Versatile Adsorption Processes for the Capture of Carbon Dioxide from Industrial Sources - FlexICCS

1/9/2016 – 31/08/2019 £1,072,672

EPSRC
Engineering and Physical Sciences Research Council

Engineering

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Carbon Nanotube / PVA Composite Aerogels for CO_2 Capture

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Previous Related EPSRC Projects

Adsorption Materials and Processes for Carbon Capture from Gas-Fired Power Plants – AMPGas
Brandani (PI), Campbell, Ahn, Ferrari, Wright, Yui
2012-2016 £1,111,261

Nanotubes for Carbon Capture
Campbell (PI), Brandani, Donaldson, Shackley, Winskel
2011-2012 £246,761

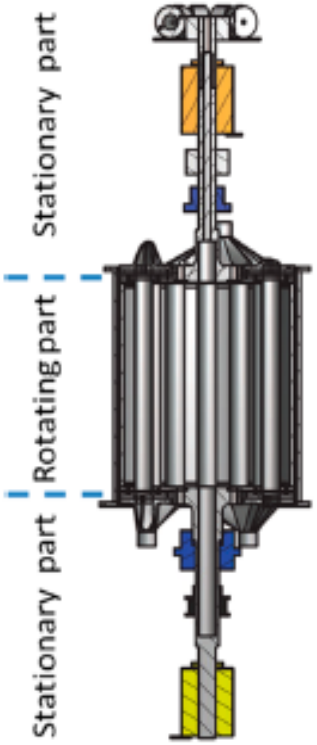
Development of an efficient carbon-based material to use in a small-scale CO_2 capture system suitable for gas power stations or small to medium sized industrial plants

Concentration of CO_2 in the flue gas is typically low, ca. 4%

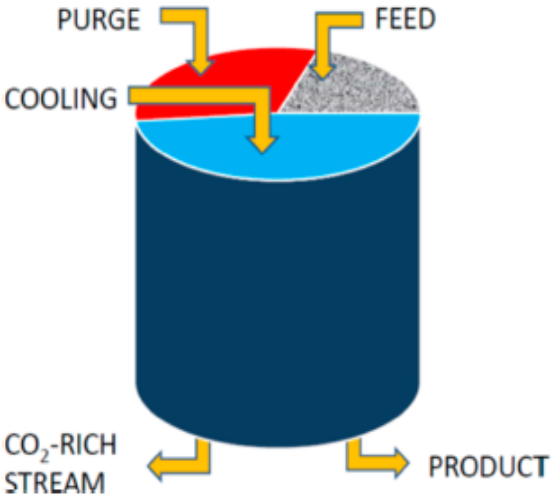
→ Need an adsorbent that is highly selective at low partial pressures of CO_2

Large volumes of gas

→ Need a short cycle time to reduce size and cost of capture plant



Rotary Wheel Adsorber



S.Brandani

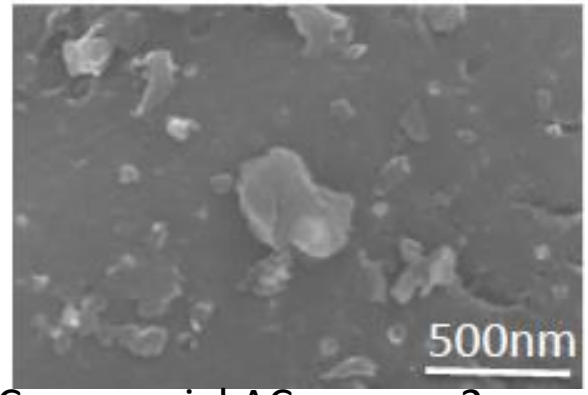
Need material with

- High and specific CO_2 uptake capacity
- good thermal conductivity (for a thermal swing adsorption process)
- ability to heat via ohmic heating
- Stability towards H_2O

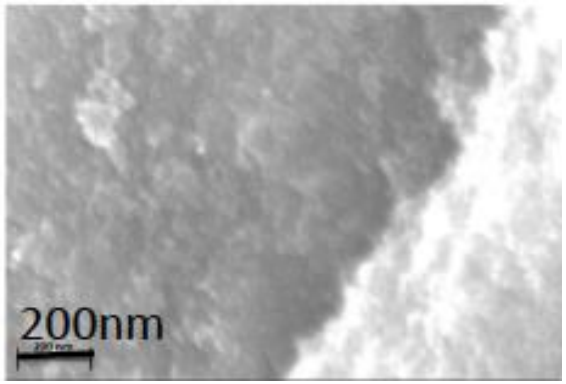
→ Functionalized porous carbon

Ind. & Eng. Chem. Res.**55** (2016) 3840

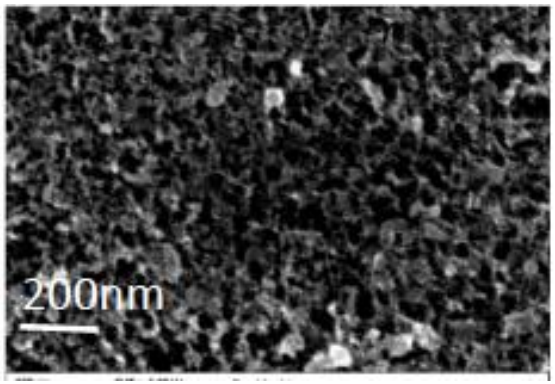
Activated carbon as the container for liquid amine – optimisation of pore size



Commercial AC, pores <2nm

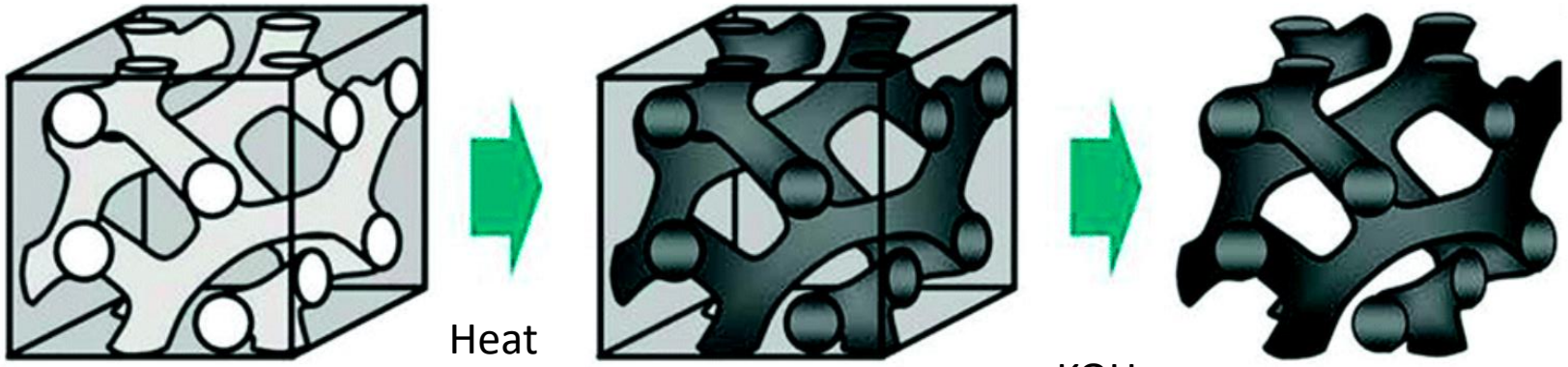


Meso-AC, pores 4-10 nm



Meso-AC, pores 5-30 nm

Meso-AC synthesised using silicagel templates



Silica gel
Sucrose
H_2SO_4

Heat
Anneal in Ar

Caramel-like
Carbon/silica composite

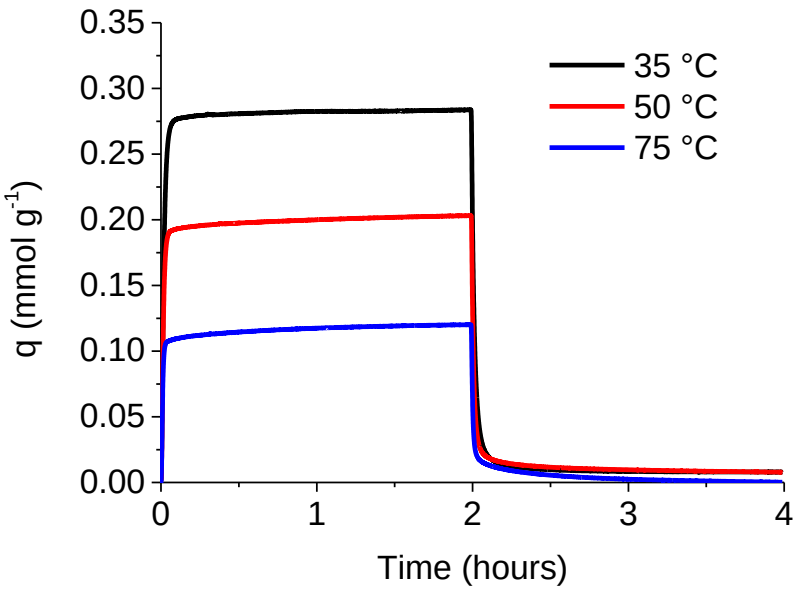
KOH

Mesoporous
carbon

Gibson et al.,Micropor. & Mesopor. Mat. **208** (2015) 129

CO_2 Uptake Microporous-AC (pore width 2 nm), 0.1 bar CO_2

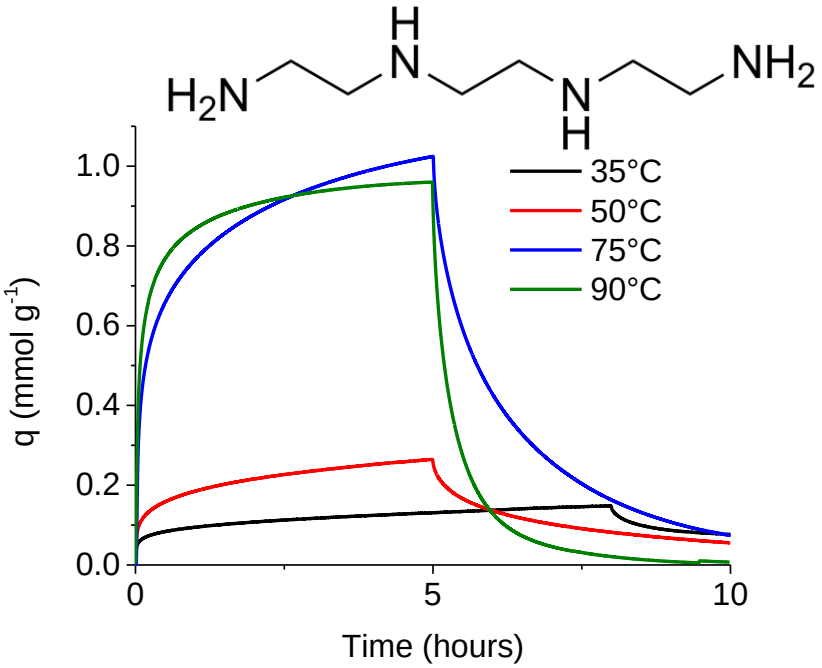
Calgon AC (unmodified)



Physisorption
ΔH_{ads} -27 kJ/mol

- Microporous carbon
- CO_2 capacity ↓ as temperature ↑

Calgon AC-TETA(100:50 w/w)

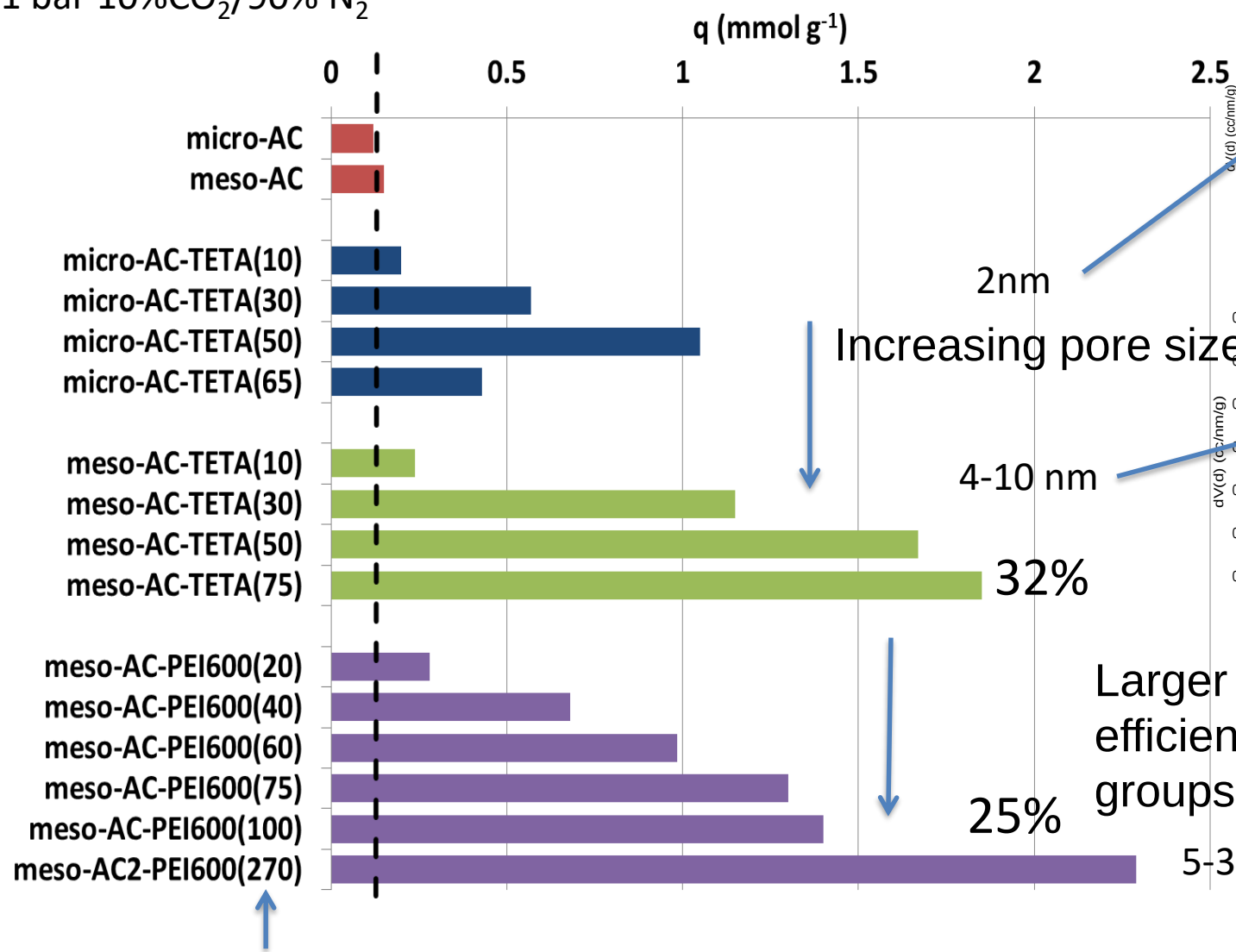


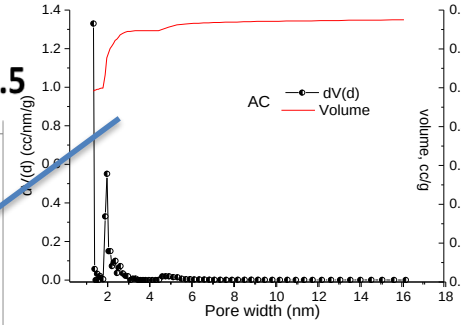
Chemisorption
ΔH_{ads} -90 kJ/mol

- Microporous carbon impregnated with triethylenetetramine (TETA)
- CO_2 capacity ↑ as temperature ↑

AMPGas

1 bar 10%CO_2/90% N_2

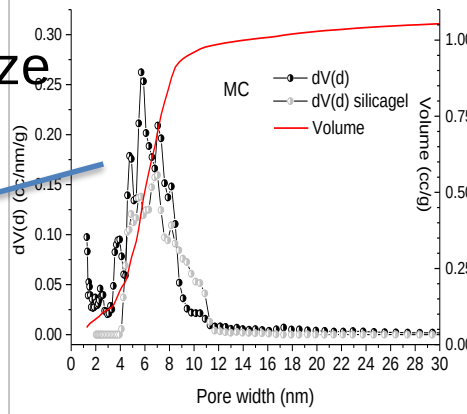




2nm

Increasing pore size

4-10 nm



32%

25%

Larger amine – less efficient use of amine groups but nonvolatile

5-30 nm pores

Weight of amine: 100 weight carbon in support

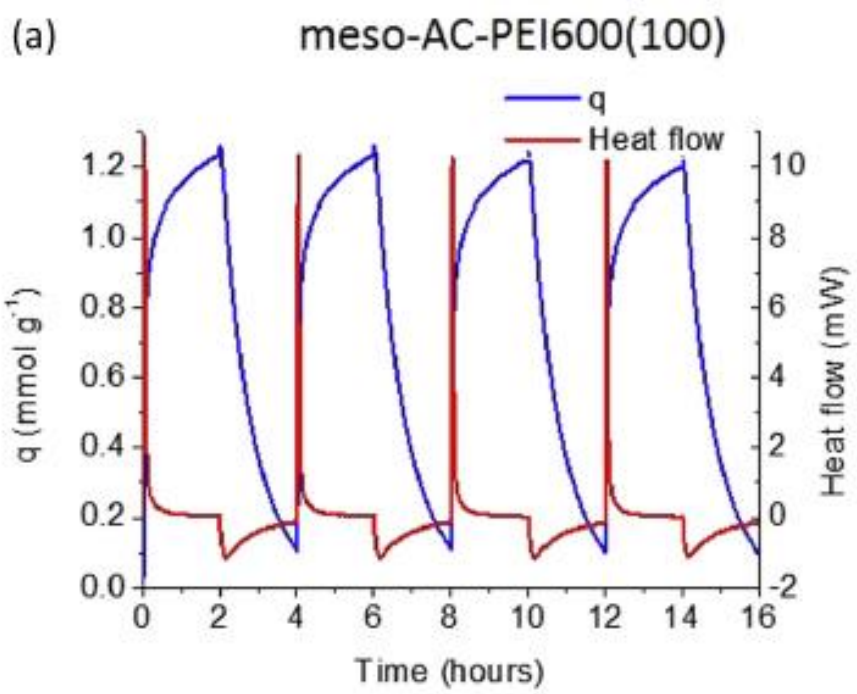
The larger pore-size material combined with high molecular weight polyimine is already a viable material for use in the RWA

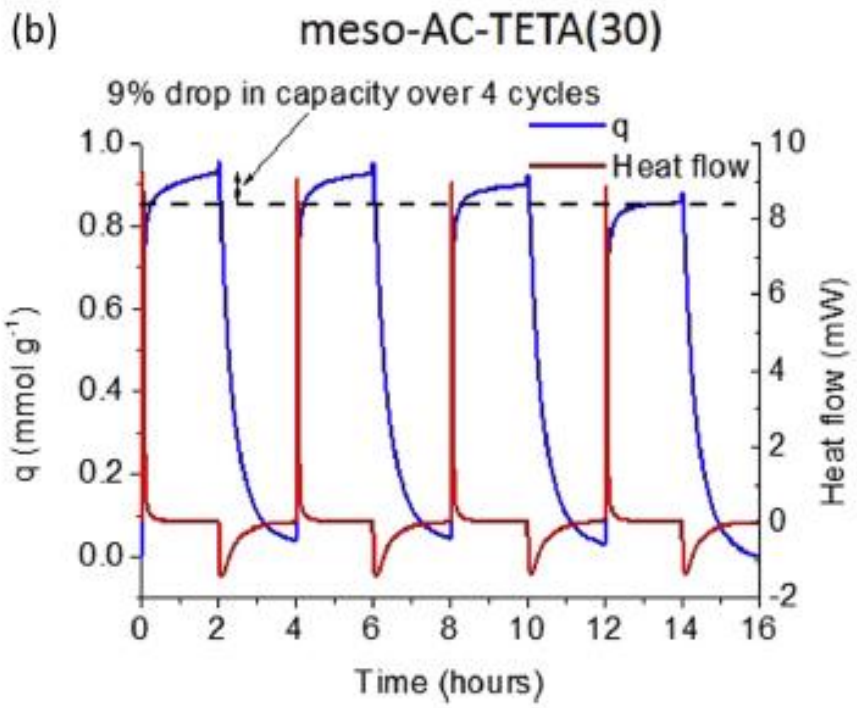
AMPGas

Micropor. & Mesopor. Mat. **208** (2015) 129

Stability over multiple cycles:

Loss of TETA from pores but PEI remains stable over many cycles. However kinetics of adsorption/desorption poorer for PEI





Increase Pore Size - Aerogel Formation

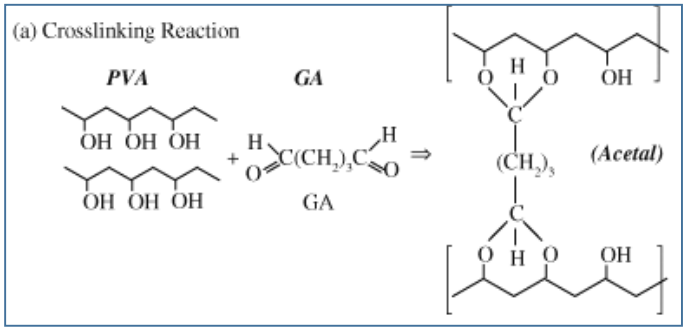
oxidised MWCNT powder

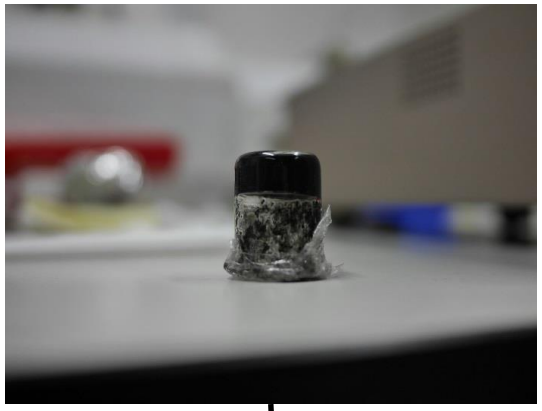
PVA aq. solution

sonication

Dilution with water to a desired volume (usually 4mg CNT/ml and 4-12 mg PVA/ml); + crosslinking agent

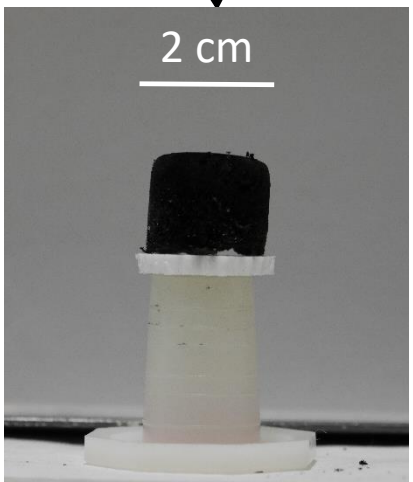
gelation



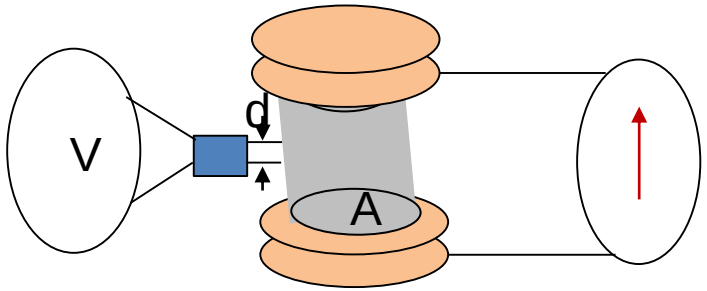


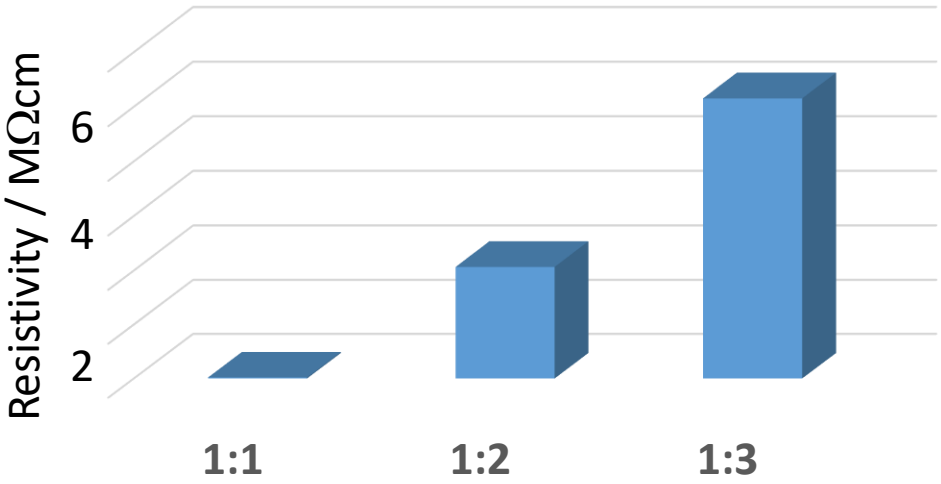
Lyophilisation (freeze-drying)

CNT/PVA ratio (wt/wt):
1:1 1:2 1:3
Aerogel densities:
<10 – 30 mg/cm^3
Available pore volume:
>40 cm^3/g
(ca. 3 cm^3/g for porous carbon)



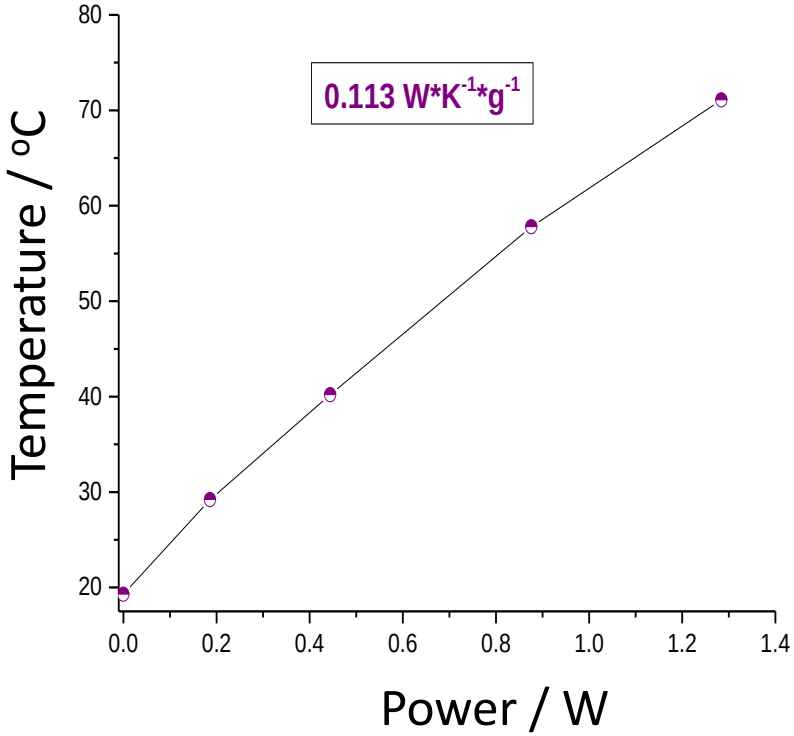
Resistivity Measurements & Ohmic Heating





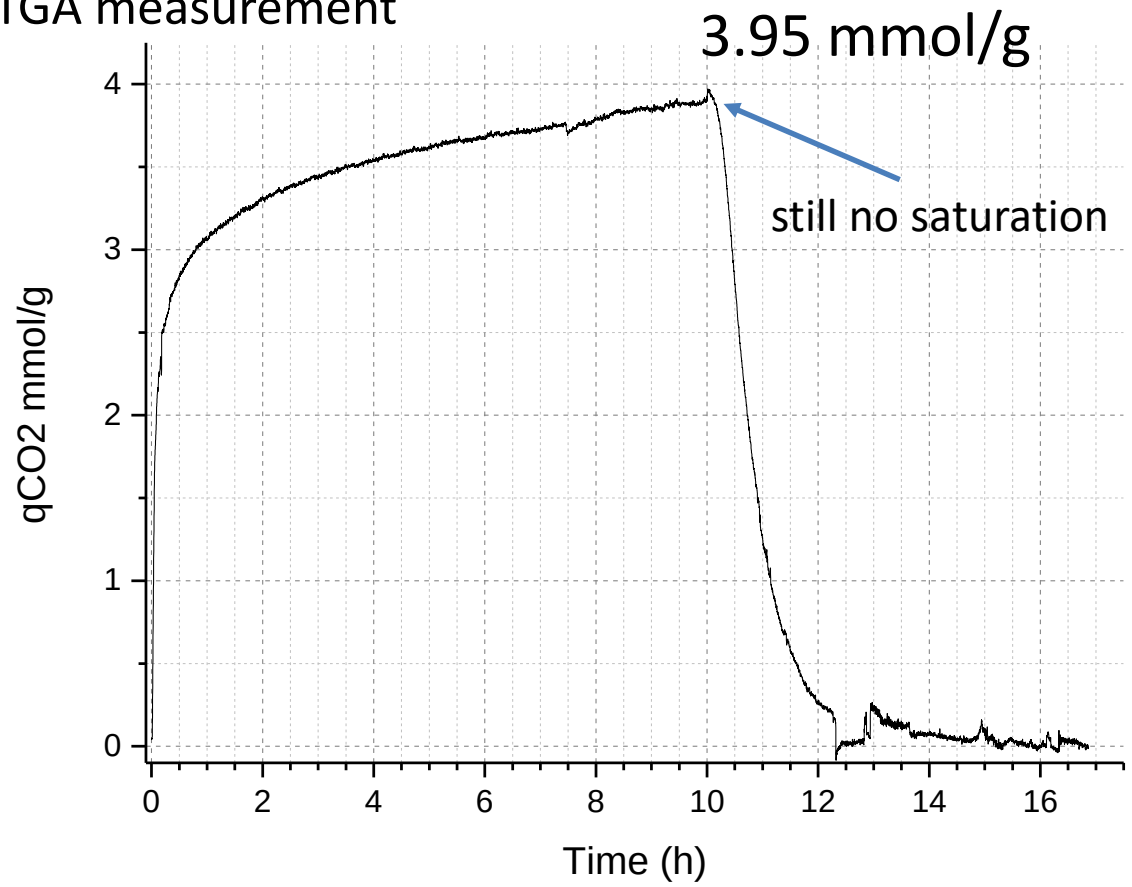
CNT/PVA wt	1:1	1:2	1:3
ρ, MΩ*cm	0.02	2.06	5.15
density, mg/cm³	12	22	32

CNT:PVA 1:2
Impregnated with 5.5 PEI-600



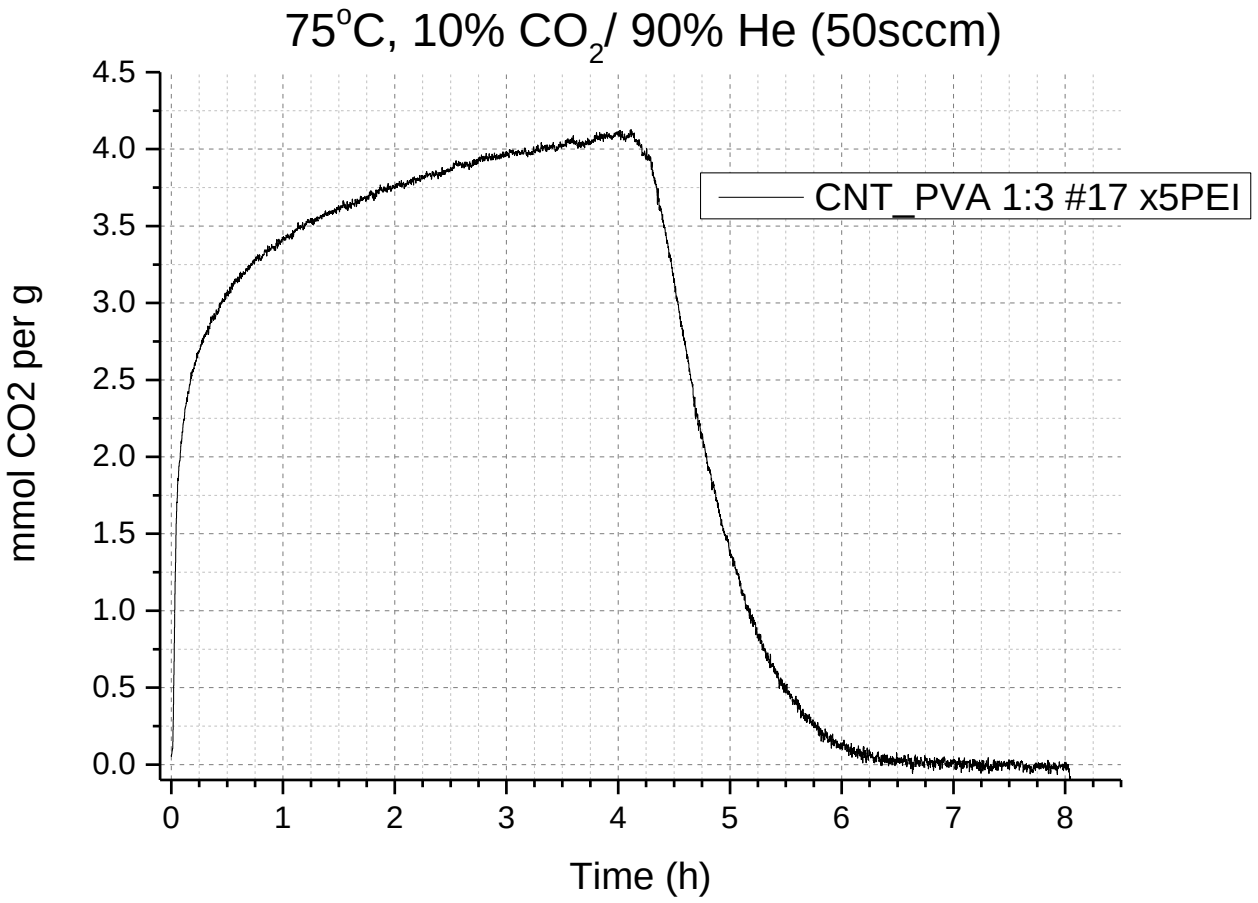
CNT:PVA 1:1 + 5 PEI 0.1bar (dry) CO_2 75°C

TGA measurement



5 PEI	Av. Uptake @ 4 hrs
1:1	3.2±0.2 mmol/g
1:2	2.6 ±0.4 mmol/g
1:3	2.6 ±0.4 mmol/g

Max. theoretical CO_2 uptake (dry conditions) for material containing 83 % wt PEI should be equal to 10 mmol/g;



Fast initial rise – reaction with surface amine groups

Slow increase: slow diffusion of CO_2 through amine

1:3 material

> 4 mmol/g (compared to 2.6) after 4 hours (water impurity)

Comparison with other carbon-based chemisorption materials in the literature

CNT:PVA	PEI modified	4 mmolg^{-1} at 75^{o}C and 0.1 bar
Commercial carbon	PEI modified	3.5 mmol g^{-1} at 75 °C and 1 bar
Nanoporous carbon	PEI modified	1.09 mmol g^{-1} at 75 °C, 1 bar
Mesoporous carbons	PEI modified	4.82 mmol g^{-1} at 75 °C, 1 bar
Activated carbons	TREN, TETA modified	1.96 mmol g^{-1} at 25 °C, 1 bar
MWCNTs	APTES modified	1.7 mmol g^{-1} at 60 °C, 1 bar
MWCNTs	PANI modified	11.7 mmol g^{-1} at 25 °C, 11 bar
Phenolic-resin-derived carbon	Oxidation	2.9 mmol g^{-1}at 25 °C, 1 bar
Carbon nanofibers	Oxyfluorination	3.68 mmol g^{-1} at 0 °C and 1 bar
Porous carbon	Loaded CuO	0.30 mmol g^{-1} at 25 °C and 1 bar
Activated carbon	Loaded NiO	2.23 mmol g^{-1} at 25 °C, 1 bar
MWCNTs/MIL-101	Nil	1.35 mmol g^{-1} at 25 °C, 10 bar
CNTs/phenolic resin	Nil	1.2 mmol g^{-1} at 25 °C, 1.5 bar
CNTs/ACF	PEI modified	2.75 mmol g^{-1} at 60 °C, 1 bar
Mesoporous carbon nitrides	Nil	2.35 mmol g^{-1} at 25 °C, 1 bar

Wang, J., L. Huang, et al. (2014). "Recent advances in solid sorbents for CO2 capture and new development trends." Energy & Environmental Science **7**(11): 3478-3518.

Conclusion

Porous carbons impregnated with liquid amines have properties that make them favourable for capture processes from dilute gas streams - but large amines block small pores

CNT/PVA aerogels impregnated with PEI show CO_2 uptake of ca. 4 mmol/g at 0.1 bar (comparable to best alternative materials)

- Stable in water (improved performance)
- High selectivity
- Possible to rapidly heat using electrical swing
- Mechanically stable
- Monolithic form

BUT: slow CO_2 diffusion through amine