EFFECTS OF INITIAL SURFACE OXYGEN LEVEL ON
POROSITY EVOLUTION & SURFACE CHEMISTRY FOR
PITCH-BASED ACTIVE CARBON FIBRES

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Introduction
Oxygen containing functionalities are part of
the overall group of so called surface sites,
which play a major role in controlling the
surface reactivity of carbon materials [1].
Since such sites influence both carbon
gasification and polar adsorptivity, they are of
interest in relation to the manufacture and final
properties of adsorbent and many other carbon
types. In this study we have produced pitch
based carbon fibres with differing surface
oxygen levels using an ozone based oxidation
treatment. We have then correlated the effect
of initial surface oxygen level with porosity
development by CO₂ activation and with
surface chemistry of the resulting carbon
fibres.

Experimental
Pitch P3200 fibres were supplied by Anshan.
The fibres have been surface oxidised using an
O₂/O₃ fluidised bed apparatus with exposure
times between 30 and 60 minutes [2,3]. Fibre
surface compositions have been investigated
by X-ray photoelectron spectroscopy (XPS)
with a Kratos 5-channel Axis instrument using
monochromated Al kα radiation (1486.6 eV) at
a residual vacuum of 1.3x10⁻⁶ Pa as in our
previous studies [4]. Fibre activation has been
carried out by a batch method using CO₂
gasification. Porosity studies have been
carried out using nitrogen adsorption at 77 K
with a Omnisorb 100CX (Coulter Electronics).

Results & Discussion.
Table 1 contains nitrogen adsorption and XPS
data for the base and activated pitch fibres.

Fibres with initial surface oxygen levels of 5
atomic % have been O₂/O₃ oxidised to give
oxygen levels of 9 and 11 atomic %. All 3
materials have then been activated in CO₂ at
1123 K for 12 hours. Nitrogen adsorption at
77 K leads to type I isotherms with the
saturation uptakes (V₀) of the oxidised
precursors being above those of the non-
oxidised base materials (Table 1 and Figure 1).
The uptakes of the 9% materials are slightly
higher than those of the 11%.

Although the total pore volumes increase with
initial surface oxygen level for activation
under the same conditions, inspection of the
low-pressure data shows that activation causes
some loss of low-pressure adsorption and
consequently the isotherms cross at p/p₀ = 2x10⁻⁵
for the 9% material and 2.5x10⁻⁵ for the 11.4%
(Figure 2). This may be due to the widening
of supermicropores by activation or pore
blocking by chemisorbed oxygen or a
combination of both of these phenomena.

Dubinin-Radushkevich analysis of the data
shows a linear plot over much of the pressure
range for the base material whilst the data for
the two oxidised materials both show positive
upturns in the higher pressure regions (log₂
p/p₀ ~5) due to pore widening (Figure 3). The
D-R data also display low-pressure negative
deviation i.e. at high log₂ p/p₀ values, which
correspond to the adsorption loss discussed
above and shown in Figure 2. This occurs
above the highest value of log₂ p₀/p shown in
Figure 3.

XPS data indicate that the levels of surface
oxygen measured post-activation for these
materials are lower than those recorded pre-
activation (i.e. post ozone oxidation). Figures
4 and 5 give respectively typical oxygen 1s
envelopes from the base and 9% materials.
Both contain peaks at binding energy values
of 532.1 eV and 533.5 eV which are due to
double bonded (C=O) and single bonded (C-
OH/C-O-C) species respectively. The spectra
show that the ozone oxidation leads to a relative increase in single bonded groups. The fibres also show low levels (∼1 atom %) of sulphur. This has an average photoelectron binding energy of 163.8 eV which equates to elemental sulphur or a sulhide species. The levels of oxygen which are residual on the activated fibres are too low to allow accurate identification of chemical shifts.

Scanning electron micrographs (Figures 6 and 7) show that the activation leads to the formation of etch pits in the pitch fibre surfaces. No pits are observed in the un-activated materials.

Conclusions
Pre-treatment of pitch fibres by O₂/O₃ oxidation leads to increased total pore volumes, compared to the un-oxidised starting material, for activation under the same conditions (CO₂/1123 K/12 hours). C-OH/C-O-C and C=O species are detected at the pitch fibre surfaces with the double bonded species more prominent on the base material and the single bonded groups most prominent after oxidation. Pitting of the surface is observed post activation.

Table 1: Chemical and physical characteristics of fibres.

<table>
<thead>
<tr>
<th>Surface Composition(XPS), atom%</th>
<th>N₂ Adsorption data</th>
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<tbody>
<tr>
<td></td>
<td>Vₒ, cm³ g⁻¹</td>
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<tr>
<td>P3200</td>
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<tr>
<td>Base</td>
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</tr>
<tr>
<td>O₂/O₃ 1</td>
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<tr>
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<tr>
<td>O₂/O₃ 2-act</td>
<td>96.4</td>
</tr>
</tbody>
</table>

References

Figure 1: Adsorption isotherms for nitrogen at 77 K on base and CO₂ activated pitch fibres

Figure 2: Low p/p⁰ data for nitrogen on pitch fibres

Figure 3: DR plots for nitrogen at 77 K on base and CO₂ activated pitch fibres

Figure 4: XPS Oxygen 1s peak envelopes from base P3200 pitch fibres
Figure 5: XPS oxygen 1s peak envelopes from O$_2$/O$_3$ oxidised P3200 pitch fibres

Figure 6: SEM of Pitch Fibre oxidised to 9\% [O]$_T$ and then CO$_2$ activated.

Figure 7: SEM of pitch fibre oxidised to 11\% [O]$_T$ and then CO$_2$ activated.