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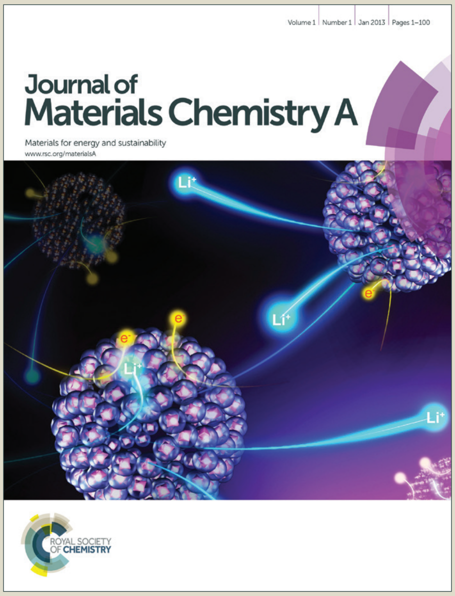

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ARTICLE TYPE

Enhancing the carbon yield of cellulose based carbon fibres with ionic liquid impregnates.

Nolene Byrne*[a] Jingyu Chen,[a] and Bronwyn Fox[a,b]

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Here we show that ionic liquids (ILs), protic or aprotic in nature containing an phosphate anion can be used as effective impregnating compounds resulting in a 50% improvement of the carbon yield of cellulose based carbon fibres and a 70° C reduction in the onset of the depolymerization temperature. Using ^{13}C NMR and FTIR we characterize the carbonized fibres with and without IL impregnates. The oxidative step in the formation of carbon fibres from cellulose precursors is very important in determining the final material properties, as such we examine this stage and show that the IL reduces the onset of the cellulose depolymerization temperature while improving the oxidative stability. This work highlights the ability for ILs to act as novel impregnates which can successfully reduce the formation of tar and volatile substances during the carbonization of cellulose based carbon fibres resulting in improved carbon yield and a significant cost savings due to reduced maintenance and wear of equipment.

Carbon fibre reinforced composites are rapidly becoming one of the leading materials to meet the light weight high strength requirements of the aerospace, automotive and sports equipment industries[1]. Carbon fibre is produced by carbonization of carbon containing precursors[2, 3]. The precursors are generally wet spun into a white precursor fibre and then undergo a series of oxidative and carbonization steps which converts the white fibre into the black carbon fibre. Commercial carbon fibre are based on rayon, polyacrylonitrile (PAN) and pitch with PAN-based fibres the most communally used precursor[2]. A major limitation associated with carbon fibre is the cost of the precursor which comprises as much as 50% of the cost of the final product. Low cost alternatives, to PAN, are currently being sought by industry with the use of cellulosic or lignin based precursors featuring as potential alternatives[4, 5]. A limitation with cellulosic based carbon fibres is the low carbon yield while the theoretical carbon yield of cellulose fibres is 44%[4]. In reality this is usually as low as 10% due to the depolymerization of the macromolecular chains and oxygen taking the carbon away as carbon monoxide, carbon dioxide or aldehydes. This compares to a carbon yield for PAN of between 50 and 55% [6, 7]. Therefore new methods to improve the carbon yield of cellulose is currently being sought [8, 9].

Here we explore, for the first time, the use of ionic liquids, ILs, as impregnate chemicals towards improving the carbon yield of cellulose based carbon fibre. The design flexibility of ILs makes these solvents a versatile class of materials[10]. Indeed ILs have themselves been shown to be excellent carbon precursors[11, 12]. Typically Impregnate chemicals are based on nitrogen, sulfur and phosphorus [9, 13] containing compounds as such we have focused our attention on the following ILs triethylammonium phosphate [TEA]H_2PO_4, triethylammonium hydrogen sulphate [TEA]HSO_4, 1-methyl imidazolium phosphate [HMIM]H_2PO_4, 1-methyl imidazolium hydrogen sulfate [HMIM]HSO_4 and cholineH_2PO_4. We also included 2 phosphonium ILs, tibutyl(ethyl)phosphonium diethylphosphate CYPHOS IL 169 and tributyl(methyl)phosphonium methylsulfate, CYPHOS IL 108 since the thermal degradation temperature of these ILs is better than the imidazolium ILs[14]. To achieve the impregnation we used a solution containing 50wt% water and 50wt% of the IL (since some of the ILs had melting points above room temperature). The cotton fibre was submerged in the IL solution for 24 hours. The excess solution was removed by pad mangle and the fibre dried at 100°C for 5 minutes. To determine what influence the IL had on the char yield the weight loss profile of the IL impregnated cellulose was measured using Thermal gravimetric analysis, TGA as shown in Figure 1.

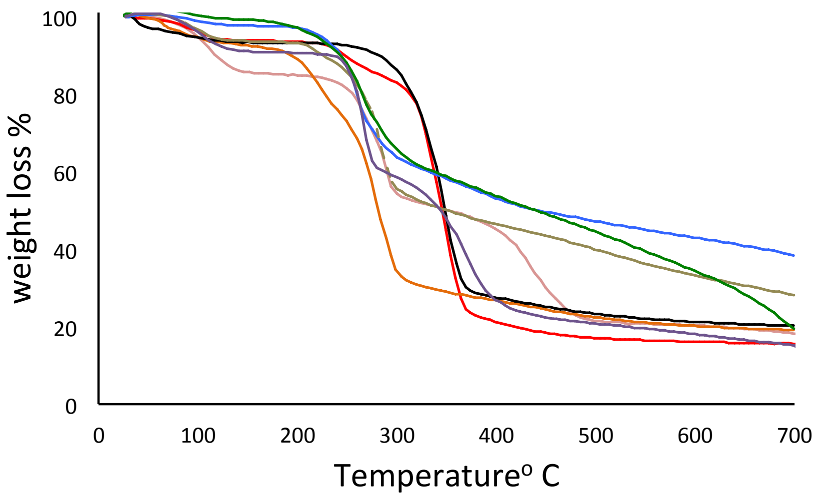

Figure 1: TGA curves for cotton impregnated with IL where [TEA]H_2PO_4 (blue), [TEA]HSO_4 (orange), [HMIM]HSO_4, (purple), [HMIM]H_2PO_4 (green), cholineH_2PO_4 (army green), CYPHOS IL 169 (pink) and CYPHOS IL 108 (red). The black line is cotton without impregnate.

Table 1: Temperature of depolymerization and carbon yield for the various samples investigated

Sample	T of decomposition (°C)	Carbon yield at 600°C (%)
As received cotton	310	26
[TEA]H_2PO_4	230	43
CholineH_2PO_4	257	33.2
[HMIM]H_2PO_4	225	34.4
[TEA]HSO_4	230	20.1
[HMIM]HSO_4	251	18.1
CYPHOS IL 169	261	20.5
CYPHOS IL 108	230	16.1

Table 1 shows the onset temperature for the depolymerization reaction of cellulose with and without the various IL impregnates[4]. The carbon yield taken as the weight loss value at 600°C is also included in Table 1[15]. It can be seen that significant improvements, up to 50%, in the carbon yield occurs with the following ILs [TEA]H_2PO_4, [HMIM]H_2PO_4 and cholineH_2PO_4, whereas the ILs with the dihydrogen sulfate anion did not perform well. The phosphonium ILs also had a null or negative effect on the carbon yield. The onset temperature for the cellulose depolymerization has been reduced in all cases with the addition of the IL. The poor carbon yield of cellulose is often linked to the formation of levoglucosan[16, 17] and the loss of oxygen containing compounds. The higher carbon yield observed for the cellulose in the presence of the phosphate ILs is likely linked to a change in the depolymerization pathway towards the formation of carbonyl and carbon-carbon compounds. It should be noted that the carbonized samples impregnated with [HMIM]HSO_4 and [TEA]HSO_4 became very brittle and fragile (see SEM images in supplementary file for fibre integrity after carbonization). The onset temperature for the depolymerization reaction was also significantly reduced in the presence of the phosphate containing ILs, for the cotton impregnated with [TEA]H_2PO_4 a reduction of 70° C this equates to a significant saving with respect to furnace temperature for the total conversion of the white precursor fibre to the black carbon fibre.

Given the significant enhancement in carbon yield of the cellulose fibres when impregnated with ILs containing the $H_2PO_4^-$ anion, we further characterized the carbonized samples which had been impregnated with [TEA]H_2PO_4, [HMIM]H_2PO_4 and cholineH_2PO_4 using FTIR and ^{13}C NMR. Figure 2 a-d shows the FTIR spectra of the cotton fibres with and without IL impregnate before and after carbonization respectively. The shared difference in the spectra before and after carbonization is the disappearance of the large OH peak at 3000 cm^{-1}, the loss of the OH peak is common for all samples and due to the dehydration caused during the depolymerisation of the cellulose. Pyrolysis of cotton is known to occur via two competitive pathways[18], the first involves the chain scissions or depolymerization caused by the evolution of oxygen containing compounds and results in low carbon yield. The second pathway involves rearrangement of the polymer chain, formation of carbonyl groups and carbon – carbon double bonds, if this second pathway is favoured higher carbon yields will result. For all samples which have been carbonized a new peak at 1730 cm^{-1} appears, this peaks represents the carbonyl group, C=O [19, 20]. It can be seen that this 1730 cm^{-1} peaks is considerably broader for all the IL samples compared with the cotton only or cotton impregnated with [TEA]HSO_4 (see Figure S2 supplementary information). This supports the TGA data, which showed the improved carbon, yield for the phosphate based ILs, suggesting that these ILs encourage pyrolysis of the cotton to occur via the second pathway,that is via polymer chain rearrangement resulting in the formation of carbonyl groups. It is likely that the IL is reacting with the hydroxyl groups on the polymer chain resulting in the rearrangement and prevent the formation of levoglucosan. An additional peak at 1107 cm^{-1} is also present in the IL samples only, this can be assigned to C-N stretching vibration[21] suggesting carbonized components of the IL is present. Figure 3a shows the ^{13}C NMR and b) the XRD spectra, of the carbonized samples impregnated with $[TEA]H_2PO_4$, $[HMIM]H_2PO_4$ and $cholineH_2PO_4$ respectively. The ^{13}C spectra for the 3 samples impregnated with the phosphate based ILs show the expected polyaromatic turbostatic carbon structure[4, 22], the broadness in the peak is due to chemical shift anisotropy effects. Little to no difference in the carbon spectra is observed for the 3 different phosphate based IL impregnated samples, since each of these ILs significantly improved the carbon yield, it is likely that the depolymerization pathway undertaken by the cellulose during the carbonization is similar for each of the phosphate IL impregnated samples, any small differences which might exist would not be seen due to the CSA present in this measurement. The XRD spectra shows two peaks are present for each of the samples a sharp peak at 24.4 degrees represents the carbon turbostatic structure [22] and an amorphous peak assigned to the original cellulose structure[23], however often an amorphous structure can be present in carbonized cellulose[22]. The XRD spectra for each sample is very similar again suggesting similar conversation rates from cellulose to carbonized carbon is not significantly different depending on IL, below we show that the temperature of the oxidation step can impact the depolymerisation temperature.

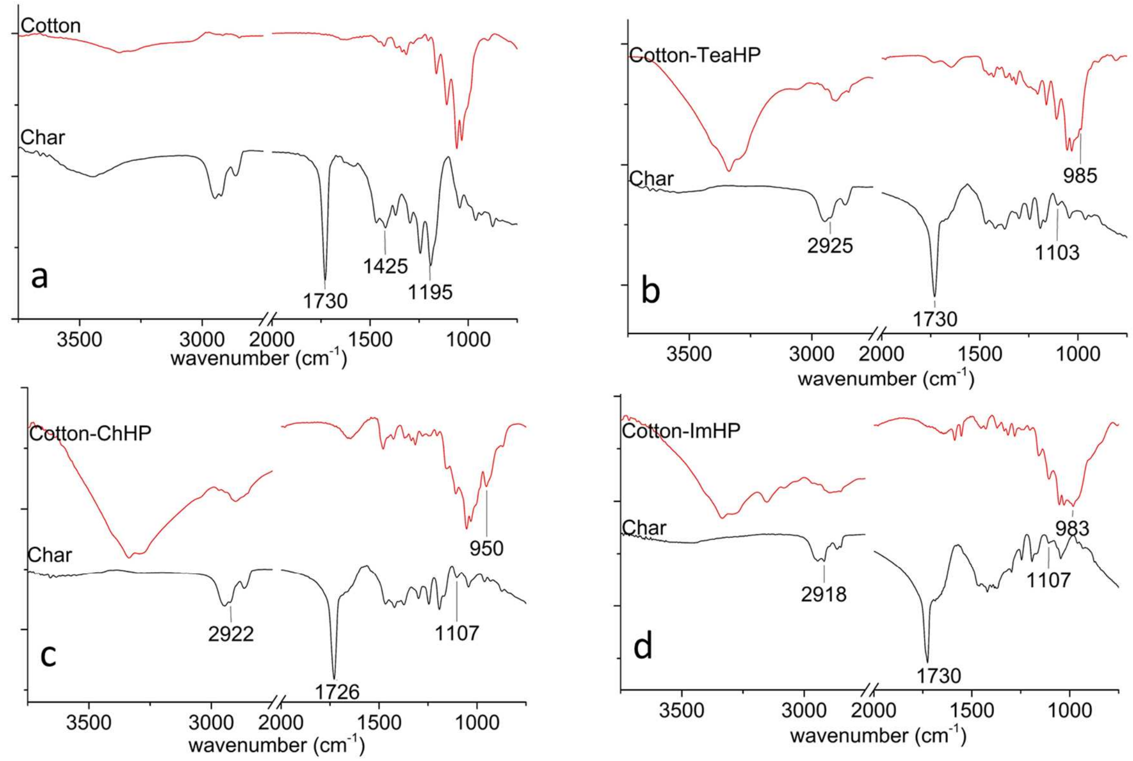

Figure 2. FTIR spectra of a) cotton without impregnates and impregnated with b) $[TEA]H_2PO_4$, c) $cholineH_2PO_4$, and d) $[HMIM]H_2PO_4$ before (red) and after pyrolysis (black).

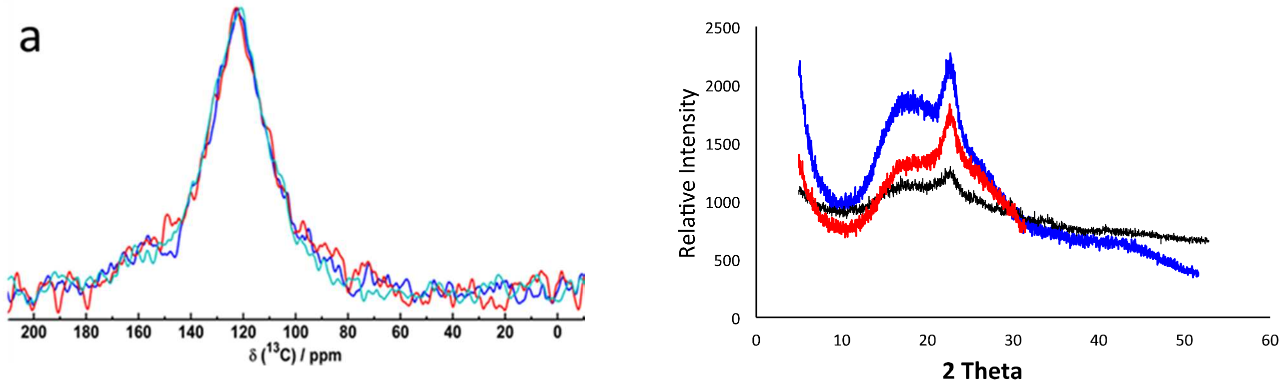

Figure 3 a) ^{13}C NMR spectra (direct) of the carbonized spectra and b) XRD spectra for the carbonized samples impregnated with [TEA]H_2PO_4 (blue) [HMIM]H_2PO_4 (red) *and cholineH_2PO_4 (green). The black curve is cotton only.*

The oxidative step in the carbonization of cellulose based carbon fibres is very important in achieving the desirable material properties indeed the carbon yield can be modified by changes in the oxidative treatments used. As such, we have examined the changes in the structure of the cellulose at varying temperatures within the oxidative region impregnated with [TEA]H_2PO_4 using FTIR and DSC shown in Figure 4. This IL was selected as it showed the greatest carbon yield according to TGA and is a synthetically simple, cheap and benign protic IL (The [choline]H_2PO_4 which improved the carbon yield by 45% is bio compatible[24], traditional most fire retardants are based on the carcinogenic formaldehyde). Figure 4a shows the FTIR spectra for the cotton impregnated with [TEA]H_2PO_4 as the oxidation temperature increases a decrease in the OH and CH regions occurs (3000-4000 cm^{-1} and 3000-2800 cm^{-1} respectively) while a new peak representing the carbonyl groups appears at 1700cm^{-1}.

The DSC of the samples oxidized at different temperatures show that the addition of the [TEA]H_2PO_4 reduces the decomposition temperature, of the cellulose, the depolymerisation temperature is shown with a * in Figure 4c. The temperature at which the depolymerisation reaction occurs for native cotton was measured to occur at around 325° C. For the cotton impregnated with [TEA]H_2PO_4 we observed a 70° C reduction of this (shown in figure 1). Here it can be seen that as the oxidation treatment temperature is increased the temperature of the depolymerisation reaction is decreased, comparing the sample oxidized at 100°C the depolymerisation reaction occurred at 230° C, whereas for the sample oxidized at 150°C the depolymerisation reaction occurred at 179° C.

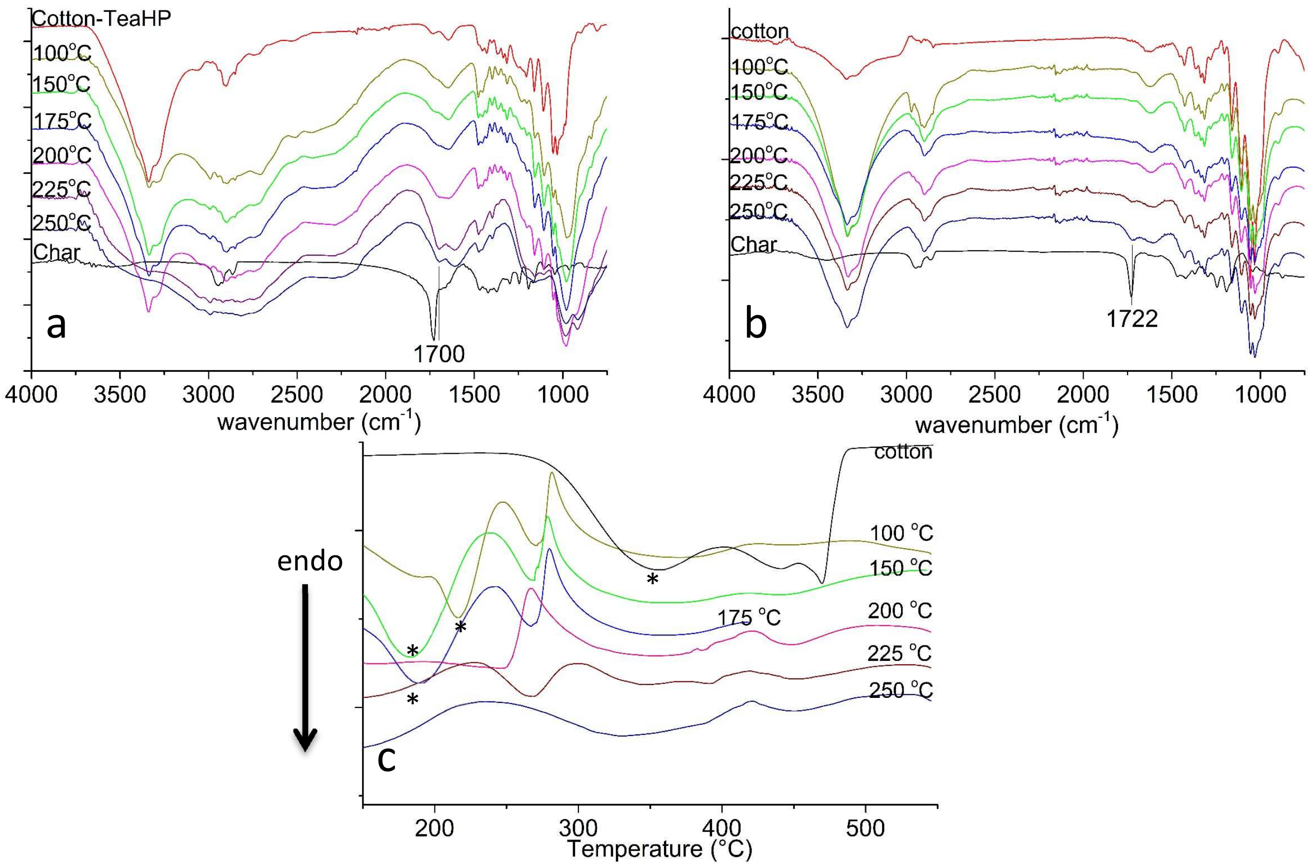

*Figure 4 FTIR of a) [Tea]H_2PO_4 impregnated samples and b) non impregnated samples. Oxidized at different temperatures as given on the graph c) DSC of the [Tea]H_2PO_4 impregnated samples oxidized at the same temperatures, black curve is cotton as received, * marks the depolymerization reaction temperature.*

Generally regenerated cellulosic fibres are preferred over the native cellulosic fibres, cotton or ramie due largely to the lower degree of orientation due to the discontinuous filament structure and the impurities which are present. Recently the use of ILs as solvents for the wet spinning of cellulosic fibres has been reported in the context of carbon fibre[25]. We show that the use of impregnates can also be applied to IL regenerated cellulosic fibres. Here the regenerated cellulosic fibres are wet spun from AMIMCl, into water[16]. Figure 5 a shows the TGA curve of the IL regenerated cellulosic fibres with and without [Tea]H_2PO_4, again a doubling in the carbon yield is measured and again the onset temperature for the depolymerization reaction is reduced.

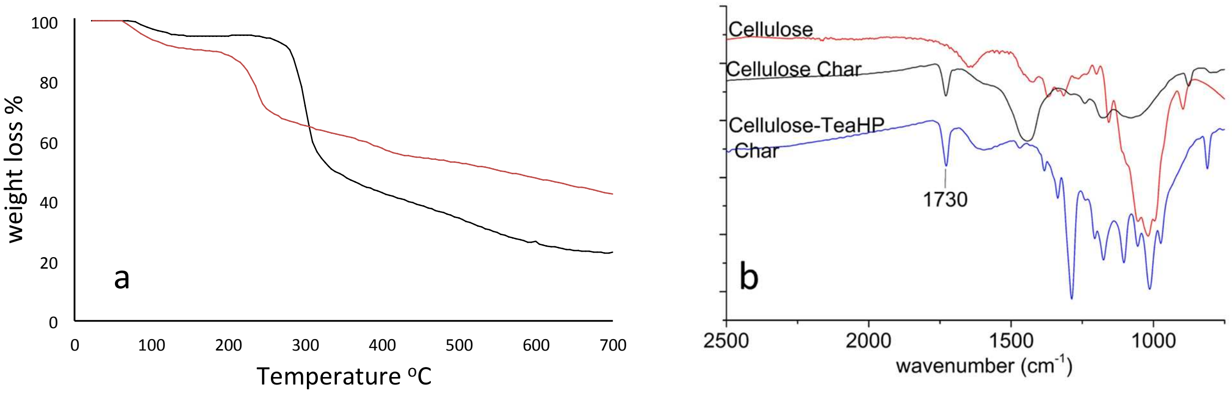

Figure 5: a) TGA curves of IL regenerated cellulose fibres with (red) and without (black) [Tea]H_2PO_4 and b) FTIR spectra of IL regenerated cellulose fibres, before carbonization, carbonized and carbonized with [Tea]H_2PO_4 impregnate.

Conclusions

A significant improvement in the carbon yield of cellulose based fibres was reported when these fibres were impregnated with ILs. This was combined with a reduction in the temperature for the depolymerization reaction by 70 degrees. We found that ILs containing the phosphate anion had the greatest effect on lowering the depolymerization temperature and improving the carbon yield. We showed that the IL, [Tea]H_2PO_4 enhanced the oxidative stability. The improvement in the carbon yield with the use of the IL impregnates is likely due to a reduction in the formation of volatile oxygen species due to a preferred reaction between the cellulose hydroxyl groups and the IL.

Notes and references

[a] *Institute for Frontier Materials, Deakin University, Geelong, Victoria 3216 Australia* [b] *Carbon Nexus, Deakin University, Geelong, Victoria, 3216, Australia*
E-mail: nolene.byrne@deakin.edu.au,

† Electronic Supplementary Information (ESI) available: [FTIR spectra]. See DOI: 10.1039/b000000x/

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Enhancing the carbon yield of cellulose based carbon fibres with ionic liquid impregnates.

Nolene Byrne*[a] Jingyu Chen, [a] and Bronwyn Fox[a,b]

We report on the use of ionic liquids as novel impregnates to enhance the carbon yield of cellulose based carbon fibres. It was found that ILs which contain a phosphate anion improved the carbon yield the most, with a 50% increase in carbon yield reported. Additional the use of the ionic liquid impregnate lowered the depolymerization temperature by 70°C this reflects a significant potential saving in the energy costs of carbonization.