Toluene insoluble	% m/m	28.6	P	ppm	5
B-resins	% m/m	21.1	Zn	ppm	158
Coking residue Alcan	% m/m	59.7	Na	ppm	144
Ash(700°C)	% m/m	0.13	Pb	ppm	119
C/H- ratio, pitch	-	1.74	S	% m/m	0.47
Mesophase content	% m/m	<1.0			
Mesophase content,> 10 µm	%	<0.2			
Dynamic viscosity, 140 °C	mPa.s	46800			
Dynamic viscosity, 160 °C	mPa.s	5760			
Dynamic viscosity, 180 °C	mPa.s	1380			

Table 3.2. Properties of Pitch 2

<b>Pitch 2</b>					
<b>Property</b>	<b>Units</b>	<b>Range</b>	<b>Element</b>	<b>Units</b>	<b>Range</b>
Softening point, Metler	°C	109.6	P	ppm	10
QI	% m/m	12.5	Ca	ppm	81
TI	ppm m/m	25.4	Pb	ppm	100
B-resins	% m/m	12.9	Zn	ppm	150
Ash	% m/m	0.3	Ti	ppm	13
Coking value	% m/m	58.7	Cr	ppm	2
Specific gravity		1.342	Mn	ppm	4
Viscosity 140	mPa.s	9159	Si	ppm	245

Viscosity 160	mPa.s	1663	Fe	ppm	179
Viscosity 180	mPa.s	468	S	ppm	0.61
			Na	ppm	130

Table 3.3. Properties of calcined coke used in this study

<b>Property</b>	<b>Units</b>	<b>Range</b>
Vibrated bulk density	cm <sup>3</sup> /g	0.85
L <sub>c</sub>	Å	25
S	%	2.9
Elements		
Ca	ppm	100
Fe	ppm	190
Mn	ppm	3
Na	ppm	65
Ni	ppm	280
P	ppm	4
Pb	ppm	<10
Si	ppm	150
Ti	ppm	17
V	ppm	505

Table 3.4. Butt properties used in this study

Property	Units	Value
VBD	cm <sup>3</sup> /g	Not available
Impurities		
S	%	2.3
Ca	ppm	444
Fe	ppm	1494
Mn	ppm	13
Na	ppm	4023
Ni	ppm	238
P	ppm	29
Pb	ppm	19
Si	ppm	148
Ti	ppm	16
V	ppm	406
Zn	ppm	25

### 3.2 Wettability test

The wettability system consisted of a tubular furnace (Thermolyne 21100), two graphite crucibles, one for the coke bed and the other for the pitch, and a digital camera (B/W, SUP, KC model). First, the coke bed was prepared using coke particles with a particle size between 100 and 125  $\mu\text{m}$  [13]. Then, ground pitch was put in its crucible. These two crucibles were placed in the furnace, the pitch crucible being above the one for the coke. The system was heated under a nitrogen atmosphere to 183.5 °C and kept at that temperature for 45 min to heat uniformly both the coke and the pitch. To reduce the humidity and oxygen concentrations, the nitrogen gas was passed through the filters (Chromatographic Specialties, Oxygen Trap C36084 and Chromatographic Specialties, Glass Moisture Trap - C36150) before it entered the system. The pitch becomes liquid at this temperature. By applying a small pressure to the line connected to the pitch crucible, a drop of pitch was dropped onto the coke surface. The change in drop shape was recorded by capturing its image at desired time intervals until the pitch penetrated into the coke bed.

At the end, the images were saved and the contact angles as a function of time were determined using the software FTA32. A picture and a schematic diagram of the wettability system are shown in Figure 3.2. The tests were carried out with all non-modified and modified pitches using the same coke [13].



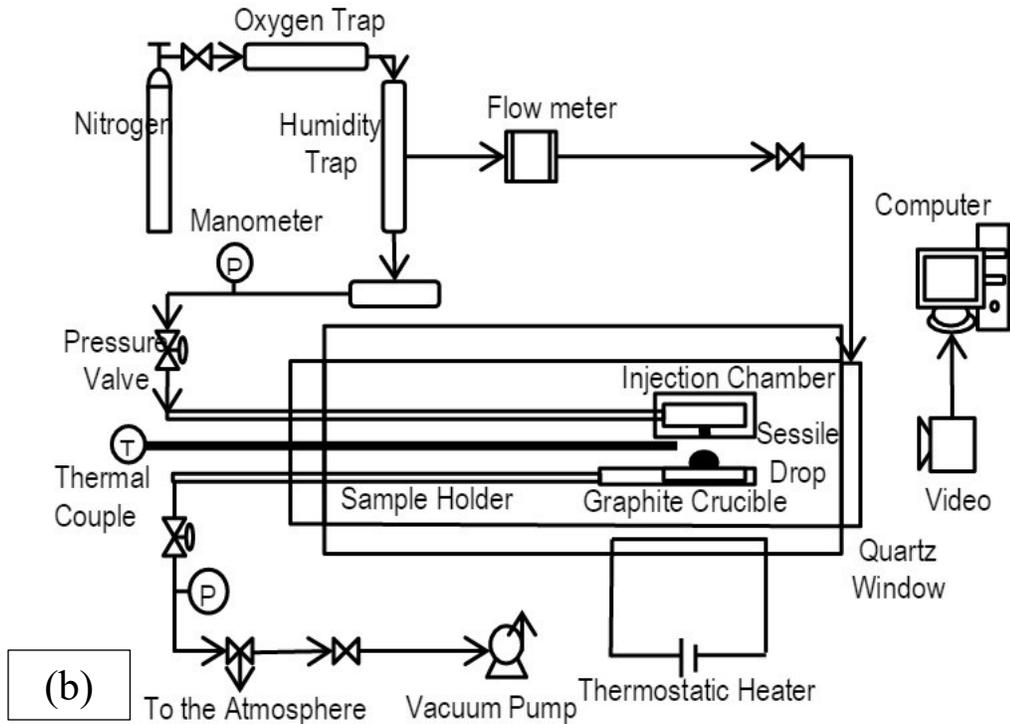


Figure 3.2. a) Wettability system and b) a diagram of the wettability system at UQAC [34]

### 3.3 Pitch modification

Figure 3.3 shows the device used to modify a small quantity of pitch for the characterization tests at the UQAC carbon laboratory. The chemical additive was first measured using the desired additive and pitch percentages and the anode recipe (particle size distribution) to be used. Then, the additive was placed at the bottom of a glass test tube and covered with pitch to prevent the escape of the additive during heating. A clean rod for mixing the pitch and additive was placed in the center of the glass test tube. Then, nitrogen ( $N_2$ ) was passed at the top of the glass test tube to prevent the oxidation of pitch above the softening point (110 to 120 °C). A thermocouple connected to an electronic thermometer (Fluke 52 II) was inserted from the top and lowered until it was close to the bottom of the glass test tube. The test tube was heated with air coming from a heat gun (Master Appliance

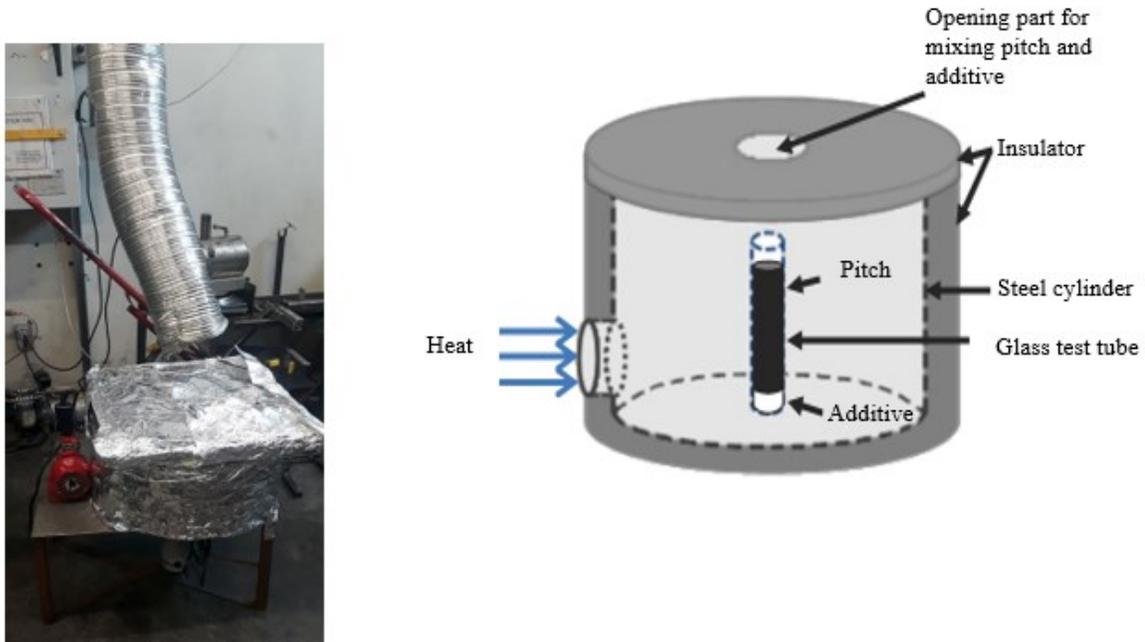


Figure 3.3. Pitch modification system at UQAC [4]

Corp. Model VT-750C). When the pitch reached the target temperature of 180 °C (or 50 °C above the softening point), the temperature was maintained between 180 °C and 190 °C. Then, the pitch and the additive were stirred for one minute in the glass test tube. The temperature was not allowed to exceed 200 °C to prevent pitch oxidation reactions. After cooling, the modified pitch was kept in a plastic bag to use for the wettability. The modification of a larger quantity of pitch to fabricate the laboratory anodes was done in a steel container instead of a glass test tube following the same procedure used for pitch modification in small quantity.

### **3.4 Production and characterization of laboratory anodes**

Sieved coke fractions and pitches were obtained from the industry. The pitch and the aggregate (coke and butts) were preheated separately. It is important to control the pitch temperature so that the pitch remains in liquid form and does not start to carbonize before and during the mixing. The preheated raw materials were mixed in an intensive mixer in the anode production laboratory of the UQAC to produce the anode paste (Figure 3.4). Once the anode paste was ready, it was transferred to the mold and compacted in the vibrocompactor using a predetermined pressure, speed, and amplitude to produce green anodes. After this step, the anode block was taken out from the mold and cooled in the ambient air. The green density of the anodes produced was determined before baking. The last step was the baking of green anodes in an electrical furnace (Pyradia, Model No B07D02029021SVCCH) under the conditions similar to those used in the industry to obtain baked anodes (Figure 3.5). They were placed into the furnace and covered with packing coke to prevent their oxidation at high temperatures and to keep them intact during the period when the pitch is in liquid form. After baking, the anodes were cooled, cored, and characterized.

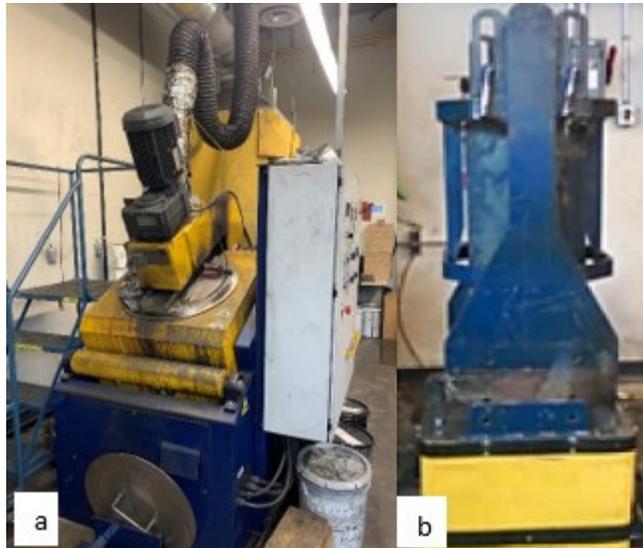


Figure 3.4. Anode manufacturing system at UQAC: a) Mixer b) Vibrocompactor



Figure 3.5. Electrical anode baking furnace at UQAC

In this project, 32 anodes were produced using the same anode recipe (predetermined percentage of each coke particle size fraction with varied pitch percentages). Two types of pitch and two additives were used. The anodes were divided into two groups. One group of green anodes was manufactured using pitch P1 and the other with pitch P2. Two types of additives (Add1 and Add2), three additive concentrations (0 %, c1 %, and c2 %), and three

pitch percentages (between 15 %-18 %) were used. The anodes made with 0 % additive were the standard anodes. Based on the previous studies [17], the additive concentration was chosen as  $(0.5 \% < c1 \% < c2 \% \leq 5 \% \text{ g/g})$ .

Finally, the anode blocks were baked in the electrical baking furnace and their properties were measured. Table 3.5 summarizes the experimental plan.

Table 3.5. Summary of modified and non-modified pitches used in the anode manufacturing

<b>Anode</b>	<b>Pitch</b>	<b>Additive</b>	<b>Additive concentration</b>	<b>Pitch percentage (%)</b>
Anode 1	P1	0	0	16
Anode 2	P1	0	0	17
Anode 3	P1	0	0	18
Anode 4	P1	Add1	c1	16
Anode 5	P1	Add1	c1	17
Anode 6	P1	Add1	c1	18
Anode 7	P1	Add1	c2	16
Anode 8	P1	Add1	c2	17
Anode 9	P1	Add2	c2	18
Anode 10	P1	Add2	c1	16
Anode 11	P1	Add2	c1	17
Anode 12	P1	Add2	c1	18
Anode 13	P1	Add2	c2	16
Anode 14	P1	Add2	c2	17
Anode 15	P1	Add2	c2	18

Anode 16	P2	0	0	15
Anode 17	P2	0	0	16
Anode 18	P2	0	0	17
Anode 19	P2	0	0	18
Anode 20	P2	Add1	c1	15
Anode 21	P2	Add1	c1	16
Anode 22	P2	Add1	c1	17
Anode 23	P2	Add1	c2	15
Anode 24	P2	Add1	c2	16
Anode 25	P2	Add1	c2	17
Anode 26	P2	Add2	c1	15
Anode 27	P2	Add2	c1	16
Anode 28	P2	Add2	c1	17
Anode 29	P2	Add2	c1	18
Anode 30	P2	Add2	c2	16
Anode 31	P2	Add2	c2	17
Anode 32	P2	Add2	c2	18

### 3.4.1 Core characterization done at UQAC

After baking the anode blocks, four cores (50 mm in diameter and 180 mm in length) were taken (Figure 3.6). The samples were dried for 17 h at 80 °C, cooled down to the room temperature, and characterized. Their apparent density, electrical resistivity, air

permeability, coefficient of thermal expansion, CO<sub>2</sub> and air reactivities, and compressive strength were measured.

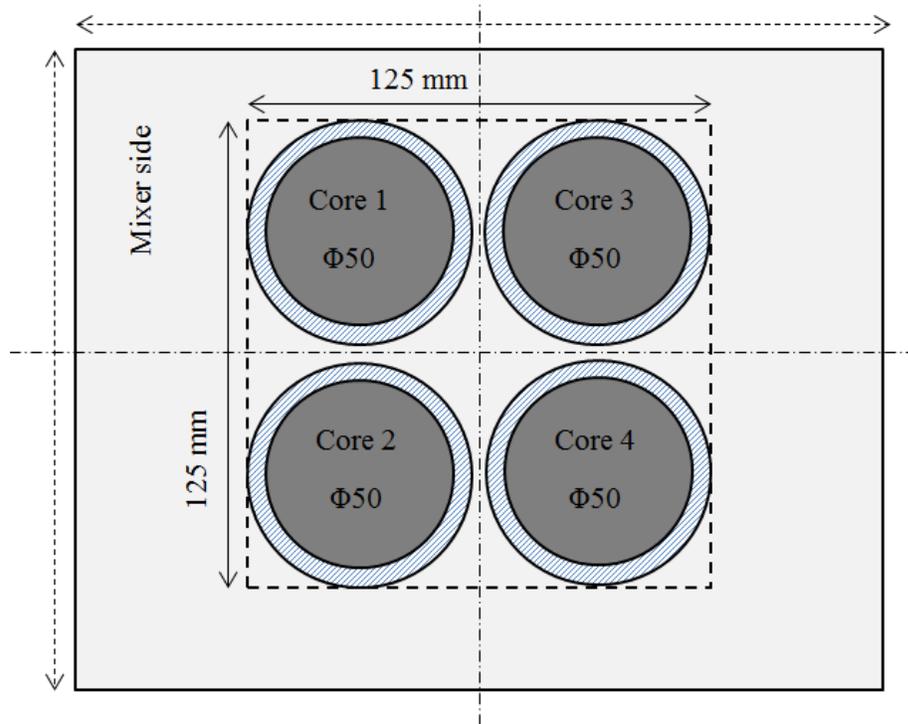


Figure 3.6. Position of cores in an anode block [7]

### 3.4.2 Bulk density measurement (ASTM D 5502-00)

In order to measure the density of the laboratory anodes and cores, their mass and volume were measured. First, the mass was determined using an electronic balance with an accuracy of 0.01 g (Figure 3.7).



Figure 3.7. Electrical balance with an accuracy of 0.01 g

Their dimensions (length, width, and height or diameter) were measured using a digital caliper and a ruler as shown in Figure 3.8 to reduce the risk of error during the measurement.



Figure 3.8. Instruments for measuring the dimensions of anodes and cores:

(a) Digital caliper, (b) Ruler

The density of the anode blocks was calculated using the following equation:

$$\rho = m / (l \times h \times w) \quad (\text{Eq. 3.1})$$

l: length (cm)

w: width (cm)

h: height (cm)

m: mass of anodes (g)

The average diameter as well as the average height of the cores were determined according to the ASTM standard ASTM D5502-00. The height of the core was the average of four height measurements as shown in Figure 3.9 (left side). The diameter was the average of eight diameter measurements as shown in Figure 3.9 (right side).

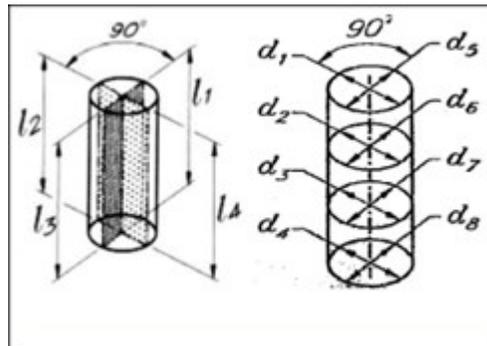


Figure 3.9. Measurement of the average length (left side) and the average diameter (right side) of cores [4]

The volume of the cores was determined using Eq. 3.2.

$$V = \pi \cdot h_{(\text{average})} \cdot d_{(\text{average})}^2 / 4 \quad (\text{Eq.3.2})$$

V: core volume (cm<sup>3</sup>)

d<sub>(average)</sub>: average diameter of core (cm)

h<sub>(average)</sub>: average height of the core (cm)

After determining the volume of a core, its density was calculated from Eq. 3.3.

$$\rho = M / V \quad (\text{Eq.3.3})$$

$\rho$ : Density of the core ( $\text{g}/\text{cm}^3$ )

M: mass of the core (g)

### **3.4.3 Characterization tests done at RioTinto**

After the characterization measurements at UQAC, the cores were sent to Rio Tinto for other characterization tests. First, 100 mm and 50 mm samples in length were cut from each baked core. The reactivity tests were carried out with 50 mm-long samples. The 100 mm-long samples were used for all other characterization tests. For each test, samples from all four cores were tested with the exception of the reactivity ones. In this case, samples from two cores were used for the measurement of  $\text{CO}_2$  reactivity and samples from the other two cores were used for air reactivity tests. All the tests were carried out at Rio Tinto using baked cores produced at UQAC.

### **3.4.4 Core Apparent Density (ASTM D 5502-00)**

Baked apparent density is measured from the baked anode core mass divided by the calculated baked core volume. The baked cores from UQAC were cut into 100 mm and 50 mm samples in length, and the apparent density was measured using Rio Tinto procedures.

### **3.4.5 Electric resistivity and permeability**

A current is passed through the anode core from one surface to the opposite surface. The corresponding voltage drop is measured. Then, it is possible to determine the specific electrical resistivity across the core. The average value of the four measurements gives the specific electrical resistivity of the anode. The anode electrical resistivity and permeability

were determined with the equipment from QUATRA (Montréal, Qc, Canada), using Rio Tinto procedures.

#### **3.4.6 Carbon dioxide and air reactivities**

Instruments QUATRA (Montréal, Qc, Canada) are used for CO<sub>2</sub> and air reactivities. The measurements are performed at 960 °C (CO<sub>2</sub>) and 525 °C (air), respectively, following Rio Tinto procedures.

## Chapter 4

### Results and discussion

#### 4.1 Wettability of coke by pitch

In the present study, the two pitches with different QI contents (high QI pitch (HQI pitch) and low QI pitch (LQI pitch)) were studied to determine the wettability of a calcined petroleum coke by these pitches using the sessile-drop method. In this test, the contact angle, which indicates the wettability, is measured. A smaller contact angle indicates a better wettability of coke by pitch.

Figure 4.1 shows the wettability results for the non-modified HQI and LQI pitches and those modified with additive 1. As it can be seen from this figure, the modified and non-modified LQI pitches gave smaller contact angles compared to those of the modified and non-modified HQI pitches, meaning that non-modified and modified LQI pitches wet better the coke relative to the HQI pitches.

As it can be seen in Figure 4.1 modifying the HQI pitch with additive 1 (1% and 2%) resulted in lower contact angles and an improvement of the wettability of the coke compared to the those of the non-modified HQI. Also, it is found that the higher the percentage of additive 1 is, the smaller contact angle is. This shows that the modification with 2% additive improved the wettability of coke compared to that of the non-modified pitch and the one modified with 1% additive 1.

The LQI pitch modified with additive 1 (1% and 2%) after 300 s showed a slightly better wettability compared to the non-modified pitch. Increasing the additive concentration did not affect the coke wettability further.

As shown in Figure 4.1, additive 1 was more effective for HQI pitch compared to LQI pitch. However, the modified HQI pitch wetted the coke less than the modified LQI pitch. In all cases, the contact angle decreased with increasing time, meaning that the wettability increased with time.

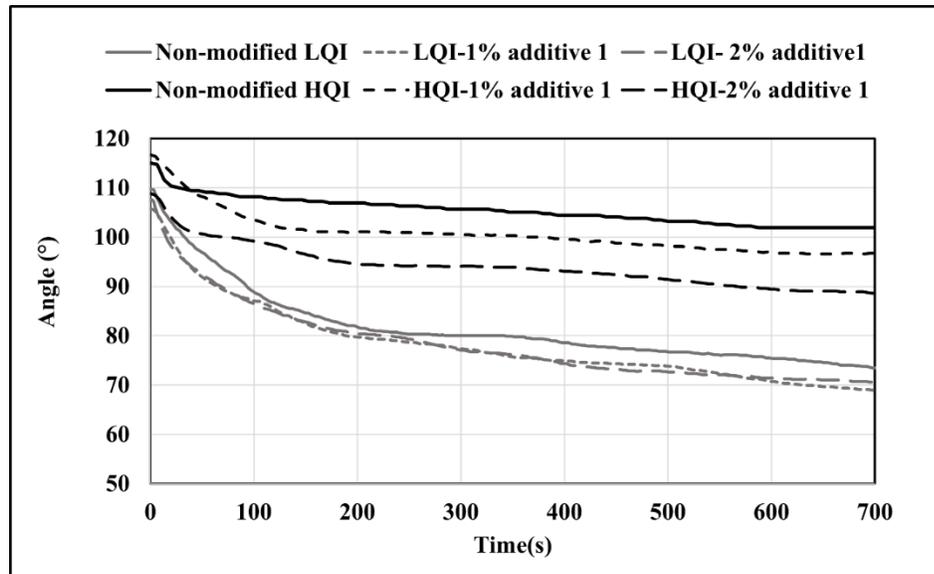


Figure 4.1. Comparison of the wettability of non-modified HQI and LQI pitches and pitches modified using different additive 1 concentrations (non-modified, 1%, 2%)

Figure 4.2 displays the wettability behavior of the coke with the LQI and HQI pitches modified with additive 2. As shown in Figure 4.2, the non-modified LQI pitch showed a significantly smaller contact angle and a better wettability compared to those of the non-modified HQI pitch.

As it can be seen from Figure 4.2, the wettability of the LQI pitch increased as the concentration of the additive 2 increased, meaning that the LQI pitch modified using both 1% and 2% additive 2 resulted in a better wettability compared to that of the non-modified LQI pitch. Up to 300 s, 2% additive 2 showed a smaller contact angle (better wettability)

compared to the contact angle obtained using 1% additive 2 for the LQI pitch. However, after 300 s, 1 % and 2 % additive 2 had a similar contact angle. As a result, the modification of LQI pitch by additive 2 improved the wettability.

As Figure 4.2 shows, the HQI pitch modified with 2% additive 2 showed a significantly better wettability compared to the non-modified HQI pitch and HQI pitch modified with 1% additive 2. Modification of the HQI pitch with 1% additive 2 did not improve the wettability.

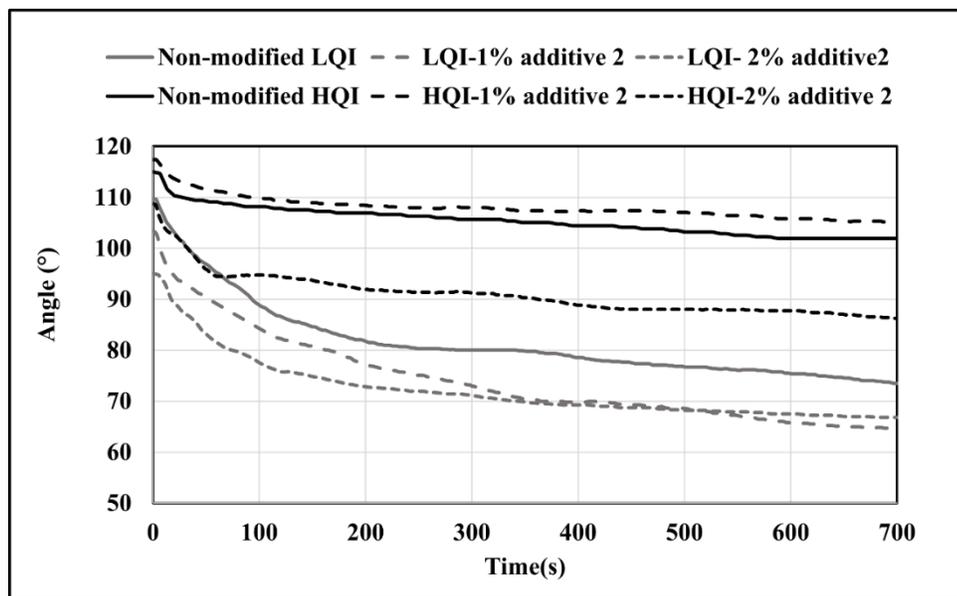


Figure 4.2. Comparison of wettability of the non-modified HQI and LQI pitches modified using different additive 2 concentrations (non-modified, 1%, 2%)

#### 4.2 Baked anode properties

All figures show the dimensionless properties to respect the confidentiality of the results in the present work. The dimensionless value is defined as the value of the of each property divided by its highest value. The dimensionless values have the same trends as their corresponding dimensional values.

### 4.2.1 Apparent density

Figure 4.3 illustrates the density of the anodes made with the non-modified pitches and pitches (HQI and LQI) modified with 1 % and 2 % additive 1 at different concentrations of pitch (15 %, 16 %, 17 %, and 18 %).

The densities of anodes produced with non-modified pitches (both LQI and HQI) increased with the increasing pitch content. However, the anodes made with the modified pitches reached a maximum density with increasing pitch content (LQI at 17 % anode pitch content and HQI at 16 % anode pitch content), and then the density decreased if the pitch content is further increased (Figure 4.3).

The anodes fabricated with the modified LQI pitch had slightly lower anode densities relative to those of the LQI standard anodes at 17 % anode pitch content. At 18 % LQI pitch level, the anode with the non-modified LQI pitch reached a much higher density compared to those with the modified LQI pitches (Figure 4.3). Thus, the anode density was not improved with the modification for this pitch.

The densities of anodes made with HQI pitch showed a different behavior when this pitch was modified using additive 1. The anodes fabricated with the modified HQI pitch gave a better density compared to that of the standard HQI anode (made with non-modified HQI pitch). The modification of this pitch with 2 % additive 1 resulted in a higher anode density relative to that obtained with the modification of the same pitch with 1 % additive 1. The HQI pitch modified with 2 % additive 1 at 16 % pitch level gave the highest anode density compared to others. Therefore, it can be concluded that the optimum pitch percentage is 16 % for the anode production using HQI pitch modified with 2 % additive 1.

As mentioned above, the anodes made with non-modified LQI pitch and LQI pitch modified with additive 1 had lower densities than those made with the HQI pitch modified with the same additive at 16 % pitch level. At 18% pitch level, the anode made with non-modified LQI pitch had the highest density. The wettability results (Figure 4.1) indicated that the modification of HQI pitch with additive 1 improves the wettability and increasing the additive content has a positive effect on the wettability. Improvement in wettability is due to the chemical changes occurring on the pitch surface because the modification with additive enriches the surface functional groups and increases the possibility of bonding between pitch and coke. This increases the coke-pitch interactions. It is also found that the anode density increased with pitch modification. The results also showed that modifying the LQI pitch improves the wettability slightly. Therefore, it was expected that the density of the anodes made with this pitch would not be significantly improved. In this case, the expected small improvement in the density might have been offset by the voids and cracks formed during anode baking due to the volatile release.

It must be noted that the wettability results can't explain the effect of pitch content on the anode density. They can only show if the modification has the possibility of improving anode properties. Density trends observed are in good agreement with the wettability results.

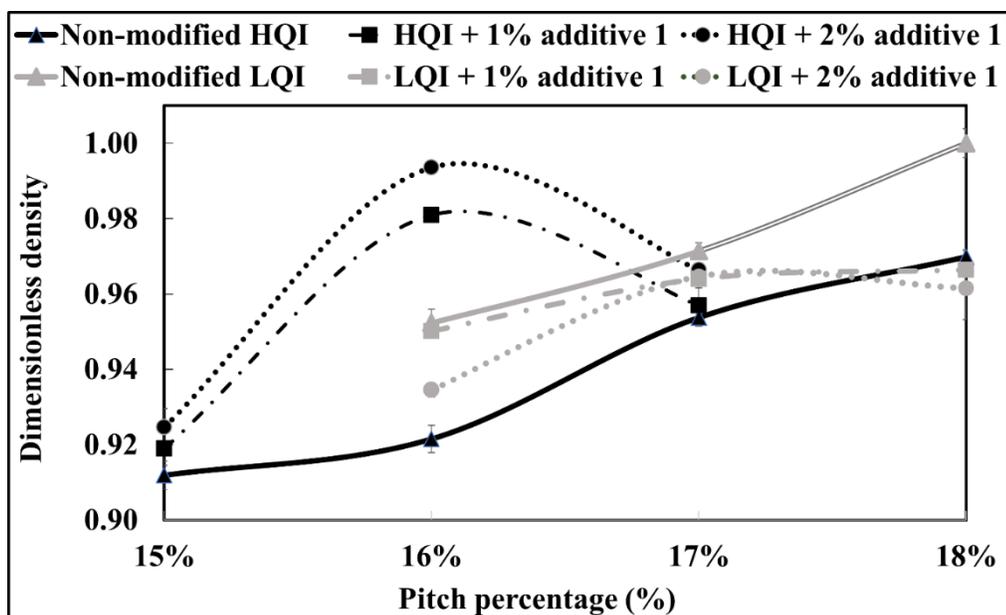


Figure 4.3. Dimensionless densities of baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 1 [53]

Figure 4.4 shows the density of the anodes made with the non-modified and modified pitches (HQI and LQI) using 1 % and 2 % additive 2 at various pitch contents (16 %, 17 %, and 18 %).

In contrast to additive 1, additive 2 increased the density of the anodes fabricated with the LQI pitch. The LQI pitch modification with the 2 % additive 2 gave a similar anode density at all pitch levels studied. Using 1 % additive 2 to modify the LQI pitch led to a maximum anode density at 17 % pitch level, and then the anode density reduced with further increase in the pitch content (18 %). An increase in anode density with the modification of the LQI pitch using additive 2 could mainly be attributed to the increased surface functional groups which leads to improved wettability.

Figure 4.4 shows that the density of the anodes made with HQI pitch modified with 1 % additive is higher compared to those of the anodes made with the non-modified HQI pitch and HQI pitch modified with 2 % additive 2.

Wettability results indicate that the modification of LQI pitch improves the wettability of coke by this pitch. For HQI pitch, the wettability decreased with the modification of the pitch with 2 % additive 2, but it is increased when HQI pitch is modified with 1 % additive 2. Consequently, density and wettability results are in good agreement.

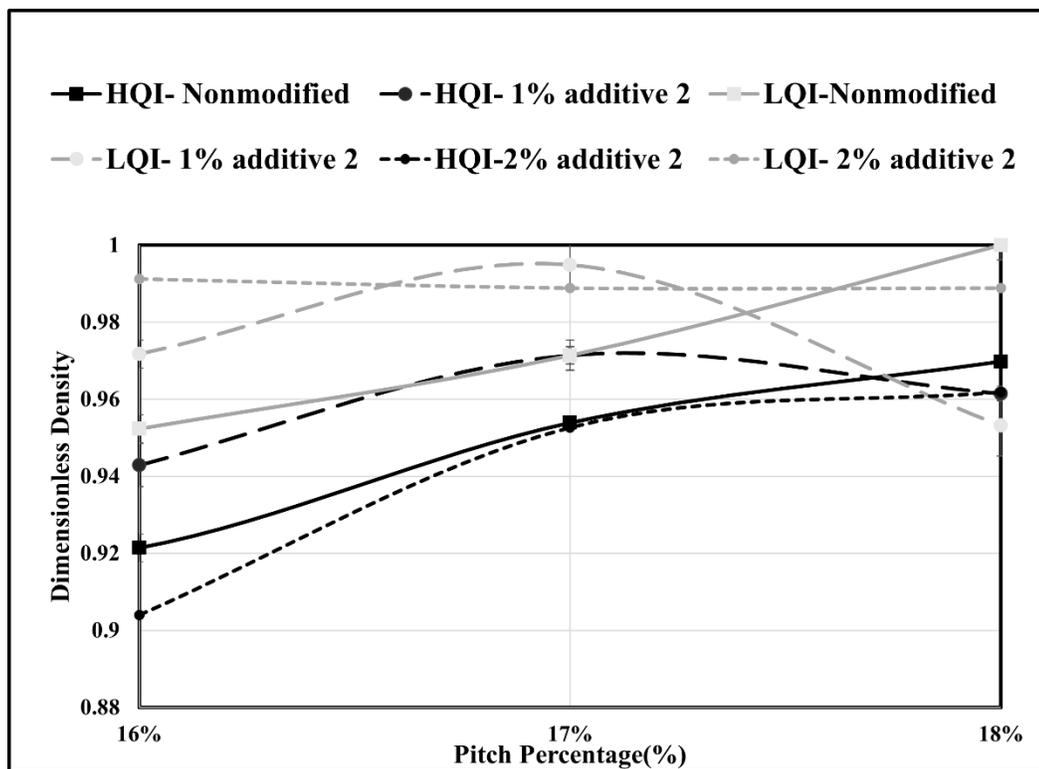


Figure 4.4. Dimensionless densities of baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 2

As it can be seen from the above results, an additive can affect different pitches differently. Also, different additives can affect the same pitch differently. This depends on the surface

functional groups added to the surface and the compatibility of these new groups with those of the coke.

#### **4.2.2 Electrical resistivity**

Figure 4.5 shows the electrical resistivities of the anodes made with the non-modified LQI and HQI pitches as well as with the modified LQI and HQI pitches using 1 % and 2 % additive 1 at various pitch levels.

In general, the electrical resistivity of the anodes containing the non-modified pitches (LQI and HQI) reduced with increasing pitch content (Figure 4.5). This is because the voids decrease as the pitch percentage of the anode increases, resulting in a lower electrical resistivity. The anode made by 18 % non-modified HQI had the lowest electrical resistivity. The anode made with the 15 % HQI pitch modified with 2% additive 1 showed the highest electrical resistivity among all the anodes produced.

The electrical resistivity of anodes fabricated with the modified HQI pitches (1 % and 2 % additive 1) decreased with increasing pitch content up to 16 %, and increased when the pitch content increased (17 %) further. The anodes made with the modified HQI pitches (1 % and 2 % additive 1) also had the highest densities at the 16 % pitch level. The high-density anodes contain more carbonized pitch, and hence they have low porosities. This decreases the electrical resistivity; consequently, the cost of production and the energy consumption decrease. Therefore, the anode density is inversely proportional to the electrical resistivity as expected.

The anode containing the LQI pitch modified with 2 % additive 1 had a higher electrical resistivity compared to those of the non-modified LQI-pitch anodes and the anodes made

with the LQI pitch modified with 1 % additive 1 at the pitch level of 16 %. For the LQI pitch contents higher than 17 %, the anodes produced with the modified and non-modified LQI pitches using additive 1 showed a similar electrical resistivity.

In general, the electrical resistivity decreased with increasing pitch content. The electrical resistivity of the anodes made with the LQI pitch is low at high pitch contents. However, at the pitch content of 16 %, the lower resistivities can be obtained by modifying the HQI pitch with additive 1.

As mentioned earlier, the pitch is costly, and the production cost increases with increasing pitch percentage. Therefore, using the modified HQI pitch, which is a lower quality pitch compared to the LQI pitch, might be more economical at the low pitch contents since the additives chosen have a low cost.

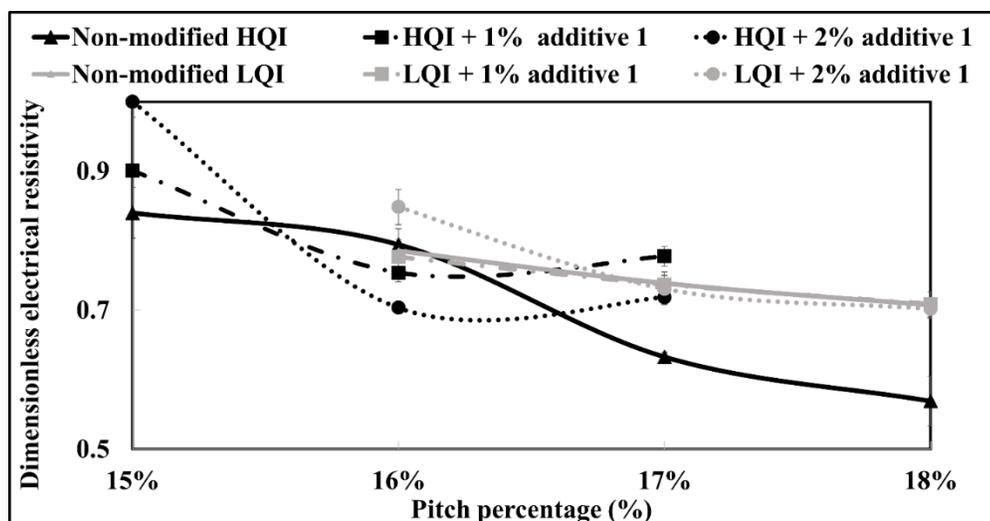


Figure 4.5. Dimensionless electrical resistivities of baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 1

Figure 4.6 shows the electrical resistivity of the anodes produced using the non-modified LQI and HQI pitches and those containing the modified LQI and HQI pitches with 1 % and 2 % additive 2 at different pitch contents.

Modifying HQI pitch with additive 2 did not improve the anode resistivity. A slight improvement was observed in the electrical resistivity of the anodes made with the LQI pitch modified with 1 % and 2 % additive 2 at 17% pitch content. The results are in good agreement with the wettability results except for the HQI pitch modified with 2 % additive 2 (Figure 4.2).

The lowest electrical resistivity is found for the anode containing 18 % non-modified HQI pitch. The highest electrical resistivity is observed for the anodes made with the HQI pitch modified with 1 % additive 2 at 15 % pitch level. The anodes made of the LQI pitches (both modified and non-modified) had more or less similar electrical resistivities at different pitch levels. It can be observed from Figure 4.6 that, at 16% pitch content, the electrical resistivity of standard anodes is less than the anodes made with the modified LQI pitch. Electrical resistivities of the anodes containing LQI pitch modified with both 1 % and 2 % additive 2 are slightly less than that of the standard anode at 17 % pitch content.

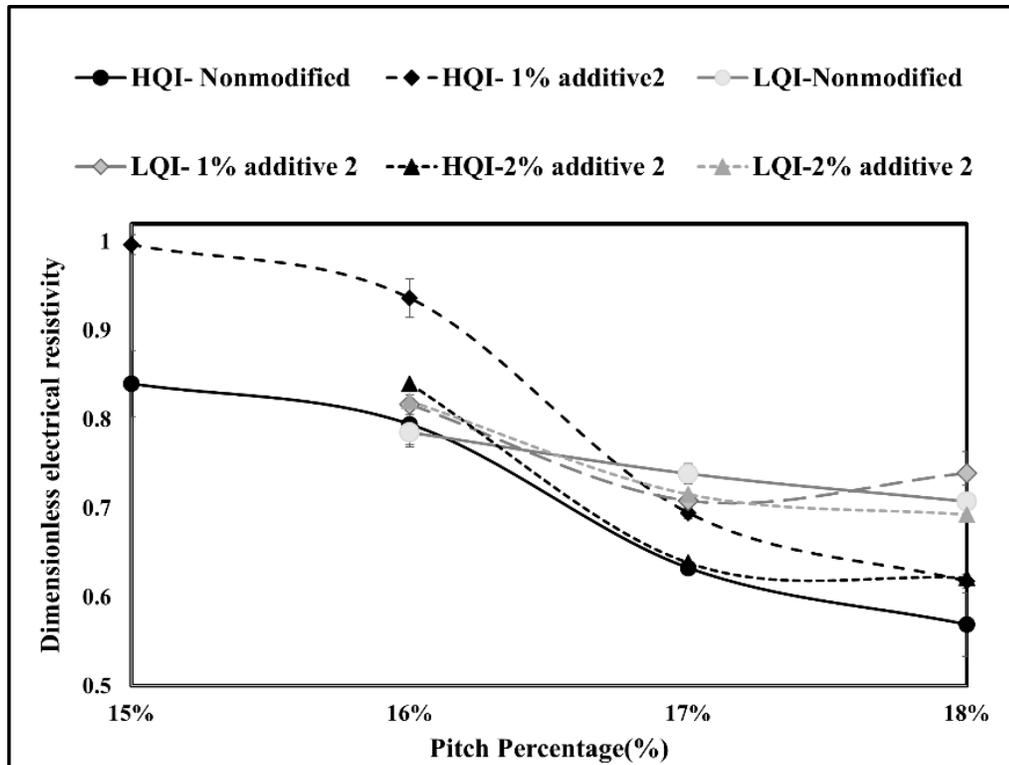


Figure 4.6. Dimensionless electrical resistivity of baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 2

Using the modified HQI pitch by additive 1 significantly decreased the electrical resistivity at 16 % pitch content. Previously, it was observed that this anode had a high density at this pitch content. In addition, using more modified HQI pitch by additive 1 increased the electrical resistivity in higher pitch contents (17 % and 18 %).

It is shown that using the LQI-modified pitches with additive 1 did not significantly decrease the electrical resistivity for these anodes.

The anodes made with the modified HQI pitch using additive 2 did not improve the electrical resistivity compared to the HQI standard anodes. But, the electrical resistivity of the anodes containing 1 % and 2 % modified LQI pitch using additive 2 decreased at 17 %

pitch content compared to the LQI standard anode at this pitch level. Overall, using additive 2 did not significantly improve the electrical resistivity for both types of pitch.

### **4.2.3 Air permeability**

Figures 4.7 and 4.8 show the air permeability results at different pitch contents for the standard anodes and those fabricated with the pitches modified with additive 1 and additive 2, respectively.

The air permeability, which usually is inversely proportional to the anode density, reduced with increasing pitch content for anodes made with non-modified pitches. It is evident that the anodes with higher densities have lower permeability because they contain less pores and voids, and they have more carbonized pitch.

Figure 4.7 shows that the anode containing the HQI pitch modified with 1 % and 2 % additive 1 at 16 % of the pitch content had the lowest permeability among all the anodes. This is in good agreement with the wettability (highest), density (highest), and the resistivity (lowest) results.

At 15 % pitch level, the permeability for the anodes made with the non-modified HQI pitch and the HQI pitch modified by 1 % and 2 % additive 1 were high. As it can be seen from Figure 4.7, the modification at this pitch percentage (15 %) increased the permeability. In addition, the densities were low and the electrical resistivities were high for these anodes. The reason might be that the anodes fabricated with 15 % HQI pitch were under-pitched and hence contain more voids and pores. The anodes containing 16 % HQI pitch had lower permeabilities compared to those of the anodes made with the LQI pitch at the same pitch level. This shows that using the HQI pitch modified with additive 1 is more economical to

achieve low permeability compared to using a higher amount of non-modified LQI pitch. This is because pitch is more expensive than the additives, and using more pitch thus increases the cost of production (Figure 4.7).

For the LQI pitch, the highest anode permeability was found for the anodes made with 16 % LQI pitch modified with 2 % additive 1. However, its permeability is still lower than the anodes made with the modified and non-modified HQI pitch at 15 % pitch level.

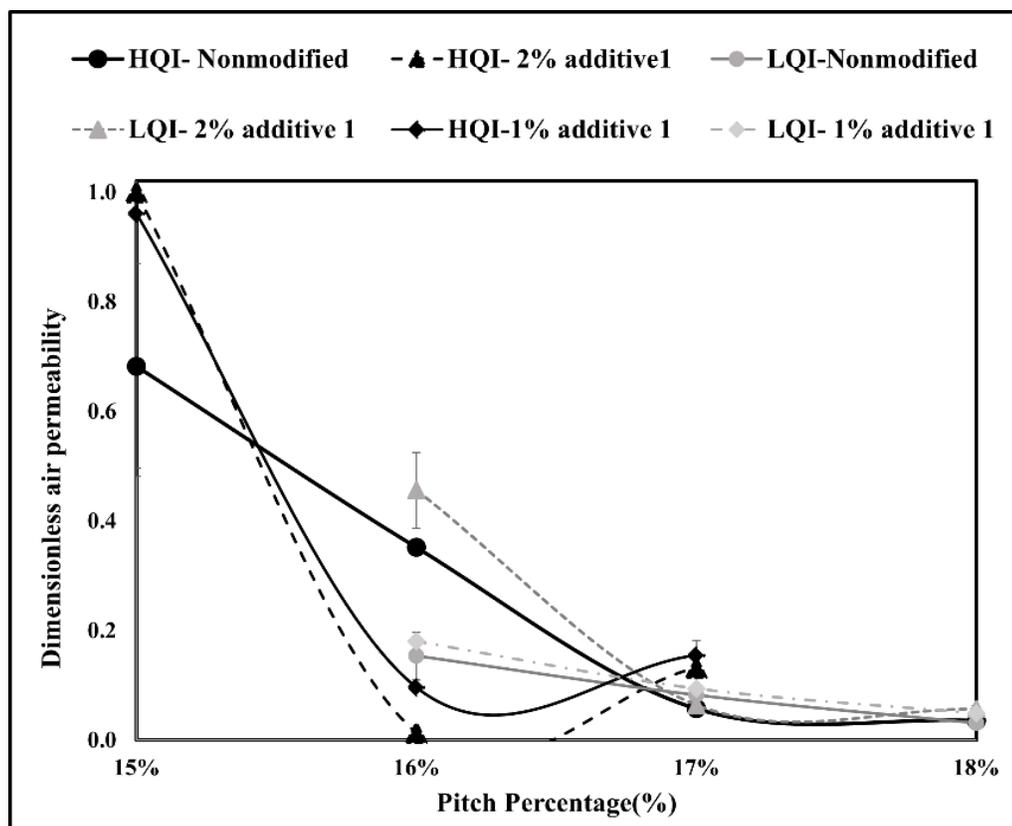


Figure 4.7. Dimensionless air permeabilities of baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 1

The air permeability as a function of pitch level for the standard anodes made with non-modified pitches and those made using the pitches modified with additive 2 is shown in Figure 4.8.

Figure 4.8 shows that the air permeability for all anodes decreased with an increase in pitch content. The air permeability of all the anodes is found to be similar at 17 % pitch content with the exception of the anodes made with the LQI pitch modified by 1 % additive 2. The anode made with the non-modified LQI pitch had the lowest permeability at 16 % pitch level among all the anodes. Wettability of coke by LQI pitches was found to be lower than those of the HQI pitches (Figure 4.2). This is in good agreement with the permeability results. However, wettability results could not indicate the effect of pitch content on anode properties as mentioned previously. The modification of LQI pitch with additive 2 did not significantly affect the permeability of the anodes at pitch contents higher than 17 %.

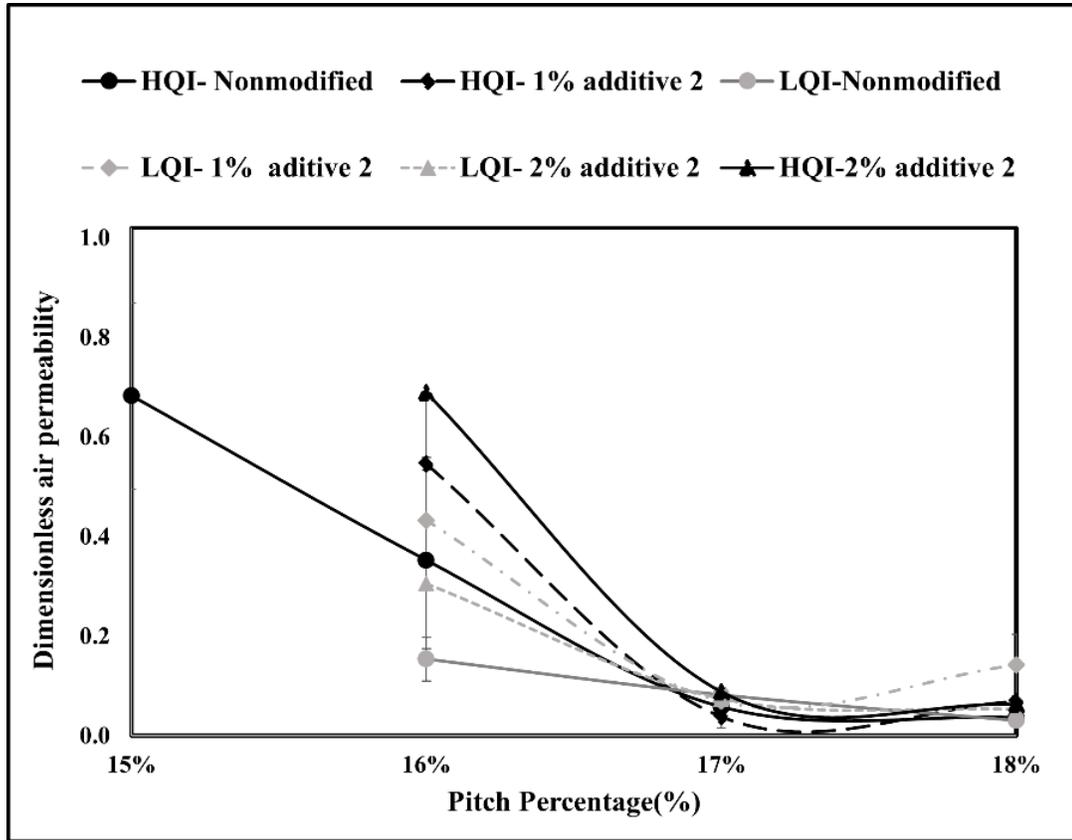


Figure 4.8. Dimensionless air permeabilities of baked anodes with non-modified HQI and LQI pitches and pitches modified using additive 2

It is observed that using the modified LQI pitch by additive 1 did not decrease the air permeability in lower pitch contents (15 %) compared to the LQI standard anode.

Air permeability for the anodes made with the HQI pitch modified by additive 1 at 16 % pitch content significantly decreased, and this anode had the lowest air permeability among all the anodes produced.

The anodes made using modified HQI and LQI pitches by additive 2 at lower pitch content had some differences in the air permeability. But, in the higher pitch contents, this anode

property is similar for these anodes. It is observed that using pitch modified by additive 2 did not reduce the air permeability compared to the permeabilities of both LQI and HQI standard anodes at the lower pitch content (16 %).

#### **4.2.4 Air reactivity**

Figure 4.9 shows the air reactivity residue for anodes made with pitches modified using additive 1. The high residue means low air reactivity (low carbon loss). The highest residue was found for the anode made with non-modified LQI pitch at 18 % pitch content, which is in accordance with the highest anode density observed (Figure 4.3). The anodes with a high density have a low porosity that reduces the amount of air entering into the anode. The lowest residue was found for the anodes made with 15 % non-modified HQI pitch (highest air reactivity). This might be attributed to an under-pitched anode with high porosity, which facilitates the diffusion of air into the anode and the reaction of air with carbon. At 16 % and 17 % pitch levels, the highest residues were found for the anodes made with the LQI pitch modified with 1 % additive 1. For anode with 16 % pitch content, the residue of the anode made with HQI pitch modified with 2 % additive 1 was similar to that made with the LQI-pitch with the highest residue.

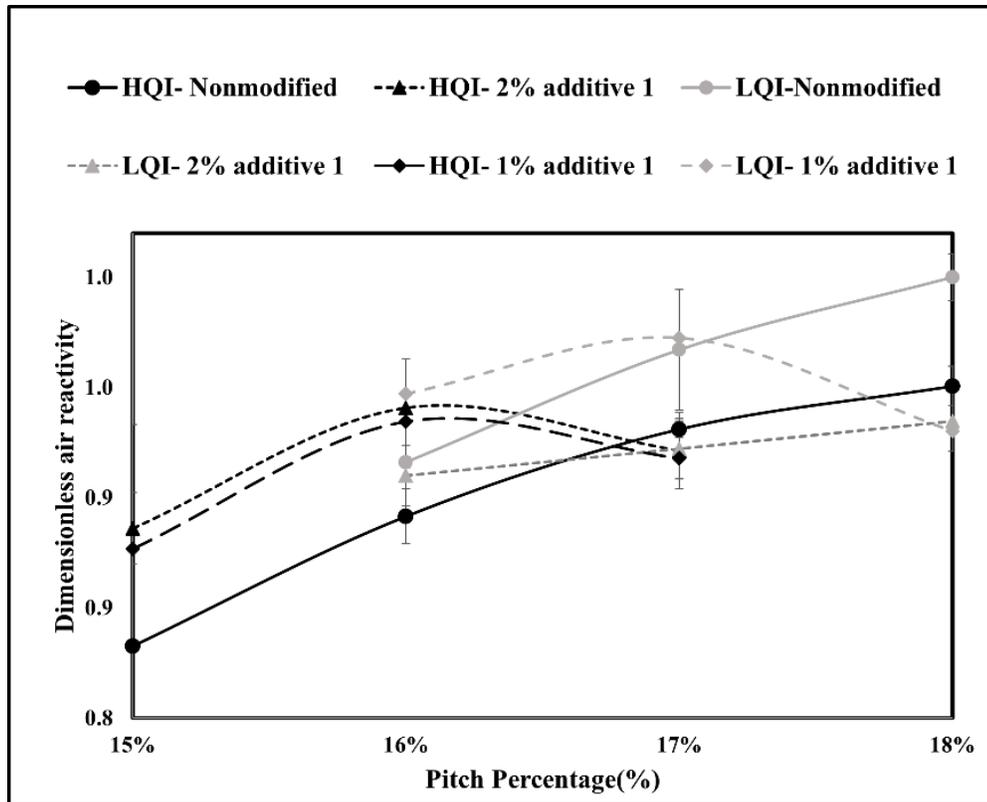


Figure 4.9. Dimensionless air reactivity residues for baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 1

Figure 4.10 shows the air reactivity for anodes made with pitches modified using additive 2. It can be seen from this figure that the highest residue (low air reactivity) was found for the standard anodes made with the LQI pitch at 18 % pitch content. This anode also had a low air permeability, a low electrical resistivity, and a high density. The lowest residue was found for the anodes containing 15 % HQI pitch. This anode also had a low density. The anodes with low densities have more porosities. Consequently, air can enter into the anode more easily allowing the reaction of air with carbon. It can be observed that the residue for the anodes using the LQI pitch modified with 1 % additive 2 is higher than that of the anode made with the LQI pitch modified with 2 % additive 2 at 17 % pitch level. For

anodes containing 16 % pitch, the highest residue was obtained for the anodes made with non-modified LQI pitch, followed by, in the decreasing order, anodes made with HQI pitch modified with 1% additive 2, non-modified HQI pitch, and HQI pitch modified with 2% additive 2.

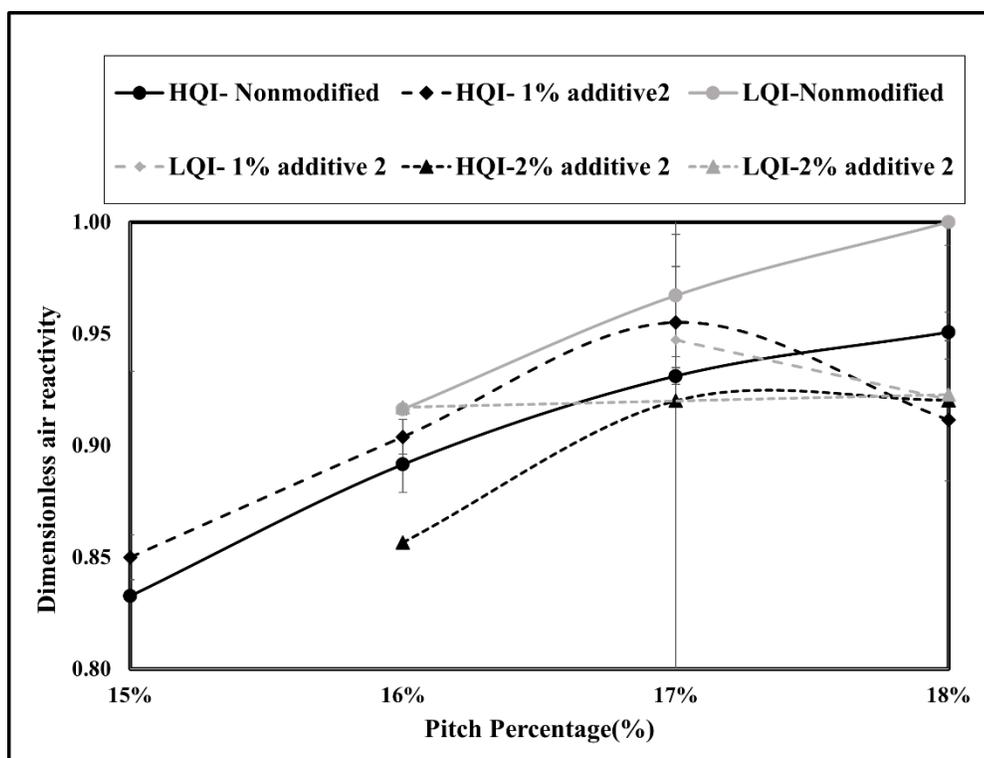


Figure 4.10. Dimensionless air reactivity residues for baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 2

Air reactivity residue for the standard anodes made with the non-modified LQI pitch is higher than the anodes made with the modified LQI pitches at 18 % pitch content. It can be observed that the modification of LQI pitch by additive 2 did not improve the air reactivity of the anodes made by the same pitch. Also, it is shown that using the modified LQI pitch

by additive 1 increased the air reactivity residue (low air reactivity) in lower pitch contents (16 % and 17 %).

It can be observed that the air reactivity residue for the anodes using modified HQI pitch by additive 1 had the higher air reactivity residue which have lower air reactivity compared to that of the standard anode made by the same pitch.

Also, it is shown that the modification of HQI pitch by 1 % additive 2 increased the air reactivity residue (low air reactivity) at 16 % and 17 % pitch content compared to the air reactivity of HQI-pitch standard anodes. The anodes made with the HQI pitch modified using 1 % and 2 % additive 1 had the higher air reactivity residues compared to the anode made with the modified HQI pitch by 1 % and 2 % additive 2 at lower pitch content.

#### **4.2.5 CO<sub>2</sub> reactivity**

The CO<sub>2</sub> reactivity residues for anodes non-modified and modified with additive 1 are shown in Figure 4.11. As shown in this figure, the CO<sub>2</sub> residues for anodes made with the non-modified HQI pitch are the highest compared to those of the anodes made with the modified HQI pitches and non-modified and modified LQI pitches (lowest CO<sub>2</sub> reactivity). The anode made with the HQI pitch modified by 1 % additive had the lowest CO<sub>2</sub> reactivity residue (high reactivity) at 18 % pitch content. The residue of the anode made with the HQI pitch modified by 2 % additive 1 was higher than that made with the HQI pitch modified by 1 % additive 1.

The CO<sub>2</sub> reactivity for the anodes made with the LQI pitch modified by 1 % additive 1 did not change compared to the CO<sub>2</sub> reactivity of the anodes made with non-modified LQI pitch at 16 % and 17 % pitch content. Modification of the LQI pitch by 2 % additive 1

increased the CO<sub>2</sub> reactivity residue (decreased the CO<sub>2</sub> reactivity) compared to the anodes made with the non-modified LQI pitch for 17 % pitch content.

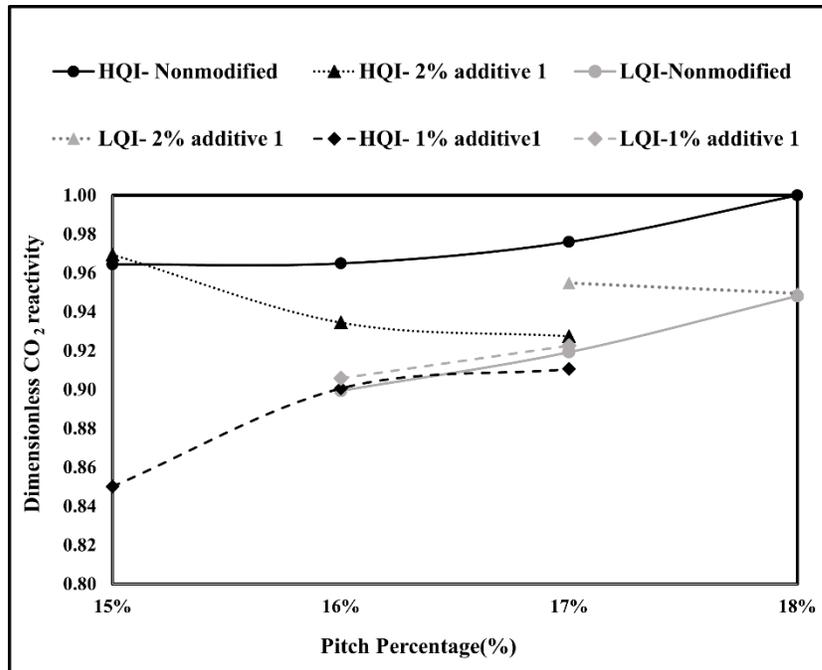


Figure 4.11. Dimensionless CO<sub>2</sub> reactivity residue for baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 1

Figure 4.12 shows the CO<sub>2</sub> reactivity residues for anodes made with modified and non-modified pitches using additive 2. It can be observed from this figure that the CO<sub>2</sub> reactivity residue for the anodes made with non-modified HQI pitch was the highest at 18 % pitch content (lowest CO<sub>2</sub> reactivity). Modification of the HQI pitch with 1 % and 2 % additive 2 decreased the residue (increased the CO<sub>2</sub> reactivity) with the exception of pitch contents between 16 % and 17 % for HQI pitch modified with 1 % additive 2.

Modification of the LQI pitch by 2 % additive 2 lowered the residue (increased the CO<sub>2</sub> reactivity) above 17 % pitch content and increased the residue (lowered the CO<sub>2</sub> reactivity)

at pitch contents less than 17 %. The residue values remained essentially the same at all pitch percentages for the anodes produced with the LQI pitch modified by 2 % additive 2.

The lowest residue was found for the anodes made with the LQI pitch modified by 1 % additive 2 at 17 % pitch percentage. At 18 % pitch level, the residue was the same as that of the anode made with non-modified LQI pitch. At lower pitch concentrations (16 %), the residue decreased (the CO<sub>2</sub> reactivity increased).

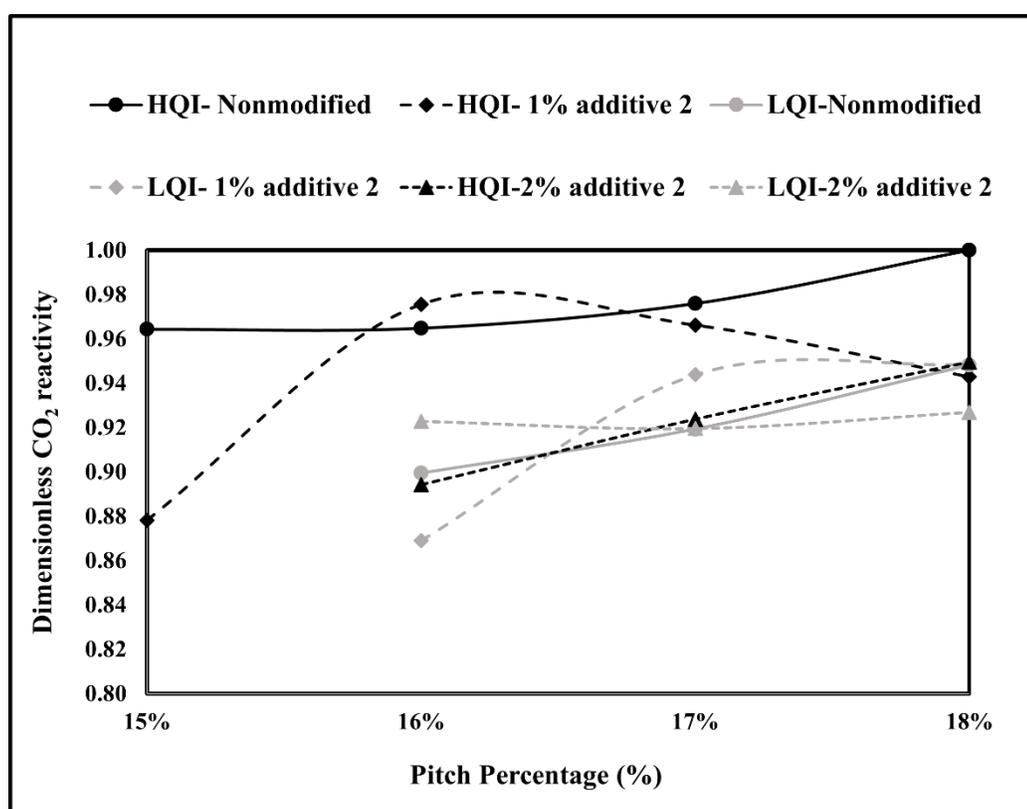


Figure 4.12. Dimensionless CO<sub>2</sub> reactivity residue for baked anodes made with non-modified HQI and LQI pitches and pitches modified using additive 2

CO<sub>2</sub> reactivity residues for the standard anodes made with non-modified HQI had usually the highest values compared to all the anodes produced. Using the HQI pitch modified with additive 1 did not help reduce the CO<sub>2</sub> reactivity compared to the standard anodes.

Using 2 % additive 2 to modify LQI pitch helped increase the CO<sub>2</sub> reactivity residue (lower CO<sub>2</sub> reactivity) at 17 % pitch content.

The CO<sub>2</sub> reactivity of the anodes made with the modified HQI pitch by 1% additive 2 at 16 % pitch content had the highest CO<sub>2</sub> reactivity residue (low CO<sub>2</sub> reactivity) compared to all the other anodes at this pitch content.

## **Chapter 5**

### **Conclusions**

In this study, the effect of the modification of HQI and LQI pitches on the anode properties was investigated. Two different additives at different additive percentages and different pitch levels were tested. The HQI pitch modified with 1 % additive 1 at 16 % pitch percentage was the best choice to produce anodes. The modification improved the anode properties which could possibly help decrease the cost of production, the energy and carbon consumptions, greenhouse gas emissions, and increase the production. The results showed that the modification of HQI pitches improves the wettability compared to that of the non-modified HQI pitch. Consequently, the wettability results are in a good agreement with the improvement in anode properties.

The modification of the LQI pitch with additive 1 improved the anode properties at higher pitch contents. Modified LQI pitches wetted the coke better than the non-modified LQI pitches. Since the pitch is more expensive than the additive, using the HQI pitch modified with additive 1 might be a good choice since the properties are improved at lower pitch contents. Using the LQI pitches modified with additive 1 in anode fabrication increased the densities of anodes at pitch contents between 17 % and 18 % compared to the anode density at the pitch content of 16 %; but, the densities of LQI standard anodes are higher than the anodes using the modified pitch with additive 1. The anode resistivity decreased by increasing the pitch content. It was observed that increasing the pitch content decreased the air permeability for all anodes made with modified and non-modified LQI pitches. It was also found that the anodes fabricated with the LQI pitch modified using 1 % additive 1 at 17 % pitch content improved properties.

Wettability measurements can point out if the modification of a given pitch with a specific additive can increase the possibility of making better quality anodes. It cannot however predict the effect of modification as a function of anode pitch content.

Pitch modification affects less the anode properties if the pitch has already a good quality (LQI pitch). On the other hand, the properties of the anodes made with a low-quality pitch (HQI pitch) can be improved with modification. If the modified pitch which was originally low quality can give better quality anodes at lower pitch percentages compared to those made with non-modified high-quality pitch, it can have economic benefits since high quality pitch is more expensive. Further work involving more laboratory anode production and characterization is needed to assess such benefits.

## **Recommendations**

Other tests such as FTIR and XPS have to be carried out to understand the mechanism of improvement brought by the pitch modification. Such information will give a better insight into the details of the mechanism.

Other additives could be tried. It might be possible to improve the pitch quality further by modifying them with additives other than the ones used in this work.

It is also possible to look at the use of the combination of different additives for pitch treatment and verify the impact on anode properties.

## References

- [1] H. Kvande, P.A. drablos, The aluminum smelting process and innovative alternative technologies, *Journal of occupational and environmental medicine*, 2014, pp. S23-32.
- [2] K.L. Hulse, Anode manufacture : raw materials, formulation and processing parameters, R & D Carbon Ltd.2000.
- [3] S.M. Hume, Anode reactivity, Influence of raw material properties, R&D Carbon Ltd, Switzerland, 1999.
- [4] J. Bureau, Étude de l'amélioration de la qualité des anodes, applied science, University of Quebec at Chicoutimi 2017, p. 188.
- [5] H. Estrade-Szwarckopf, XPS photoemission in carbonaceous materials: A “defect” peak beside the graphitic asymmetric peak, *Carbon* 2004, pp. 1713-1721.
- [6] J.L. Gauthier, Monitoring of a carbon anode paste manufacturing process using machine vision and latent variable methods, University of Laval, 2015, p. 217.
- [7] S. Ozturk, D. Kocaefe, D. Bhattacharyay, Y. Kocaefe, Modification of petroleum coke by different additives and the impact on anode properties, *The Canadian Journal of Chemical Engineering*, 2018, pp. 1707-1712.
- [8] C. Andre, K. Yasar, Le carbone dans l'industrie de l'aluminium, 2012.
- [9] A. Sarkar, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, B. Morais, P. Coulombe, Effect of Coke Granulometry on the Properties of Carbon Anodes based on Experimental Study and ANN Analysis, *Journal of Materials Science Research*, 2016, pp. 63-78.
- [10] K. Azari Dorcheh, Investigation of the materials and paste relationships to improve forming process and anode quality, University of Laval, 2013, p. 148.
- [11] S. Uthaiporn Characterization of coal and petroleum derived binder pitches and the interaction of pitch coke mixtures in pre baked carbon anodes, Department of Materials Science and Engineering, The Pennsylvania State University, 2008, p. 355.
- [12] S. Amrani, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, M. Bouazara, P. Coulombe, Evolution of anode properties during baking, *IJSET - International Journal of Innovative Science, Engineering & Technology*, 2017, pp. 301-309.
- [13] A. Sarkar, D. Kocaefe, Y. Kocaefe, D. Sarkar, D. Bhattacharyay, B. Morais, J. Chabot, Coke–pitch interactions during anode preparation, *Fuel*, 2014, pp. 598-607.
- [14] S. Ozturk, D. Kocaefe, D. Bhattacharyay, Y. Kocaefe, B. Morais, Modification of coke by different additives to improve anode properties, *Fuel* 211 (2018) 102-109.
- [15] S. Ozturk, Improvement of anode properties by coke modification with additives, University of Quebec at Chicoutimi, 2017, p. 110.
- [16] J. Bureau, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, B. Morais, Modification des propriétés du brai de goudron de houille utilisé dans la, *Canadian Journal of Chemical Engineering*, 2018, pp. 545-553.
- [17] J. Bureau, A. Rastegari, D. Kocaefe, Y. Kocaefe, H. Darmstadt, Additive Selection for Coal Tar Pitch Modification in Aluminium Industry, *Light Metals*, 2020, pp. 1329-1337.
- [18] V.N. Rubchevskiya, S.A. Ovchinnikovaa, V.M. Volokha, R.A. Begmaa, L.P. Bannikovb, V.V. Karchakova, Influence of Coking Parameters on the Quality of Tar for ElectrodePitch Production, *Ukrainian CoalChemistry Institute, Kharkov, Ukraine*, 2014, pp. 158-162.
- [19] J.R. Davis, Corrosion of aluminum and aluminum alloys 1999.

- [20] M. Pistilli, top 10 aluminum producing countries 2022. <https://investingnews.com/daily/resource-investing/industrial-metals-investing/aluminum-investing/aluminum-producing-countries/>.
- [21] K. Khaji, M. Al Qassemi, The Role of Anode Manufacturing Processes in Net Carbon Consumption, *Metals* 6(6) (2016).
- [22] D. Kocaefe, A. Sarkar, S. Das, S. Amrani, D. Bhattacharyay, D. Sarkar, Y. Kocaefe, B. Morais, M. Gagnon, Review of different techniques to study the interactions between coke and pitch in anode manufacturing, *Light Metals*, 2013, pp. 1045-1050.
- [23] Binuta Patra, A. Palchowdhury, Improvement in oxidation Behaviour of Prebake anodes used in NALCO smelter plant Proceedings of 35th International ICSOBA Conference, pp. 731-733.
- [24] Kamran Azari, Gholamreza Aryanpour, Donald Ziegler, Donald Picard, M. Fafard, Compaction properties of carbon materials used for prebaked anodes in aluminum production plants, *Powder Technology*, 2013, pp. 650-657.
- [25] Y. Xie, D. Kocaefe, Y. Kocaefe, L. Wei, S. Zou, A. Wu, Correlation between Anode Recipe and Anode Properties, *International Journal of Engineering and Innovative Technology (IJEIT)*, 2013, pp. 23-27.
- [26] R. J. T. M. M. Inzunza Evelyn, Structural evaluation of coke of petroleum and coal tar pitch for the elaboration of anodes in the industry of the aluminum, *Light Metals*, 2008, pp. 887-892.
- [27] D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, B. Sanogo, Y. Ahoutou, H. Sun, P. Coulombe, Development of techniques and tools for the determination of carbon anode quality, *Light Metal*, 2017, pp. pp 1247-1254.
- [28] Senior C L , Lignell D O , Chen Z , Sarofim A F , D.T. D, Characterization of reactivity of green and calcined petroleum coke with oxygen for application to combustion systems, *Light Metals*, 2005, pp. 597-600.
- [29] G. E.J, S. J.W, Coal- tar pitch as electrode binder for the aluminum industry, use of pitch from vertical- retort tar, Commonwealth of Australia, CSIRO Coal Research Section, North Ryde, N.S.W., 1959, p. 23.
- [30] Q. Lin, T. Li, C. Zheng, Y. Zhao, S. Song, Carbonization behavior of coal-tar pitch modified with divinylbenzene and optical texture of resultant semi-cokes, *Journal of Analytical and Applied Pyrolysis* 71(2) (2004) 817-826.
- [31] Y. Lu, Effect of pitch properties on anode properties, applied science, The university of Quebec at Chicoutimi 2016, p. 222.
- [32] X. Huang, D. Kocaefe, Y. Kocaefe , D. Bhattacharyay, Interaction of bio-coke with different coal tar pitches, *Fuel*, 2016, pp. 179-192.
- [33] X. Huang, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, Wettability of bio-coke by coal tar pitch for its use in carbon anodes, *Light Metals TMS*, 2016, pp. 133-144.
- [34] Y. Lu, D. Kocaefe, Y. Kocaefe, H. Xian-Ai, B. Dipankar, The wettability of coke by pitches with different quinoline-insoluble contents, *Fuel*, 2017, pp. 587-597.
- [35] A.N. Adams, Characterization of the pitch wetting and penetration behavior of petroleum coke and recycled butts in pre-baked carbon anodes, The Pennsylvania State University, 2004, p. 220.
- [36] M.B. Dell, R.W. Peterson, Wettability of Petroleum Cokes by Pitch, *Ind Eng Chem Prod Res Dev* pp. 190–194.
- [37] J. Cao, A.N. Buckley, A. Tomsett, Re-examining the pitch/coke wetting and penetration test, *The journal of the Minerals, Metals & Materials Society* 2002, pp. 30-33.

- [38] B. Amara, Effet du soufre sur la reactivite des anodes en carbone, Universite du Quebec a Chicoutimi, Maîtrise en ingénierie, 2017, p. 218.
- [39] V. Rocha, C. Blanco, R. Santamaria, E. Diestre, R. Menendez, M. Granda, Pitch/coke wetting behaviour, Fuel (2005).
- [40] V.G. Rocha, R. C. Blanco, E.I. Santamaría, R. Diestre, M.G. Menéndez, An insight into pitch/substrate wetting behaviour. The effect of the substrate processing temperature on pitch wetting capacity, Fuel 86 (2007) 1046-1052.
- [41] V.G. Rocha, C. Blanco, R. Santamaría, E.I. Diestre, R. Menéndez, M. Granda, The effect of the substrate on pitch wetting behaviour, Fuel Processing Technology, 2010, pp. 1373-1377.
- [42] A. Sarkar, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, B. Morais, M. Pouliot, Characterization of petroleum coke and butts used in anode manufacturing in aluminum industry, Materials Science and Technology Conference and Exhibition, 2013.
- [43] A.A. Mirchi, G. Savard, J.-P. Tremblay, M. Simard, Alcan characterisation of pitch performance for pitch binder evaluation and process changes in an aluminium smelter, Light metals, 2002, pp. 525-534.
- [44] L. Edwards, N. Backhouse, H. Darmstadt, M.-J. Dion, Evolution of anode grade coke quality, Light Metals, 2012, pp. 1207-1212.
- [45] Seh-Min. Oh, Y.-D. Park, Comparative studies of the modification of coal-tar pitch, Fuel 78(15) (1999) 1859-1865.
- [46] C. Ren, T. Li, F. Song, X. Sun , Q. Lin, Influence of additives on the permeability of impregnating coal-tar pitch, Materials Letters 60(13–14) (2006) 1570-1574.
- [47] Rocha V. G., Granda M., Santamaría R., Blanco C., Diestre E. I., M. R., Pyrolysis behaviour of pitches modified with different additives, Journal of Analytical and Applied Pyrolysis, pp. 276-283.
- [48] Rocha V.G., Granda M., Santamaría R., Blanco C., Diestre E.I., M. R., Improvement of pitch/coke interactions by addition of surface tension modifiers in carbon, Carbón Instituto Nacional del, Brown University, Providence, RI, 2004.
- [49] E. Commission, h, EUR 18584 EN, 1999.
- [50] Y. Lu, Interaction du bio-brai avec le coke - Effet du bio-brai sur la formulation d'anode, Université Laval, 2020, p. 204.
- [51] B. Amara, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, J. Côté, A. Gilbert, Partial Replacement of Petroleum Coke with Modified Biocoke during Production of Anodes Used in the Aluminum Industry: Effect of Additive Type, Applied Sciences 12(7) (2022).
- [52] B. Amara, F.-E. Faouzi, D. Kocaefe, Y. Kocaefe, D. Bhattacharyay, J. Côté, A. Gilbert, Modification of biocoke destined for the fabrication of anodes used in primary aluminum production, Fuel 304 (2021).
- [53] D. Kocaefe, J. Bureau, A. Rastegari, K. Rajan, Y. Kocaefe, Effect of the modification of high-QI pitch with an additive on anode Submitted to The canadian journal of chemical engineering 2023.