Short-Range Ordered Structure of Activated Carbons

Luca Cervini, John M. Griffin, Nathan S. Barrow
l.cervini@lancaster.ac.uk

Some structure models

Structure of porous carbons:
- carbon content > 95 % (elemental analyses)
- graphitic domains (powder X-ray diffraction)
- defects in the structure (transmission electron microscopy)
- pore walls are aromatic (nuclear magnetic resonance)

Synthesis facts:
- carbonization occurs progressively
- oxygen content reaches minimum at > 800 °C
- porosity of carbon is small
- carbon atoms are removed during activation

Using TEM only:
- single graphene-like sheets
- defects e.g. non-hexagonal rings
- no ordered region
- closed structures
- void spaces

Using TEM and PXRD:
- stacked graphene-like sheets < 5
- closed and graphitic domains also > 5
- void spaces

Using PXRD only:
- perfect graphitic domains
- up to 5 sheets
- disordered linkers
- void spaces

Combining TEM and PXRD leads to more detailed pictures but still incomplete:
- **before activation, what separates the ordered domains ?**
- **what is the exact structure of pores ?**

My new model

- Created to rationalize pore size distributions of PEEK-Derived Carbons (PDCs).
- Used to propose and predict activation mechanisms.

Scheme of the graphite-like domains, the sheets contain defects

Packing mode of the graphite-like domains

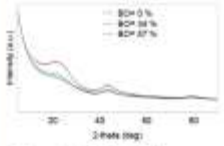
- ordered domains made of distorted graphite-like structures with up to 4 sheets,
- disordered domains made of very distorted sheets,
- before activation, all gaps between the ordered domains are filled with disordered domains because the initial porosity is very small.

- etching of sheets proceeds from the edges inwards,
- little rearrangement of the structure at moderate burn-offs.

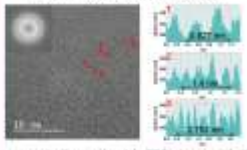
- pore sizes obtained increase step-wise as multiples of the interlayer distance, and can be incremented by one interdomain distance,
- the pore size distribution depends on the probability of etching of adjacent sheets.

Characterization of 900 °C Steam-Activated Samples

Powder X-Ray Diffraction

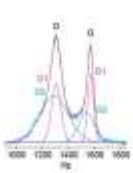


Transmission Electron Microscopy



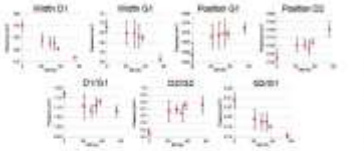
In agreement with several models, PDCs show graphite-like domains made of few distorted sheets, and some proportion of disordered domains unidentifiable by TEM or PXRD

Raman Spectroscopy

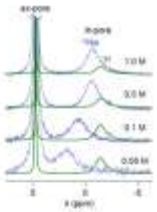


- Typical G and D bands are evidence for sp2-sized graphitic domains (G) with defects (D).
- Good fit using two components,
- 1: sharp --> ordered, graphite-like domain,
- 2: broad --> least ordered domain.

- Width, position and ratio of bands depend on the size of the sp2 domains,
- During steam activation, both domains are etched, and
- The proportion of disordered material decreases.



Nuclear Magnetic Resonance

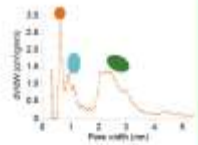


Carbon with BDH 36 % saturated with NaCl

- Only one in-pore peak: water diffuses fast between all types of pores, and particle is homogeneously activated.

- NICS of ^{23}Na decreases with [NaCl].
- [Na$^+$] is smaller in smaller pores: spontaneous desalination.

Gas Adsorption



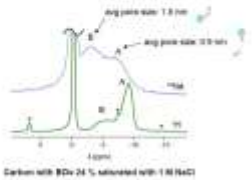
- Quantachrome Instruments,
- Nitrogen gas at 77 K,
- QSDFT Slit/cylindrical pores

- With increasing activation time, the volume of each pore increases,

- The sizes are however discrete values and do not increase continuously or beyond 3-4 nm,

- This suggests these pores are found in an ordered structure.

700 °C Activation



Carbon with BDH 24 % saturated with 1 M NaCl

- Peaks A and B correspond to spatially distinct pore networks,
- Each network has various pore sizes in close proximity (exchange-averaged into A or B),
- Water diffuses slowly between A and B.

- [Na$^+$] is much higher in B than A, as we previously observed.

Activation Mechanism

Macroscopic length scale, ~ 0.1 - 100 um

- At 900 °C, mesopores are present throughout the particle,
- Solvents diffuse quickly between meso- and micropores: 1 peak in NMR.

- At 700 °C, mesopores are more scarce,
- Some micropores are too far away from mesopores: 2 peaks in NMR.

Microscopic length scale, ~ 0.1 - 10 nm

- Similar mechanism at 900 and 700 °C,
- Ordered and disordered domains are etched simultaneously,
- At 700 °C, metastable oxydation debris decrease the apparent pore sizes,
- The etching process depends on the activating agents.

Conclusion and Outlook

- In activated carbons, pores have a slit-like geometry and possess defined sizes,

- Regions of the pore network with small average sizes take up less ions,

- New 2D material for water desalination ?
  - only subnanometre pores sizes
  - hydrophobic pore walls
  - open-ended pores for membrane

e.g. expanded graphite, or similar graphene oxide framework