Evolution of Mechanical Properties of Carbon Anodes during Baking

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Abstract

To be considered as a good quality product, carbon anodes must not only have a low electrical resistivity, but also a high mechanical resistance to crack generation and propagation. To obtain such anodes, a good understanding of the evolution of their mechanical properties during baking is crucial. Traditional mechanical characterization approaches consist of baking anode samples at specific temperatures and performing the tests at either room temperature or slightly lower than that of the baking level. In the latter case, it is well-known that numerous chemical reactions take place during the tests which affect the results. In this paper, an innovative approach is proposed to ensure the reliability of mechanical properties measurements. The anode cores were taken from industrial green anodes removed directly from the production line of Aluminerie Alouette Inc. (AAI) and then baked to different temperatures in a laboratory furnace of the UQAC/AAI Chair. Compression tests initially performed using the Gleeble system showed that this system was not suitable for low temperature testing, at which the anode samples were in a semi-solid state. To overcome this problem, a new setup was installed on a classical CRIMS press which accurately measures the Young's modulus, compressive strength, and particularly, Poison's ratio.

Keywords: Carbon anodes; baking process; mechanical properties; high temperature mechanical property testing.

1. Introduction

Carbon anodes are used in aluminium smelters both as an electrical conductor and a carbon source for the electrolytic process. Their production process begins with the formation of a green anode, which is composed of solid petroleum coke particles, coal tar pitch and recycled materials [1]. The coke particles serve as an inert carbonaceous filler necessary for the electrolysis reaction while the pitch carbonizes and binds the coke particles to each other by adhesion to their surfaces and pores while filling the empty space between the particles, thus giving the mix mechanical strength. The components are mixed together in a mixer at around 180°C, transferred to a shaping mold and then vibrocompacted to densify the mixture. Finally, the green anodes are baked using a large refractory furnace up to a temperature of 1200°C, following an average heating rate of 11°C/h. During this operation, packing coke is used to provide structural support to the green anodes and protection from oxidation by air during baking. The baking carbonizes and solidifies the compressed mixture which then acquire the necessary properties to efficiently perform in an electrolytic industrial cell.

During the baking process, carbon anodes undergo various chemical transformations, which greatly influence the final product quality. The current literature on carbonaceous materials states that since the coke particles in the anode are already calcined, evolution of the anode properties through the process is mainly caused by the binder phase changes [2-4]. At 100°C, the viscosity of the pitch decreases, caused by the modification of the crystalline structure of the pitch from amorphous to liquid. This process continues up to the softening point, which begins in the temperature range of 120 to 150°C for the lightest constituents, and stops around 200 to 250°C for the heavier ones. Between 250 to 500°C, volatilization starts as the anode simultaneously loses mass and swells. The volatilization process comprises the distillation of the condensable gases and the release of low molecular weight condensable (tar) from pitch into simpler components like methane and hydrogen, which will further increase the viscosity of the binder [5]. Subsequently, between 400 and 500°C, the material tends to solidify through the binder's polymerization and polycondensation into a semi-coke. For temperatures higher than 550°C, the pitch enters its pyrolysis phase which further carbonizes the material, bringing the anode microstructure towards its final form [5]. During this process, the volatile generation produces pressure within the anode and leads to crack generation, affecting the final quality of the product [6].

Chemical reactions have a direct impact on the evolution of the mechanical properties during the baking process. A number of authors tested the mechanical properties of carbon-based materials over the years. However, certain phenomena must be better understood to ensure the proper comprehension of the anodic carbon paste behavior during baking. In order to get the necessary information which describes the evolution of the thermomechanical properties during this phase, a new methodology has been developed. Mechanical compression tests were performed at different selected testing temperatures to describe the evolution of Young's modulus, Poisson's ratio and compressive strength. In order to have the entire history of the evolution of the mechanical properties during the baking phase, the tests were carried out on green, partially baked, and fully baked carbon anode samples. In this paper, the influence of the baking level and testing temperature on the thermomechanical behaviour of the carbon anode paste is investigated. This work will later be used in a numerical model that simulate the mechanical behavior of the anode paste during its baking phase in an industrial furnace [7] and aim to improve anode quality through a better understanding of the baking process.

2. Previous works

A few works have been carried out on carbon-based materials over the years to describe the evolution of their mechanical properties. The traditional testing approach is based on room temperature tests as a way to identify the mechanical properties of the specific material. Andersen and Zhang [8] measured the compressive strength and Young's modulus of fully baked anode samples at room temperature and in the temperature range of 200°C to 400°C. Their results showed a strong dependence of these properties on the testing temperature. D'Amours [2] measured the Young's modulus, Poisson's ratio and compressive strength of the ramming paste at room temperature as a function of the baking level for partially baked anodes up to 1000°C. The author concluded that Poisson's ratio continuously decreases from 180°C up to 1000°C while the Young's modulus and compressive strength increase quickly starting around 250°C to 450°C, and then stabilizes with a slight decrease in Young's modulus after 800°C. The same conclusions were drawn by St-Arnaud et al. [9] who measured the compressive strength, Young's modulus and Poisson's ratio of ramming paste at room temperature on larger samples.

To better understand the temperature dependency of carbon-based material mechanical behavior, some authors also tested samples at higher temperatures. D'Amours [2] measured the Young's modulus and compressive strength of partially baked ramming paste samples tested at temperatures slightly below the baking temperature. Results showed a different trend compared to the results of room temperature tests. The material acted as an incompressible viscous fluid with very low Young’s modulus for tests carried out on anode samples partially baked at 175°C, 250°C and 400°C. At 250°C, the paste begins to have some resistance but it is still weaker than those tested at room temperature. For samples partially baked at 400°C, the measured compressive strength was similar to the one observed at room temperature. However, those results were fairly scattered and the trend couldn’t be confirmed due to the small number of completed tests as well as technical difficulties encountered during the high temperature tests using partially-baked samples. In another study, Orangi [10] performed tests on ramming paste to obtain Young’s modulus and Poisson’s ratio at high temperatures. Uniaxial compression tests were carried out at 160°C and 200°C on samples baked respectively at 200°C and 250°C. The tests were carried out at temperatures below the baking temperatures to avoid further chemical evolution of the samples. However, the motives for the choice of test temperature was not explained. Orangi’s results showed that the Young’s modulus at baking temperatures under 200°C could not be obtained since the ramming paste was very soft and compression tests could not be carried out with the available apparatus.

3. Identification of the testing temperature for the mechanical tests

As shown, high temperature tests have only been used in previous works to understand the effect of the testing temperature on the mechanical behavior of the anode during the baking phase. However, they did not establish a methodology to identify the appropriate testing temperature to properly identify the mechanical behaviour of carbonaceous materials during their baking phase during high temperature tests. To solve this problem, a new approach was developed using thermogravimetric tests to identify the beginning of the volatile release phase of carbon anode samples.

3.1. Experimental setup and experimental procedure

The mechanical tests were conducted on green, partially-baked and fully baked carbon anode samples. Green and partially-baked specimens were sampled from industrial green anodes while baked specimens were sampled from industrial baked anodes. All samples were taken from the anode production line at AAI (Aluminerie Alouette Inc.). The samples (cylinder: 50 x 125 mm) were cut in a way to ensure the parallelism between both end surfaces, and then mechanical properties were measured according to standard laboratory practice [6]. For partially baked conditions, green samples were placed in a furnace which was then filled with packing coke and the anodes samples were baked up to the desired temperatures under similar conditions that are used in carbon plants to simulate industrial conditions.

3.2. Results

The baking is done in laboratory furnace under a nitrogen atmosphere with a heating rate of 11°C/h and stopped at 300°C, 400°C, 500°C, and 600°C. These temperatures were selected to capture most of the chemical and physicals evolutions that occur in anode during baking. Thus, the entire temperature spectrum was covered, with the emphasis being on the temperatures at which the mechanical properties may change. After cooling, the dimensions of the samples were measured again to check for variations [6]. The mechanical tests were both carried out at room temperature and high temperatures. For room temperature, green, partially baked (300°C, 400°C, 500°C, 600°C) and fully baked (1200°C) samples were tested. For high temperature, green anodes were tested at 120°C, 180°C and 230°C. These temperatures were chosen since 120°C is the temperature of the softening point of the pitch, 180°C is the temperature of anode vibrocompaction and 230°C is below the safe temperature just before the release of volatiles [5].

The remaining samples baked at different temperatures were tested at the safe temperature which was determined through thermogravimetric tests.

The thermogravimetric tests have been carried out on the Thermogravimetric Analyzer (TGA) at UQAC [5] using an anode sample pre-baked at 400°C following the standard procedure described previously. The tests were performed at a heating rate of 11°C/h, similar to the heating rate used in industrial horizontal anode baking furnace, and mass loss is measured using a mass balance. Figure 1 shows the thermogravimetric tests results for a sample pre-baked at 400°C. The results showed that the baking of this same sample resume not at the pre-baking level of 400°C, but rather at the same temperature where the volatile release starts when a green anode sample is baked. In the tests with a pre-baked sample, volatile release actually resumed at 300°C with a few disruptions starting as soon as 260-270°C were reached. These new results suggest that until the volatiles are entirely depleted, the sample will always resume its chemical evolution at the same temperature, regardless of its pre-baking state. Therefore, to avoid excessive volatile release and resumption of baking during the mechanical tests, a testing temperature of 250°C was selected for all partially baked samples. Table 1 presents the testing temperatures used for different anode samples.

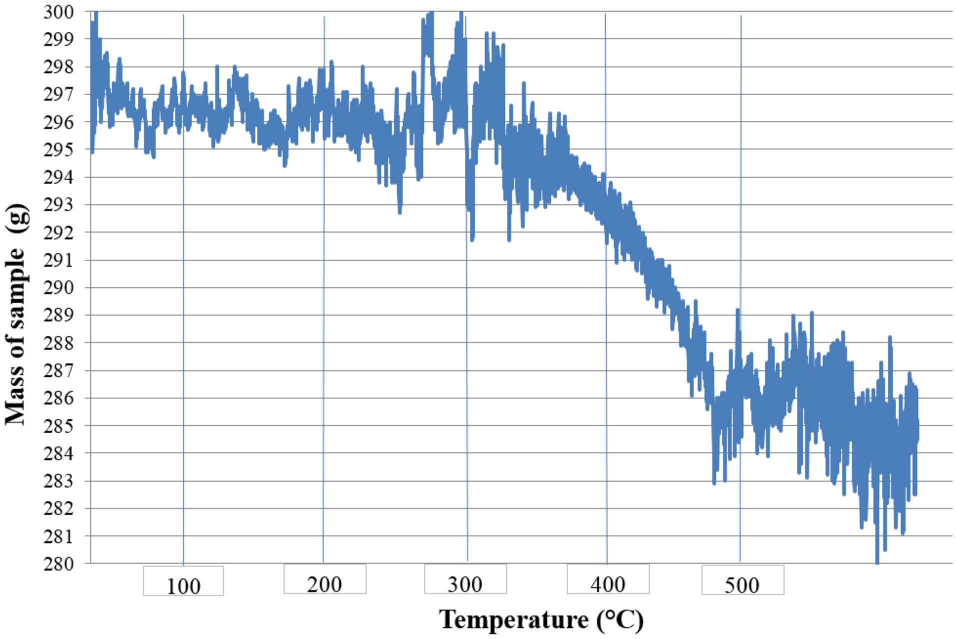

Figure 1: Thermogravimetric tests on pre-baked anode samples at 400 °C

Table 1. Testing temperatures for different anode samples

Room temperature tests		High temperature tests	
Baking level (°C)	Test temperature (°C)	Baking level (°C)	Test temperature (°C)
25 (green anode)	25	25 (green anode)	120
300	25	25 (green anode)	180
400	25	25 (green anode)	230
500	25	300	250
600	25	400	250
1200 (baked anode)	25	500	250
		600	250
		1200 (baked anode)	250

4. Mechanical tests

4.1. Experimental setup

Gleeble® 3800 Press

All room temperature tests were carried out using the Gleeble® 3800 press following a previously developed procedure [11]. Using the setup shown in figure 2, compressive strength, Young's modulus and Poisson's ratio were identified for each sample. For high temperature tests, samples baked at 500°C, 600°C and 1200°C could be carried out in the Gleeble® 3800 press. This is due the minimum preload force necessary to produce the Joule's effect required by the heating system (0.6 kN – 0.3 MPa), which cannot be sustained by the other pre-baked samples.

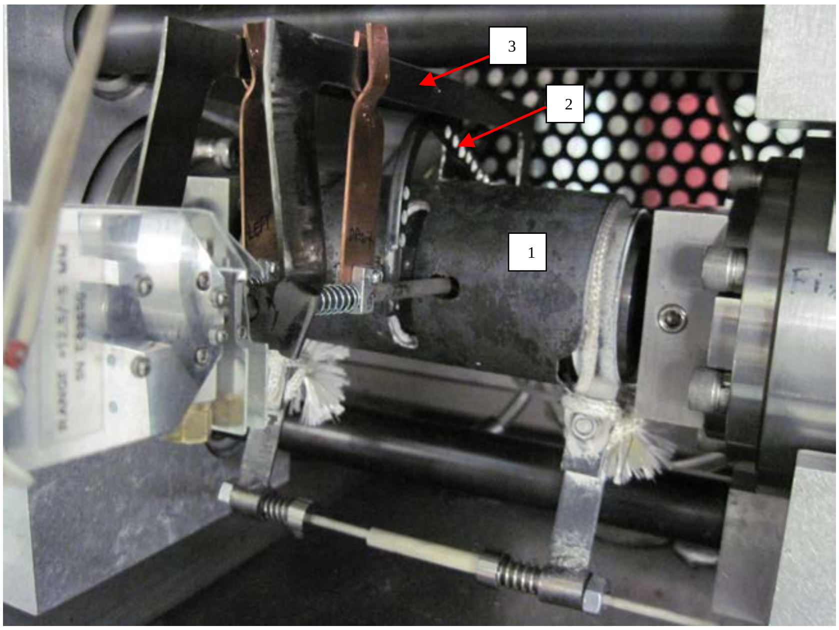

Figure 2. The Gleeble® 3800 Press system: Sample (1), radial extensometer (2) and axial extensometer (3).

CRIMS Press

To complete the remaining high temperature compression tests on softer samples (green to 400°C pre-baked samples), a new setup was developed using a CRIMS press which can measure the Young's modulus, compressive strength, and particularly, the Poison's ratio.

The CRIMS system is a high temperature testing apparatus combining a mechanical press with 100 kN maximum load and an induction furnace to heat the tested sample. Two axial LVDT were initially installed to measure the average axial displacement of the sample. The original setup was modified by adding two others radial LVDT to measure the average radial displacement, as well as two thermocouples installed inside the environmental insulation cylinder to monitor the temperature of the sample and the chamber. Each LVDT is linked to an alumina rod to allow measurement in the testing chamber. The testing chamber was further insulated to ensure the uniform temperature of the sample which is placed inside the chamber, and protected from oxidation with an inert nitrogen atmosphere. The modified setup is shown in figure 3.

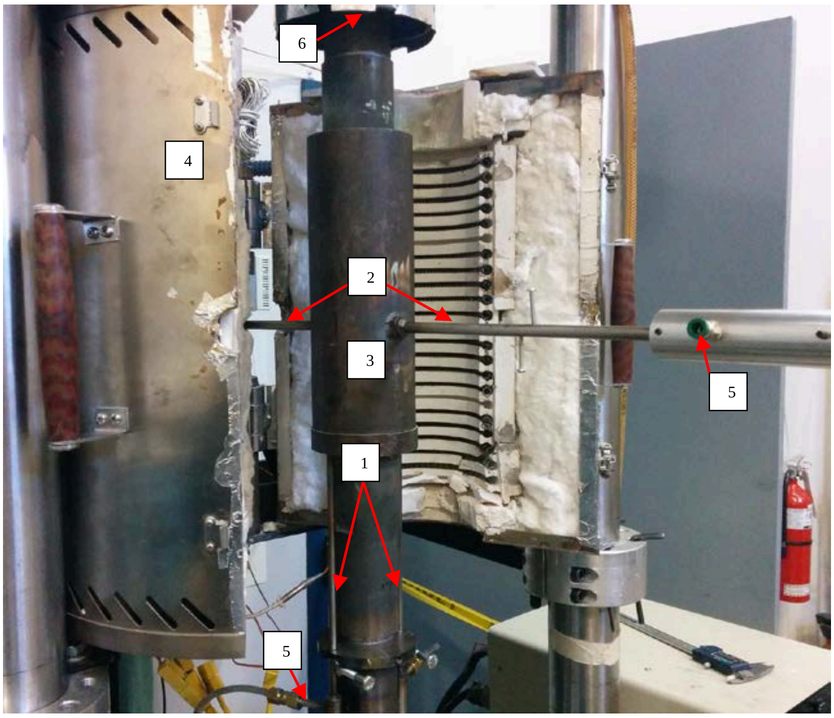

Figure 3. Modified CRIMS Press system: Axial LVDTs (1), Radial LVDTs (2), Environmental insulation cylinder (3), Furnace (4), Inert gas entry (5), Volatile uptake system (6)

4.1. Calibration

During a uniaxial compression test on the CRIMS, a measurement error was observed on the fixed radial LVDT measurements since the tip touching the sample move both horizontally and vertically, due to the sample deformation during loading. To ensure correct data collection, the generated angle due to the vertical movement must be compensated through proper calibration. Figure 4 shows the calibration sample used to determine the lateral displacement caused by vertical movement.

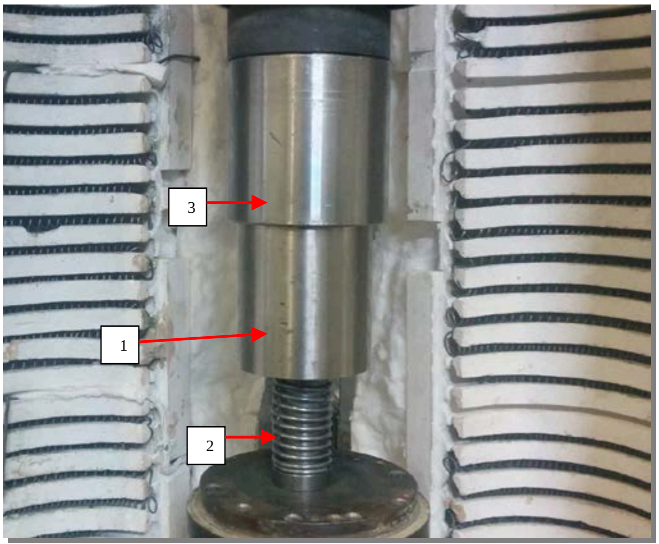

Figure 4. Radial extensometer calibration setup; Calibration cylinder (1), Insertion pin with spring (2), Spacer (3)

In this setup, the spring applies a small pressure to maintain contact between components while allowing all vertical displacement necessary for the calibration. This avoids possible deformation of the calibration cylinder. Hence, the response due to the vertical movement without radial effect is obtained. The real radial displacement is then obtained by:

$$\text{Radial displacement} = \text{Setup response} + \text{Sample response} \qquad (1)$$

In order to validate the new method, calibration tests were performed using an AA6061 aluminium sample tested at room temperature. The results were similar to those seen in the literature. For high temperature testing, calibration tests were performed at 250°C on a fully baked carbon anode samples and the results were found to be similar to those obtained with the Gleeble® 3800 press which was beforehand calibrated [11].

4.3. Experimental procedure

Two loading-unloading cycles up to 20% of the compressive stress are done prior to testing to ensure the conditioning of the carbon samples, thus closing the pores of the material and removing residual stresses induced during the preparation of the sample, following the ASTM C469M–10 standard [12]. The sample is then heated to the testing temperature and maintained for one hour to ensure its stabilization. Finally, a third load is applied to the sample until failure with a rate of 1 mm/min. For each test conditions, three samples were tested.

Young's modulus was identified using the ASTM C469M–10 standard as the average slope of the stress-strain curve of the second and third loading. Poisson’s ratio was identified as the ratio between the radial and axial deformation for these same loading curves, as stated by the ASTM C469M–10. The compressive strength was identified as the maximum stress value recorded during the third load, following the ASTM C469M–10 standard. It has to be pointed out that since the sample was heated only after the second loading using the methodology developed, Young’s modulus and Poisson’s ratio for both room and high temperature were obtained during each test, while the compressive stress was only obtained at high temperature.

4.4. Results and discussion

Room temperature tests

The evolution of the compressive strength, Young’s modulus and Poisson’s ratio at room temperature are presented respectively in figure 5, 6 and 7. The compressive strength stays almost identical through the baking process. At room temperature, the Young’s modulus decreases slowly from an average of 12 GPa for a green anode to an average of 7 GPa for a fully baked anode. This can be explained by the development of porosity during the carbonization and pyrolysis process which affect the values as well. The same logic can explain the trend of Poisson's ratio which decreases from an average of 0.22 for a green anode, to an average of 0.12 for a totally baked anode as a function of the baking level.

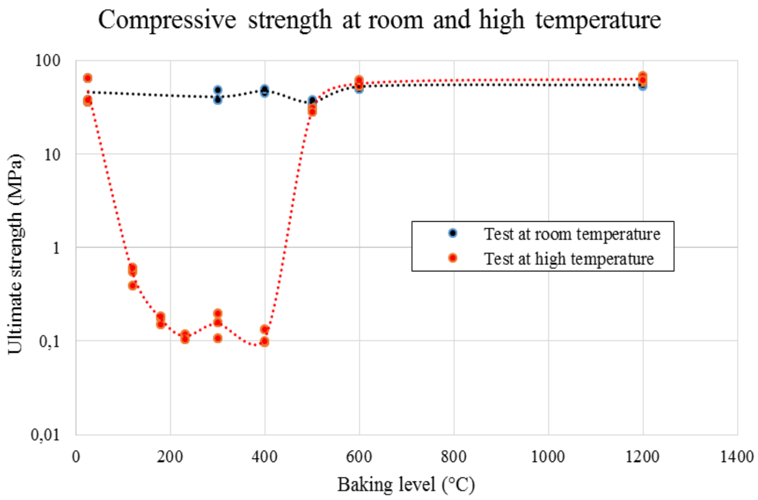

Figure 5. Compressive strength as a function of baking level. (Testing temperatures defined in table 1)

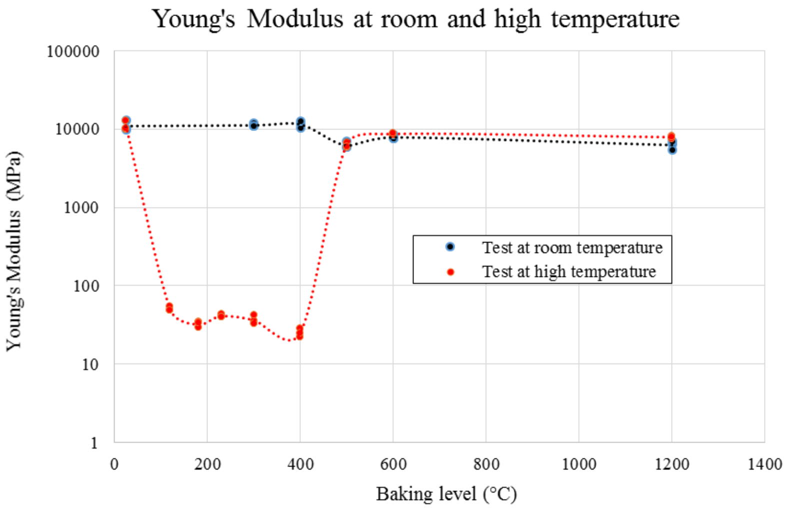

Figure 6. Young’s modulus as a function of baking level. (Testing temperatures defined in table 1)

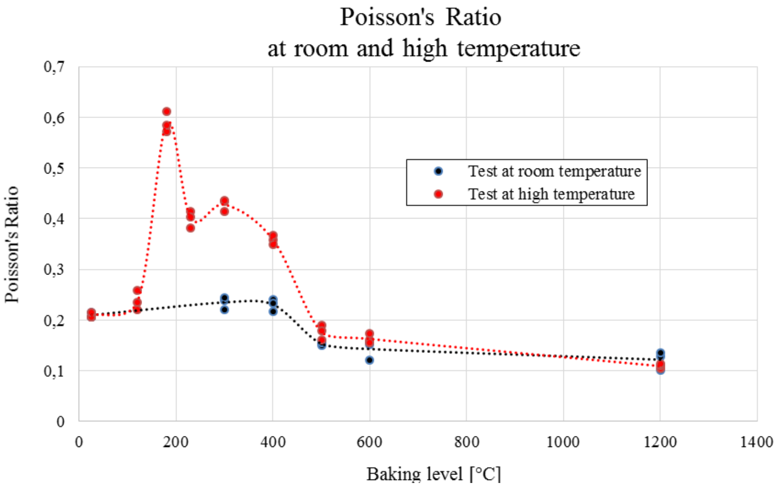

Figure 7. Poisson’s ratio as a function of the baking level. (Testing temperatures defined in table 1)

High temperature tests

The evolution of the compressive strength, Young's modulus and Poisson's ratio at high temperature are also presented respectively in figure 5, 6 and 7. High temperature tests results show a totally different trend than that of the room temperature tests results. Indeed, as shown in figure 5 and 6, the compressive strength and Young's modulus of the carbon anodes are significantly lower at around 120°C to 400°C where most of the physical and chemical transformations prior to carbonization happens, in the range of 400°C and 600°C. This could be explained by the phase change that the pitch undergoes, which could greatly affect the viscosity of the carbon paste. At these temperatures, the sample act as a viscous fluid, as previously stated by other authors, which makes axial and radial measurements difficult. Also, the progressive transformation of the pitch into a semi-coke may be responsible for the following increase and subsequent stabilization of the Young's modulus seen at 600°C. The overall results between room and 500°C could also indicate the presence of creep phenomena during the carbon paste baking since the sample acts as a viscous fluid, as shown by the high Poisson's ratio result and low compressive strength and Young's modulus values. This strain mechanism, which could be an important aspect of its mechanical behaviour evolution through the process, will be further studied in a future work.

However, Poisson's ratio results can be questionable since the measurement of this mechanical property remains a challenge due to the small magnitude of the displacement values measured during the tests. Similar to the compressive strength and Young's modulus measurement, Poisson's ratio was observed to stabilize slowly around 600°C. However, the most critical zone is between 120°C and 500°C where values up to 0.6 were obtained, which are considered to be out of the possible range for the Poisson's ratio. This could be partially explained by the release of the residual stress induced by the forming process, which could cause a volume increase during this phase. However, this explanation has to be further investigated to fully understand its proposed effect on the Poisson's ratio results.

5. Conclusions

In this paper, a new approach was presented to measure the mechanical properties of carbon-based materials at high temperature. A testing temperature of 250°C was set for the high temperature tests using thermogravimetric results for partially baked anode samples. The results showed that the chemical transformations of the material resume at similar temperatures independently of the pre-baked state of the anode while the baking process is not finished. Using a modified CRIMS press system and Gleeble® 3800 press system, the Young's modulus, Poisson's ratio and compressive strength of carbon anode samples green and partially baked at temperatures ranging from up to 1200°C were identified at high temperature. Results showed that between 120°C and 500°C, the anode paste behaves as a viscous fluid with a very low compressive strength and Young's modulus. Poisson's ratio values, which were close to incompressibility, confirmed this observation. The results also suggest that creep phenomena could be present during the baking phase, possibly affecting the final quality of the anode. This strain mechanism will be the subject of future research within the group.

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