Chapter 6
Results and discussion
Structural changes in the Söderberg electrode beyond the baking isotherm

6.1 Introduction

In Chapter 5, parameters were investigated to narrow down the temperature range of the Söderberg electrode isotherm. It was found that the baking isotherm temperature was between 450 and 475 °C. In this chapter, TMA was used to measure the dimensional changes of CTP beyond the baking isotherm temperature. The structural changes that take place during the thermal treatment of CTP beyond the baking isotherm temperature were evaluated.

6.1 Measurement of dimensional changes during three TMA thermal cycles up to 1300 °C

Dimensional changes that took place when CTP samples pre-treated at 475 °C were thermally treated in the TMA were measured over three thermal cycles. Examples for CTP 1, 4 and 9 of the associated dimensional changes that took place are presented in Figures 6.1, 6.2 and 6.3, respectively. From these figures, a significant change in dimensions in the first heating and cooling cycle is evident. The second and third cycles were characterised by small changes in dimensions. All 12 CTP samples gave similar results. CTP 1, 4 and 9 were randomly selected for illustration purposes.

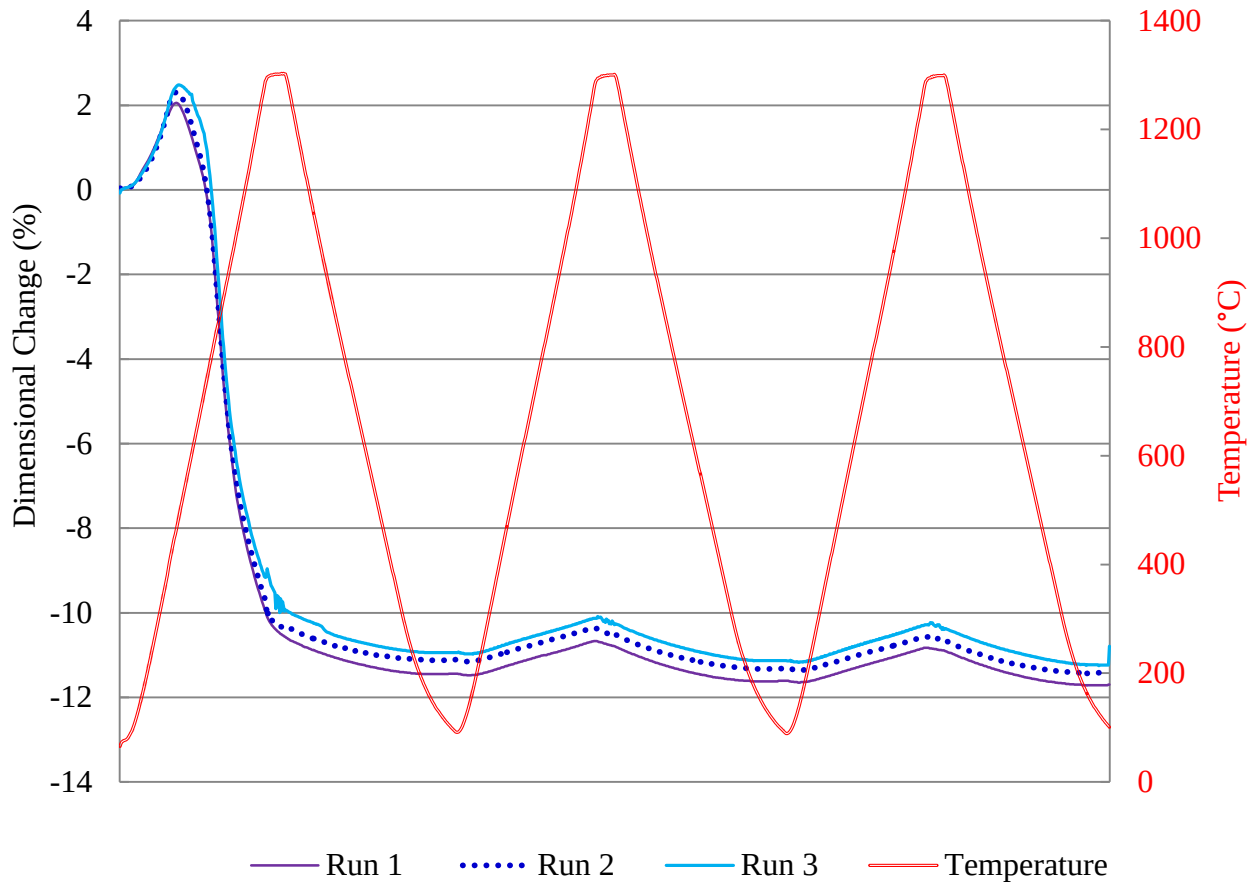

Figure 6.1 TMA behaviour of CTP 1 during three thermal cycles

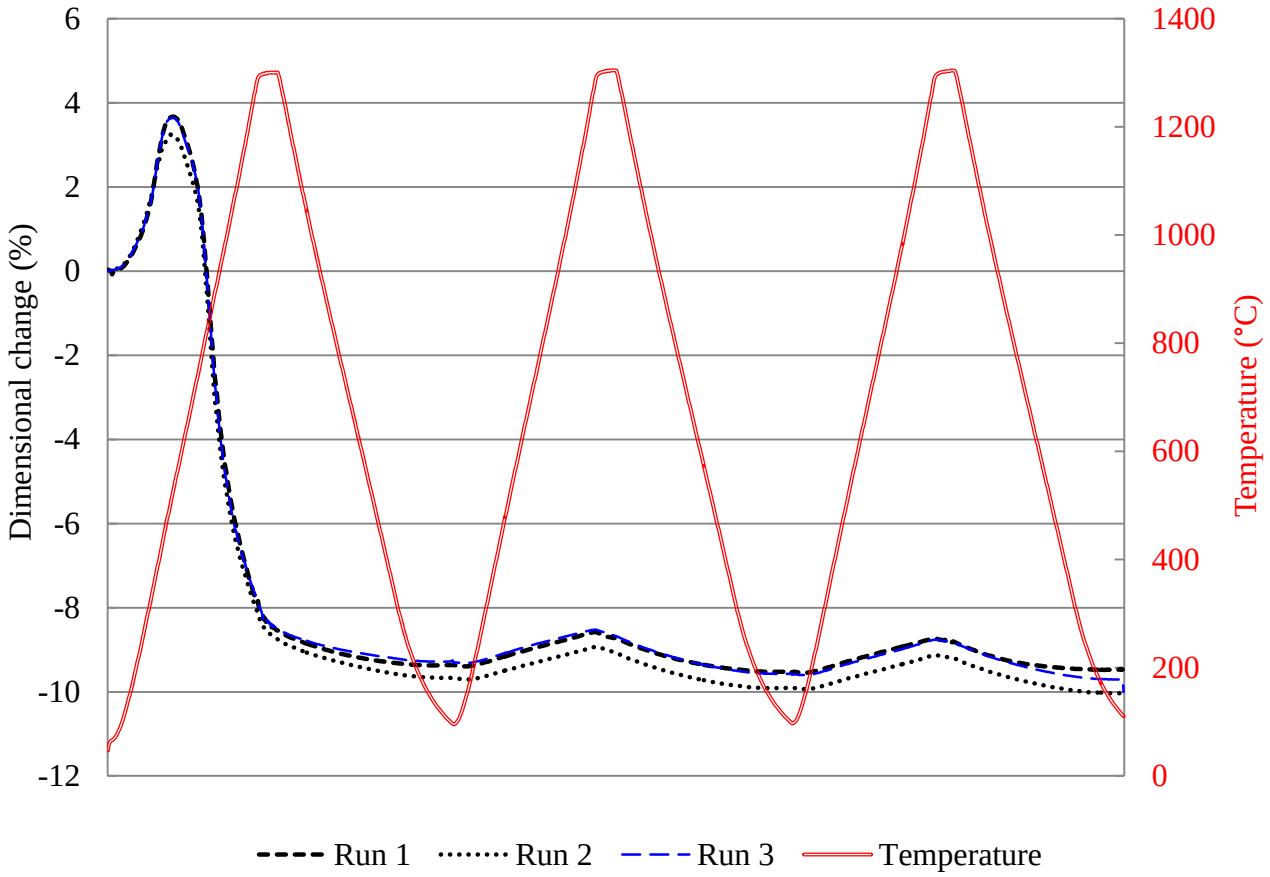

Figure 6.2 TMA behaviour of CTP 4 during three thermal cycles

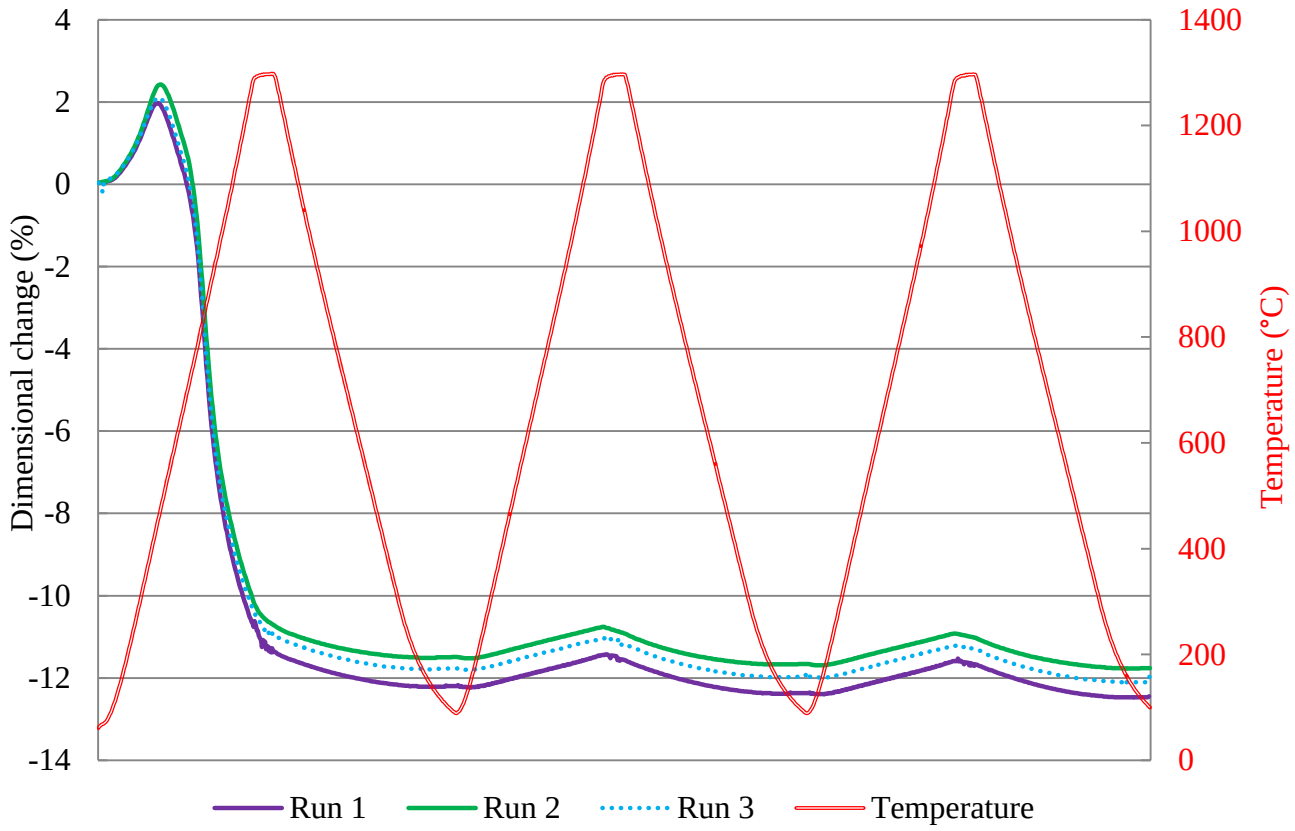

Figure 6.3 TMA behaviour of CTP 9 during three thermal cycles

From Figures 6.1, 6.2 and 6.3 it is evident that approximately 12 to 14% change in dimension occurs for all CTPs during the first TMA thermal cycle. The significant change in dimensions observed for all CTP samples during the first TMA thermal cycle is attributed to structural rearrangement, which takes place within the carbonaceous material on thermal treatment. The extent of this structural reordering will be illustrated later in this chapter (Sections 6.3). In the second and third TMA thermal cycles, much smaller changes in the dimensions occur for all samples, indicating that no more structural rearrangement of the graphene layers is taking place

within the carbonaceous structure. Average changes in dimensions for the TMA thermal cycles one, two and three for all the CTP samples are summarised in Table 6.1

Table 6.1 Dimensional change (%) for each TMA thermal cycle

Sample	cycle 1	cycle 2	cycle 3
CTP 1	12.0	2.0	2.0
CTP 2	13.0	0.5	0.5
CTP 3	12.5	1.0	1.0
CTP 4	13.2	1.0	1.0
CTP 5	12.8	1.0	1.0
CTP 6	14.0	0.5	0.5
CTP 7	15.9	0.5	0.5
CTP 8	16.0	0.5	0.0
CTP 9	13.0	1.0	1.0
CTP 10	12.0	0.1	0.1
CTP 11	14.0	2.0	2.0
CTP 12	14.0	2.0	2.0

6.2 Structural changes of the CTP on heat treatment

When CTPs are subjected to thermal treatment, they undergo chemical structural transformations. In this study, FT-IR analysis was used to investigate these changes by performing qualitative analysis aimed at establishing the functional groups lost/formed on thermal treatment (Section 6.2.1). Additionally, XRD analysis was also used to measure the DOG in thermally-treated CTP samples (section 6.2.2).

6.2.1 FT-IR analysis of CTP samples thermally treated at 700 and 1000 °C

Further investigations into the effects of heat treatment on the structure of pitch during thermal treatment were performed on samples that were thermally treated at temperatures of 700 and 1000 °C (Section 3.4.2). The FT-IR spectra from the analysis are shown in Figures 6.4 and 6.5, respectively. The FT-IR spectra of samples CTP 1, 6 and 10 were randomly selected for samples thermally treated at 700 °C, while CTP 4, 6, 7 and 9 were selected for samples thermally treated at 1000 °C. CTP samples not represented in these two figures also had similar FT-IR spectra (Appendix A). The FT-IR spectra of all CTP samples thermally treated at 700 °C had peaks in the range 3883 to 3763 cm^{-1}, which is indicative of the presence of OH groups within the samples [Painter et al., 1985]. The broad peaks at 2346 cm^{-1} are characteristic of anhydrides [McMurry, 1992; Stuart, 1996]. 1875cm^{-1} is characteristic of anhydrides. 1566cm^{-1} is due to aromatic C = C, 1255 cm^{-1} is due to aryl ethers and aryl oxygen. 948 cm^{-1} is due to out-of-plane C-H and 874 cm^{-1} is due to aromatic C-H stretching [Guillen et al., 1992; McMurry, 1992; Stuart, 1996; Alcañiz-Monge, et al., 2001]. The spectra indicate the loss of some functional groups such as aromatic and aliphatic C-H groups, which were observed in the spectra of raw pitch between 3100 and 2750 cm^{-1} (Figure 4.2, section 4.2.2) [Guillen et al., 1995; Prauchner et al., 2001; Geng et al., 2009]. The loss of the same functional groups was also observed in CTP samples that were thermally treated at 1000 °C (section 2.3.3 shows the CTP carbonisation reaction pathway).

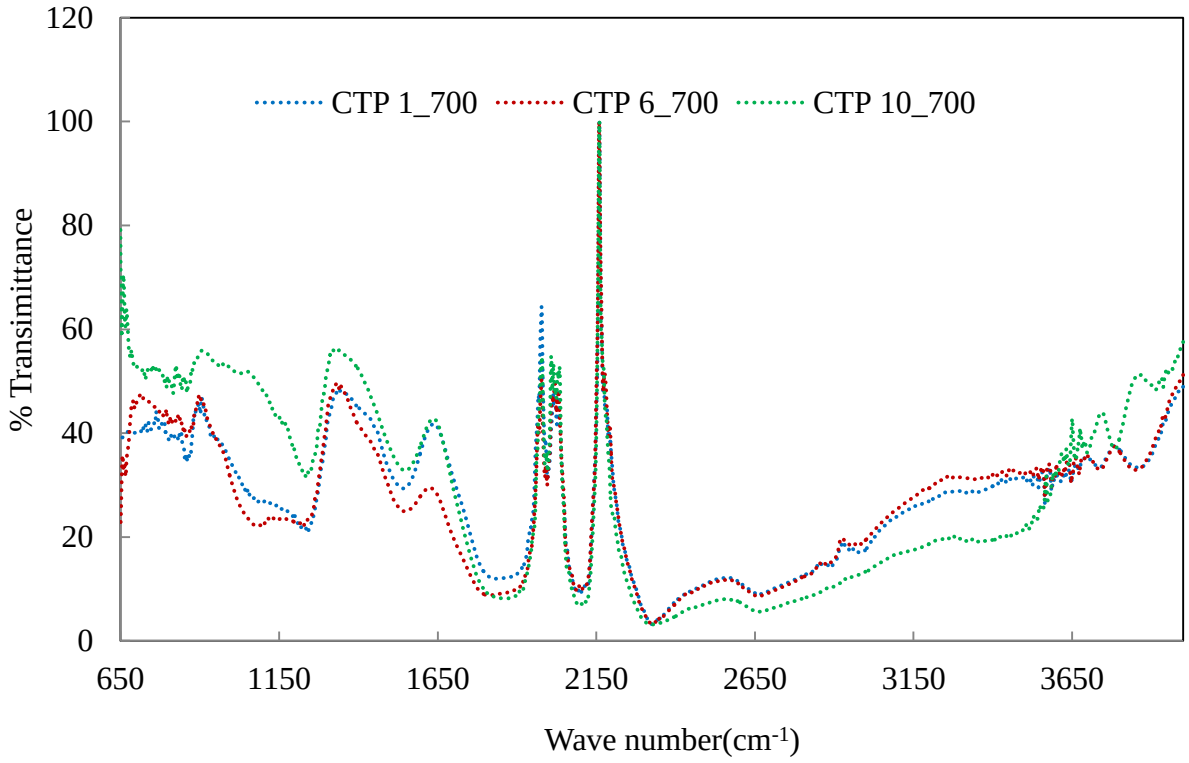

Figure 6.4 FT-IR spectra of CTP thermally treated at 700 °C

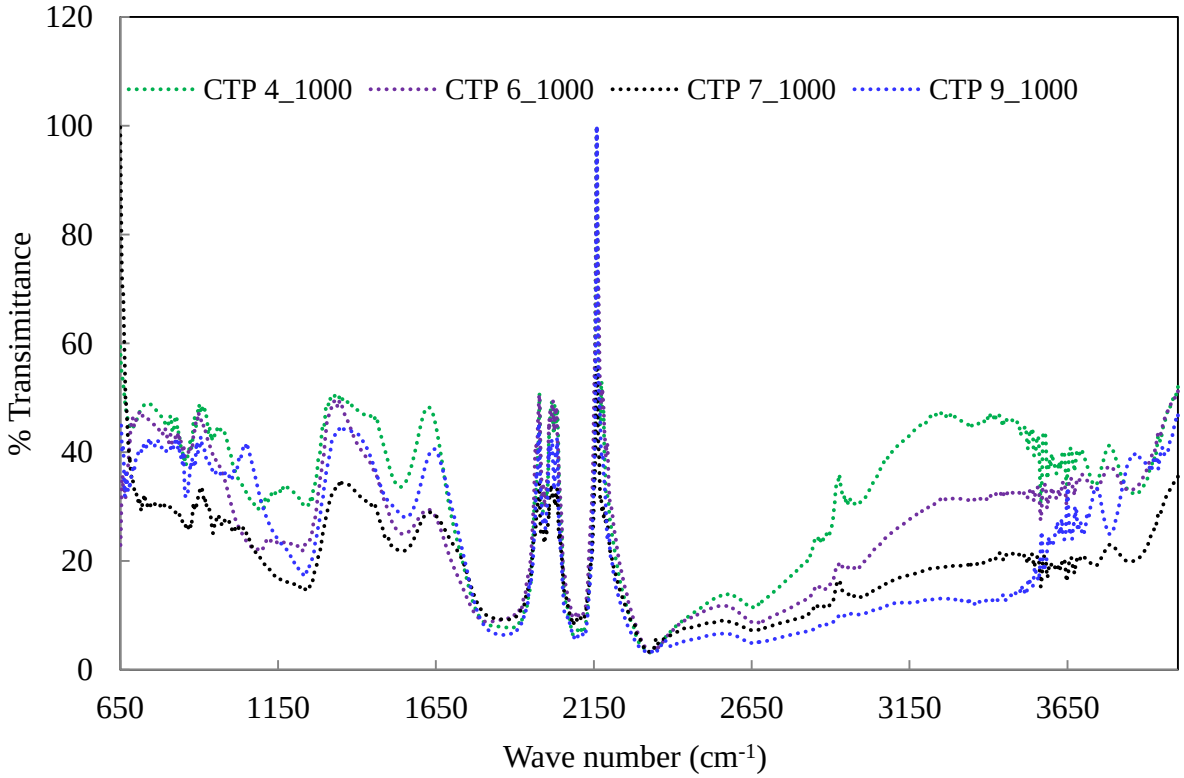

Figure 6.5 FT-IR spectra of CTP thermally treated at 1000 °C

6.2.2 FT-IR analysis of CTP thermally treated at 1300 °C and prebaked electrode graphite

FT-IR analysis was also performed on the 12 CTP samples thermally treated at 1300 °C in the TMA and also on prebaked electrode graphite. The FT-IR spectra shown in Figure 6.6 are for samples CTP 5, 6 and 7, which were selected at random for presentation purposes. The samples not shown in this figure had similar FT-IR spectra (see Appendix A).

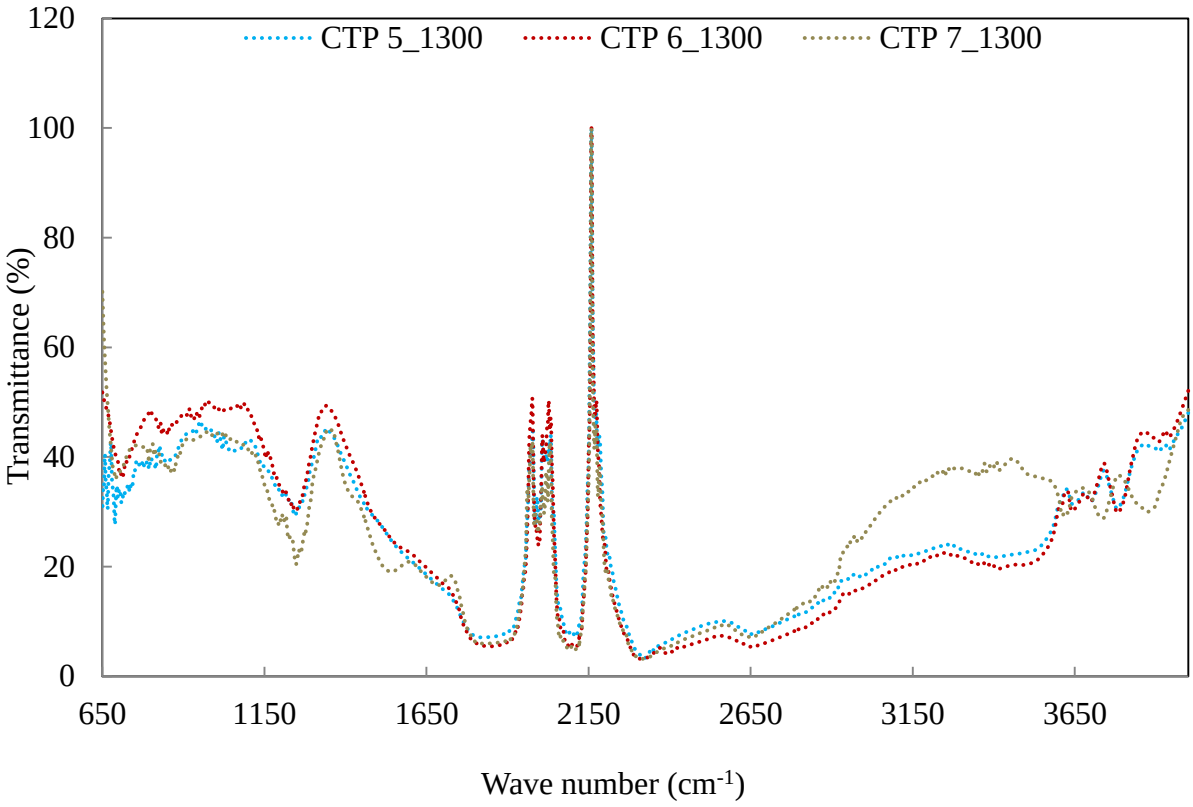

Figure 6.6 FT-IR Spectra of CTP thermally treated at 1300 °C

In order to further investigate the structural changes that occur in CTP during thermal treatment, the FT-IR spectra of CTP thermally treated at 1300 °C were compared to that of a prebaked graphite electrode. The comparative spectra are represented in Figure 6.7. From this figure, it is obvious that there are similarities in the peaks between the FT-IR spectra of the thermally (1300

°C) treated CTPs and the prebaked electrode graphite material. This indicates that similar functional groups occur in both types of materials.

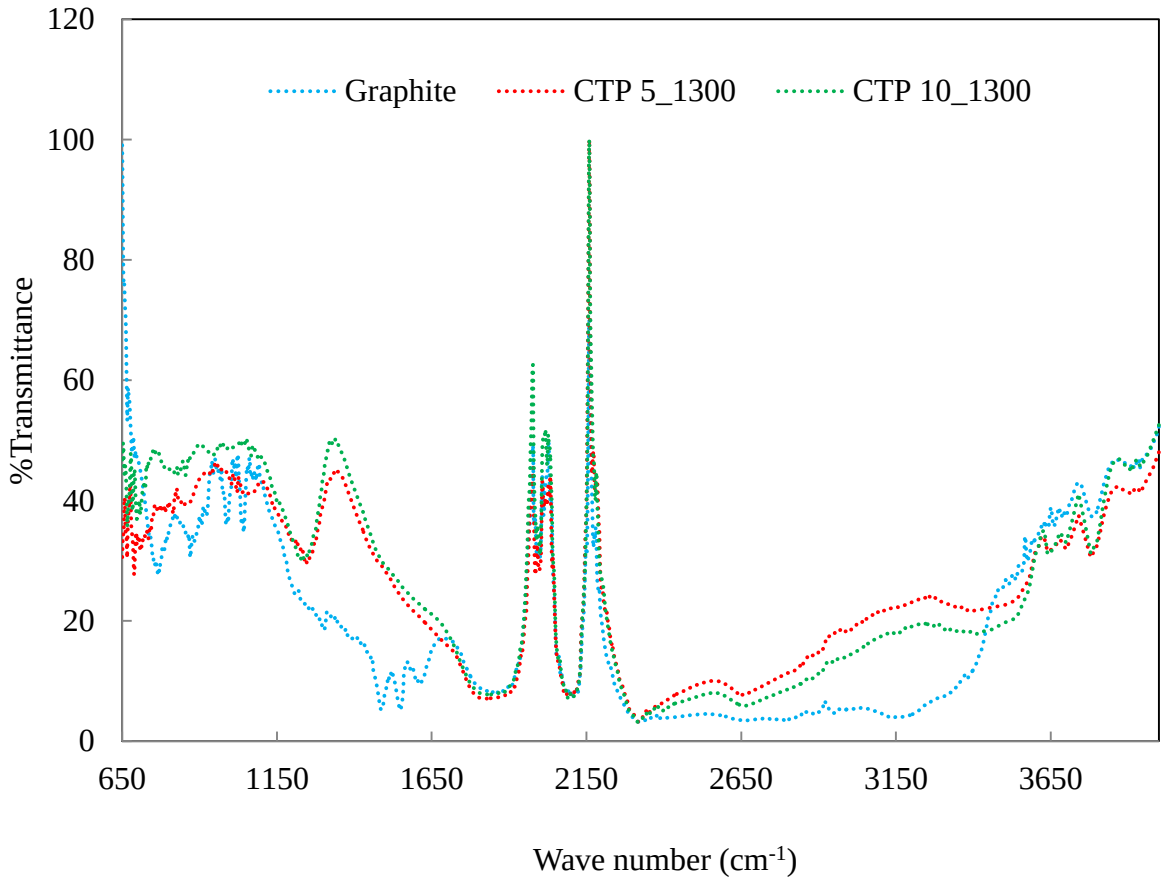

Figure 6.7 FT-IR spectra of CTP samples thermally treated at 1300 °C and prebaked electrode graphite

For the different CTP samples thermally treated at 1300 °C (Figure. 6.6), the FT-IR spectra showed a band in the region of 3498 to 3940 cm^{-1}, which was assigned to O-H bonds in samples [Guillen et al., 1992, 1995; Prauchner et al., 2001]. The peaks in the range of 2100 to 2260 cm^{-1} are reported to be due to the presence of triple bonded functional groups [Stuart, 1996] such as nitriles. The weak peak at 1597 cm^{-1} is assigned to C=O, aromatic C=C and C=C [Ibara et al.,

1989; Geng et al., 2009]. Aryl ethers and aryl oxygen are assigned to 1267 cm^{-1} [Ibara et al., 1989; McMurry, 1992; Prauchner et al., 2001; Geng et al., 2009]. The peak at 877 cm^{-1} is due to out-of-plane aromatic vibrations of C-H bonds [Guillen et al., 1992; 1995; Alcañiz-Monge., 2001; Papole et al., 2012]. Comparative FT-IR spectra of structural transformations that take place when raw CTP is thermally treated at 475, 700, 1000 and 1300 °C are presented in Figure 6.8. The FT-IR spectrum of prebaked graphite is also presented in Figure 6.8 for comparison purposes. Sample CTP 1 was selected to demonstrate the structural transitions that take place in pitch during thermal treatment at different temperatures.

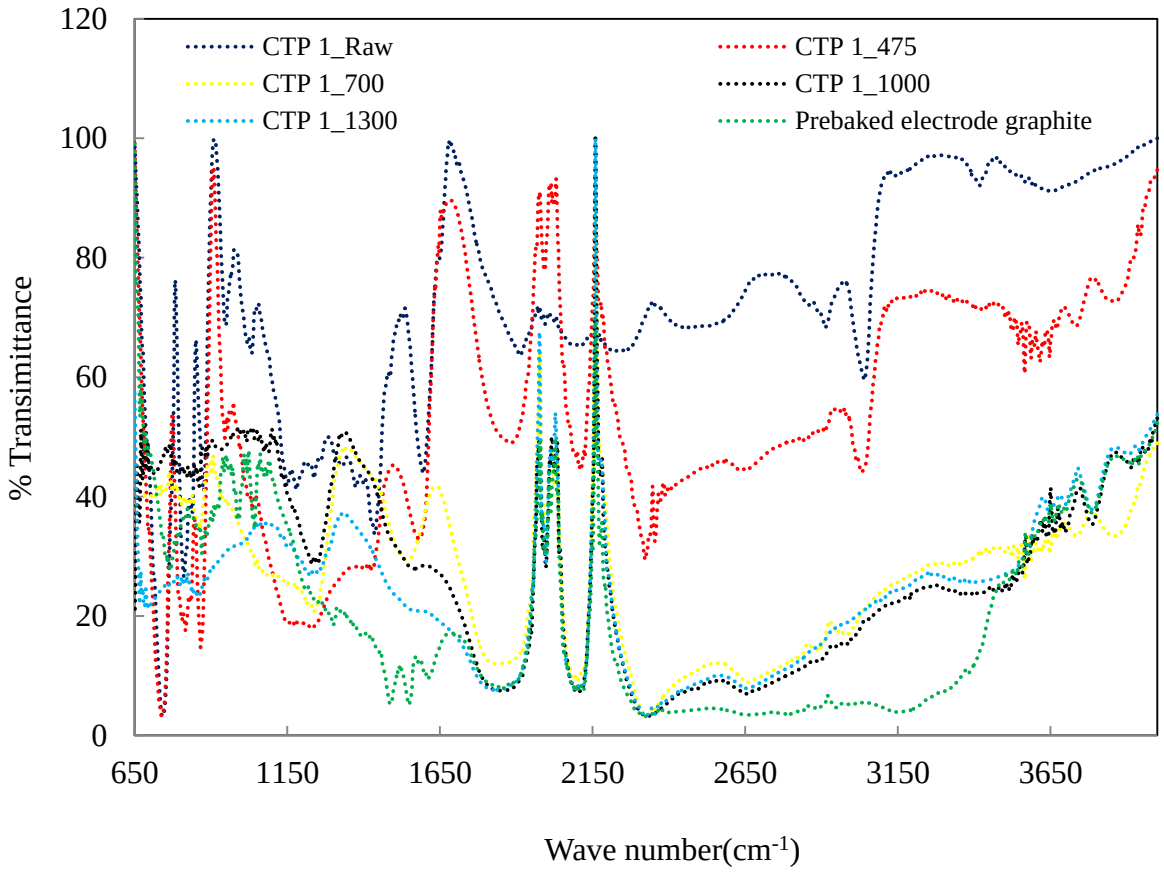

Figure 6.8 FT-IR spectra showing structural changes during thermal treatment

During the thermal treatment of CTP, there are a number of reactions that take place and these reactions lead to loss of some functional groups within the carbonaceous material [Yue and Watkinson, 1998; Alcañiz-Monge et al., 2001]. Figure 6.8 above confirms the loss of C-H aromatics, which were observed at 3000 cm^{-1}, as well as aliphatic C-H functional groups that occur between 2940 and 2835 cm^{-1}. The afore-mentioned functional groups are present in raw pitch, but they do not exist in thermally-treated samples.

6.3 XRD analysis of thermally-treated samples

In order to determine the DOG, all samples (CTP thermally-treated at 475, 1300 °C and prebaked electrode graphite) were subjected to XRD analysis as described in section 4.3.4.

6.3.1 XRD analysis of thermally-treated CTP

The XRD spectra of CTP thermally-treated at 475 and 1300 °C, as well as that of prebaked electrode graphite are presented in Figures. 6.9, 6.10 and 6.11, respectively. As can be seen, all CTP samples thermally treated are characterised by an XRD diffraction peak observed at 2Ɵ values of 20 to 40 °. A weak diffraction peak is also observed at 2Ɵ values of between 40 and 60° for samples thermally treated at 1300 °C. For the prebaked electrode graphite, the weak XRD diffraction peak is observed at 2Ɵ values in the range of 60 to 70°.

As is evident from the afore-mentioned results, the thermal treatments of CTP pitch at higher temperatures results in the structural ordering of the carbonaceous material. The DOG in carbonaceous material is an indication of crystallinity or amorphousness of the material. The degree of crystallinity of the graphitic material is indicated by the sharpness of peaks observed in the diffractogram during the analysis of the carbonaceous materials, i.e. the shaper the peak, the greater the degree of crystallinity. CTP samples thermally treated at 475 and 1300 °C all had

broader peaks at 2Θ values of 20 to 40°, if compared to the sharp peak of the prebaked electrode graphite. Although these peaks (for the CTPs thermally treated at 475 and 1300 °C) are not as sharp, they indicate partial graphitisation taking place as thermal treatment temperature increases. From section 4.2.3, it is evident that raw CTP is amorphous, but as it is subjected to thermal treatment, the crystallinity and degree of ordering are expected to increase [Hussain et al., 2000]. Ultimately, sharp and well-defined peaks are observed in the diffractogram of graphitised material, as is illustrated in the prebaked electrode graphite (Figure. 6.11).

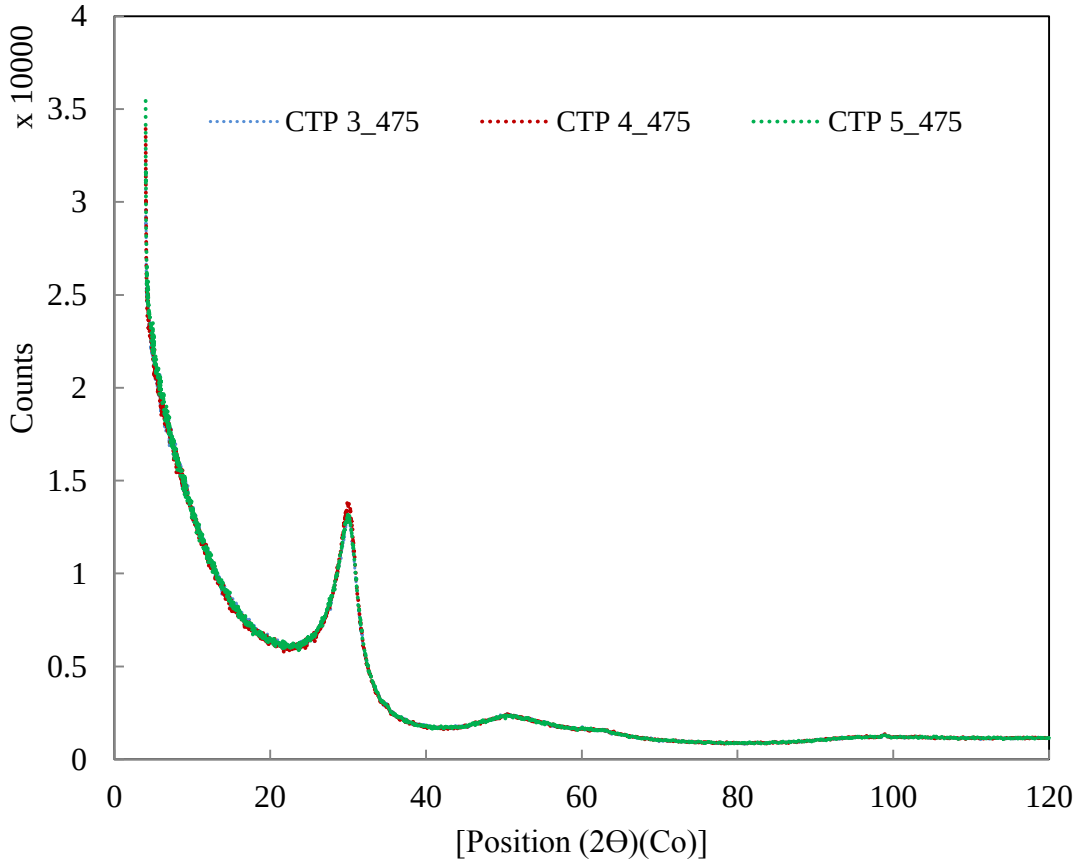

Figure 6.9 XRD diffractograms of CTP thermally treated at 475 °C

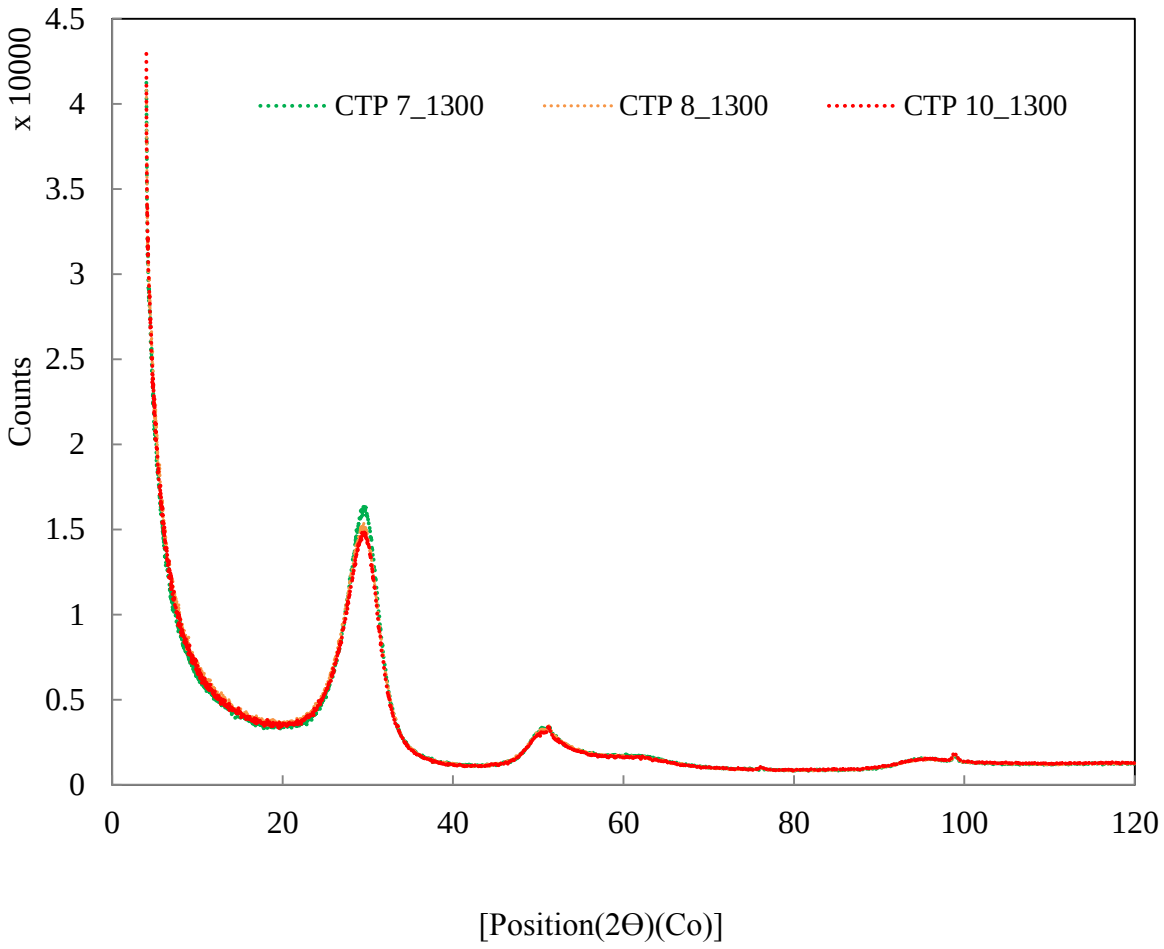

Figure 6.10 XRD diffractograms of CTP thermally treated at 1300 °C

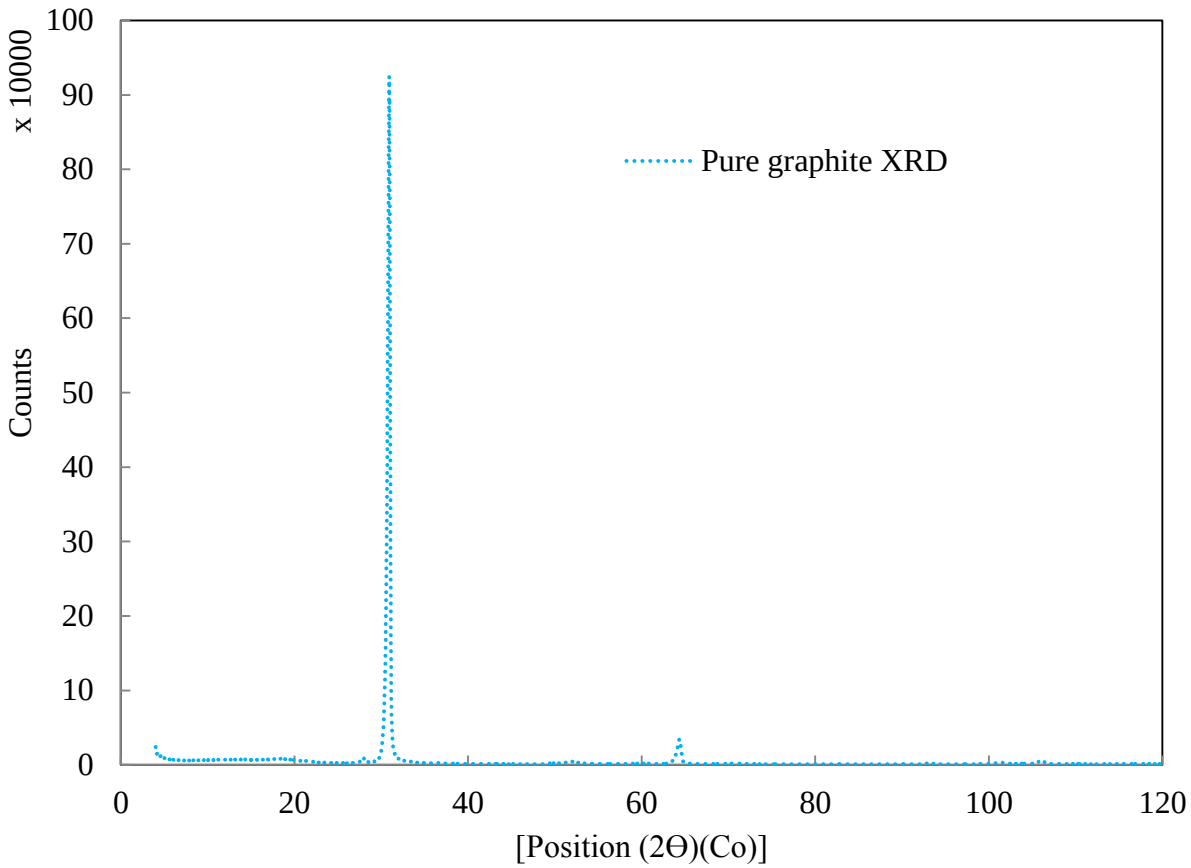

Figure 6.11 XRD diffractogram of prebaked electrode graphite

The crystallinity of the CTP material can also be evaluated by comparing the d-spacing values of raw CTP; CTP thermally treated at 1300 °C and prebaked electrode graphite. Table 6.2 below shows the different d-spacings for these three different materials.

Table 6.2 XRD d-spacing of raw and thermally treated CTP as well as prebaked graphite electrode

Sample identity	d-spacing (Å) raw CTP	d-spacing (Å) CTP thermally treated at 1300 °C	d- spacing (Å) Prebaked electrode graphite
CTP 1	3.68	3.51	
CTP 2	3.71	3.51	
CTP 3	3.78	3.51	
CTP 4	3.71	3.51	
CTP 5	3.69	3.51	
CTP 6	3.69	3.51	
CTP 7	3.71	3.51	
CTP 8	3.62	3.51	
CTP 9	3.72	3.51	
CTP 10	3.66	3.51	
CTP 11	3.74	3.51	
CTP 12	3.71	3.51	
Prebaked electrode graphite	-	-	3.37

From Figure 6.11, it was evident that prebaked electrode graphite has a very sharp and intense peak and a d-spacing value of 3.37 Å compared to a reported theoretical value of 3.354 Å for pure graphite, which is an indication of the high degree of ordering and high crystallinity within the graphitic material. The calculated DOG for the prebaked graphite electrode was 81%. The thermal treatment of carbonaceous materials at high temperatures leads to loss of impurities in the material. This also increases the crystallinity of the material due to the reorganisation of molecules within the structure [Hussain and Qadeer 2000].

In order to visualise the differences and transitions that take place during the thermal treatment of CTP, XRD diffractograms of raw CTP and CTP thermally treated at 475, 1300 °C and prebaked graphite were superimposed over each other, as illustrated in Figure 6.12. The differences in peak intensities are clearly shown in Figure 6.12 (b). CTP 6 was randomly chosen for this purpose. From the figure, the changes in the peak intensities as a function of increasing treatment temperature are clearly visible. This is also an indication of the graphitisation of the CTP taking place, as the treatment temperature increased.

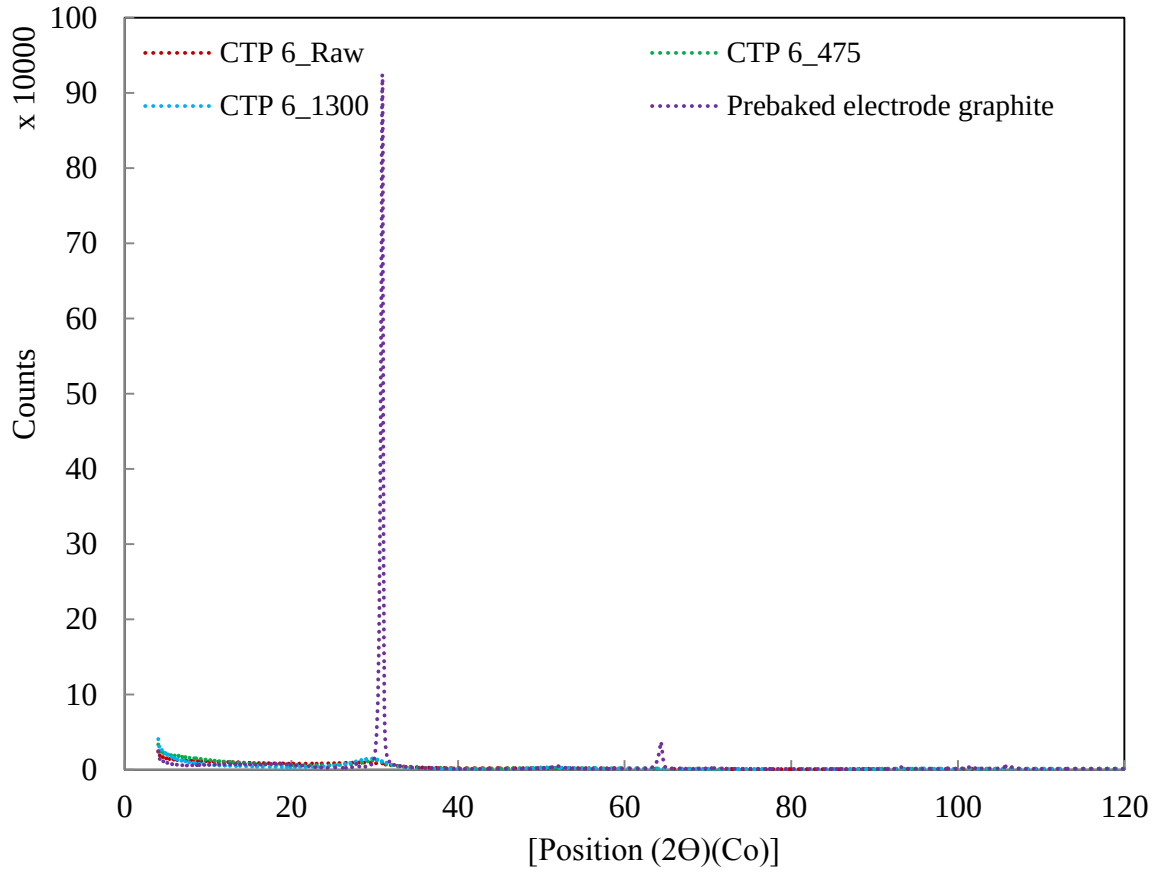

Figure 6.12 XRD diffractograms of raw pitch, pitch thermally treated at 475 and 1300 °C, as well as prebaked electrode graphite

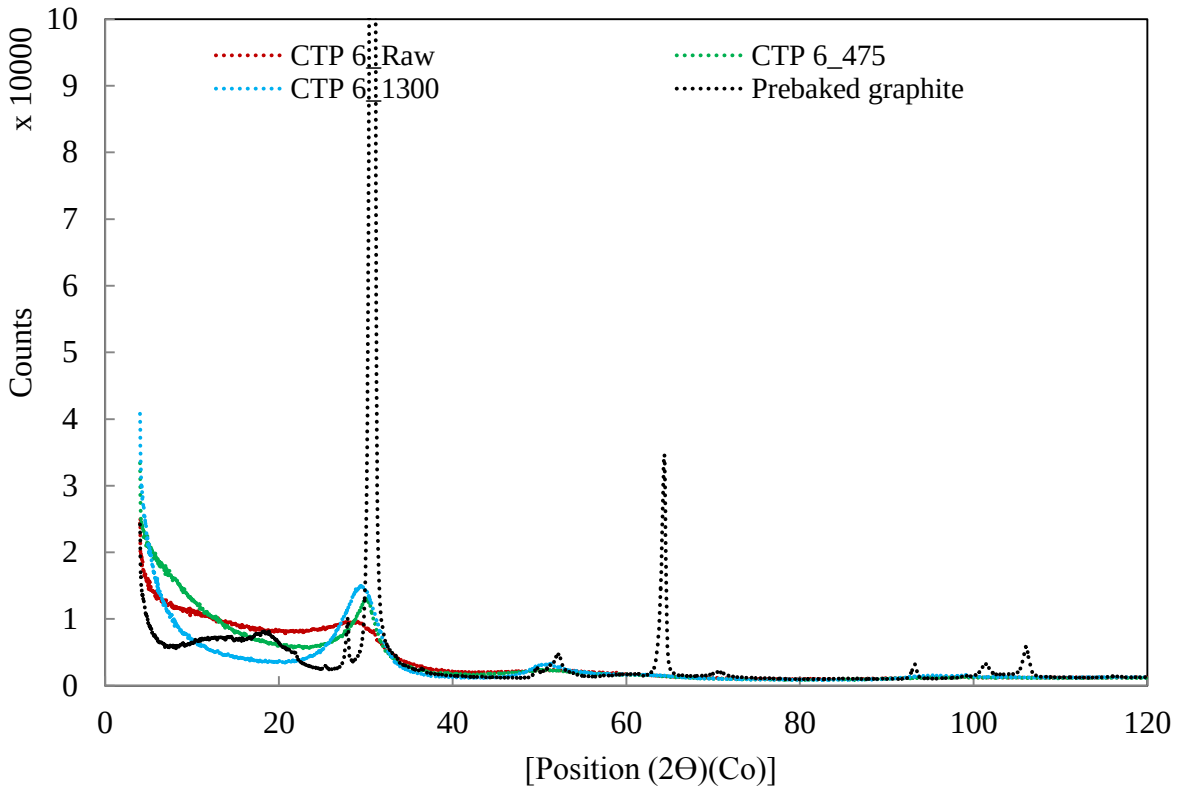

Figure 6.12 (b) XRD diffractograms of raw pitch, pitch thermally treated at 475 and 1300 °C, as well as prebaked electrode graphite (magnified)

The process of graphitisation of carbonaceous materials is temperature dependent [Feret, 1998; Manoj and Kunjomana, 2012]. The interlayer spacing (d_{002}) of graphitic materials decreases with an increase in thermal treatment temperature. The d_{002} of the prebaked electrode graphite was 3.37 Å compared to the 3.70 Å average for all CTP samples thermally treated at 1300 °C. This is supported by experimental data in Table 6.2. From Table 6.3, it can be observed that for all samples thermally treated at 1300 °C, the crystallite sizes are small (average Lc and La values are 19.8 and 15, respectively) as compared to those of prebaked graphite electrode (Lc and La values are 354 and 172, respectively)

Table 6.3 XRD lattice parameters for thermally treated CTP and prebaked electrode graphite

Sample	Lattice parameter	CTP 1300 Crystallite size (Å)
1	L_c	19
	L_a	15
2	L_c	19
	L_a	16
3	L_c	19
	L_a	14
4	L_c	20
	L_a	15
5	L_c	20
	L_a	15
6	L_c	20
	L_a	14
7	L_c	21
	L_a	15
8	L_c	20
	L_a	15
9	L_c	20
	L_a	15
10	L_c	20
	L_a	15
Prebaked electrode	L_c	354
	L_a	172

6.4 Conclusions

From the results presented in this chapter, it can be concluded that additional thermal treatment of CTP pre-treated at 475 °C resulted in significant (~12-14%) dimensional changes, as measured during the first TMA thermal cycle. However, repetitive thermal treatment, as presented by the second and third TMA cycles, resulted in very little dimensional change of approximately 2%. The observed dimensional changes are as a result of the CTP undergoing partial graphitisation in the first heating cycle. In the second and third TMA thermal cycles, there is minor additional carbonaceous structural ordering (minimal additional graphitisation) of the

material that takes place. The afore-mentioned explains the much smaller dimensional changes observed during the second and third TMA thermal cycles. The partial graphitisation of CTP was confirmed by XRD analysis performed on all samples. As the thermal treatment temperature increases, CTP is transformed from being an amorphous material to a crystalline one, as indicated by an increase in the DOG between raw pitch (-300%), pitch thermally treated at 1300 °C (-81%) and pure electrode graphite (81%) (Table 6.2 and Figures 6.11, 6.12). The changes occurring in the pitch structure, when subjected to thermal treatment, were also successfully studied by means of FT-IR analysis (Figures 6.4, 6.5, 6.6, 6.7 and 6.7).