Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information (ESI)

Increased efficiency of CO_2 capture using linear amine polymer coated carbon nanotube materials: stability under humid conditions

Z. Zhou[a], C. M. Anderson,[a] S.K. Butler[a], S. Thompson[b], K.J. Whitty[b], T.C. Shen[c], and K.J. Stowers[a†]

[a] *Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602, USA*

[b] *Department of Chemical Engineering, University of Utah, Salt Lake City UT 84112, USA*

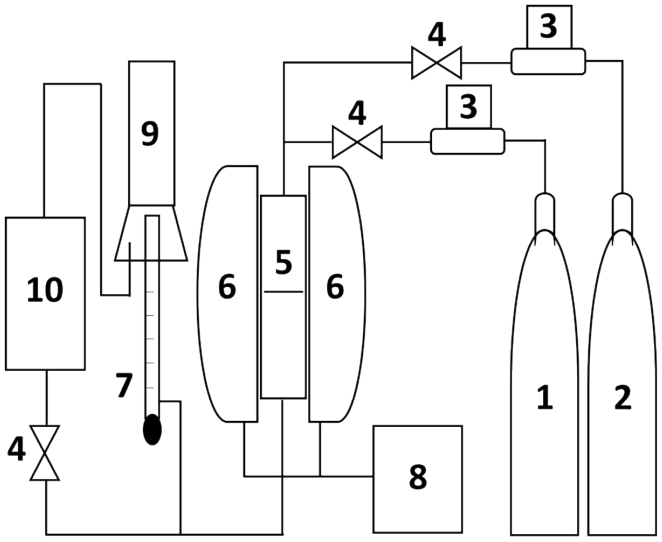
[c] *Department of Physics, Utah State University, Logan UT 84322, USA*

[†] ***Corresponding author:*** *K.J. Stowers, Email: kstowers@chem.byu.edu, Tel: +1-801-422-0835*

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Table of Contents

S1. Flow Reactor design



1: Nitrogen 2: Carbon dioxide 3: Mass flow controller 4: Valve
5: Column flow reactor 6: Furnace 7: Manual bubble flow meter
8: Temperature control 9: Exhaust 10: Mass spectrometer

Fig. S1. Flow reactor system design and details for CO_2 adsorption

S2. Material synthesis

The solubility differences of the two polymers create the need for a different method for impregnation. BPEI can dissolve in cold ethanol in a short time (< 5 min). However, LPEI is much slower (>20 min) and must be pretreated with a sonicator before heating at 40 °C. This difference in solubility stems from the difference in molecular weight of LPEI (Mn = 2500) that is higher than BPEI (Mn = 600), making it even more difficult to dissolve in polar solvents. During the evaporating process, solvents must not evaporate too fast because PEI is very viscous and will stick to the sidewalls of the beaker and cause the inefficient amine loadings. In order to improve the loading and distribution of PEI on the CNT, the size of beaker should also be carefully chosen. Oversized beaker provides too large basal area to be covered by CNT, the rest will be covered by PEI instead and thus lower the PEI loading. In turn, the beaker with too small basal area causes an increase of height of CNT and thus decreases the homogeneity of distribution of PEI.

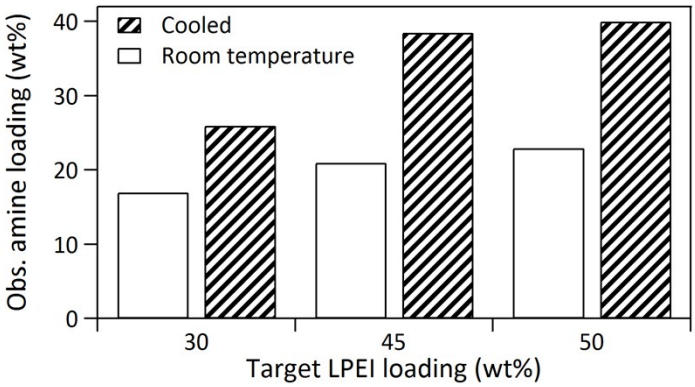


Fig. S2 The impact of cooling stage on the observed PEI loadings. PEI loadings from the TGA increased because cooled amine is easily recovered from glassware.

S3. Materials Characterization

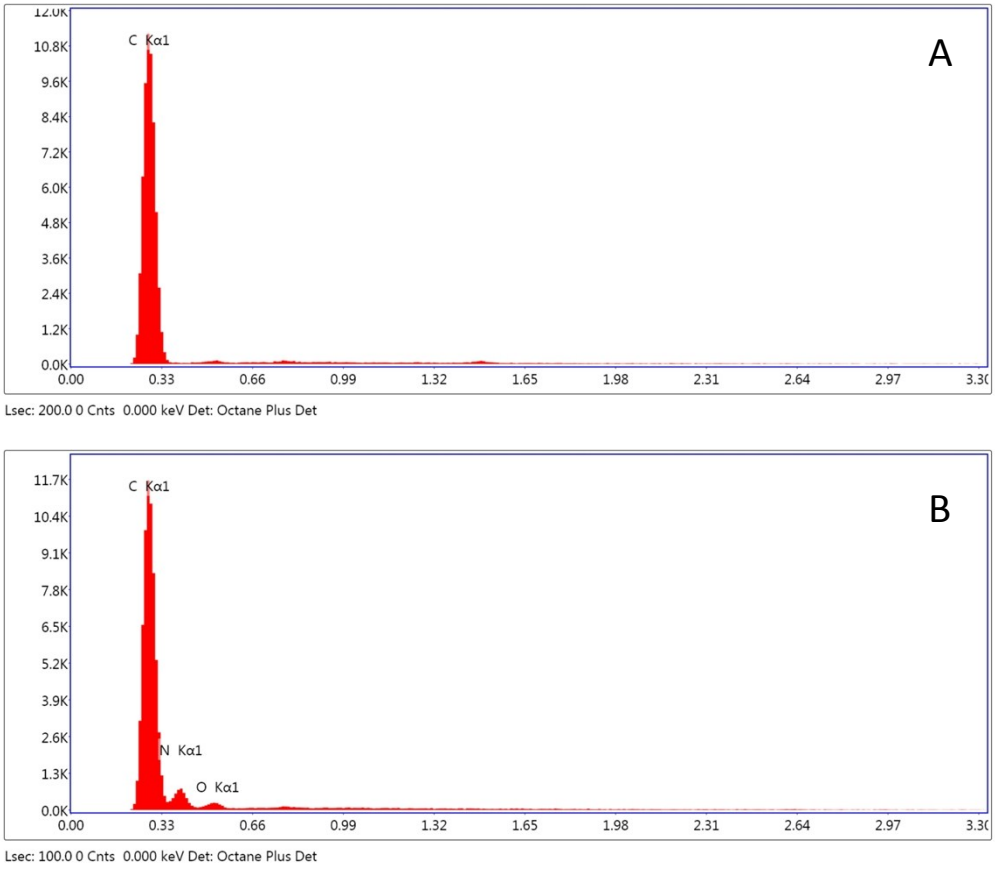


Fig. S3. EDX of A) CNT control and B) CNT-40 wt%LPEI

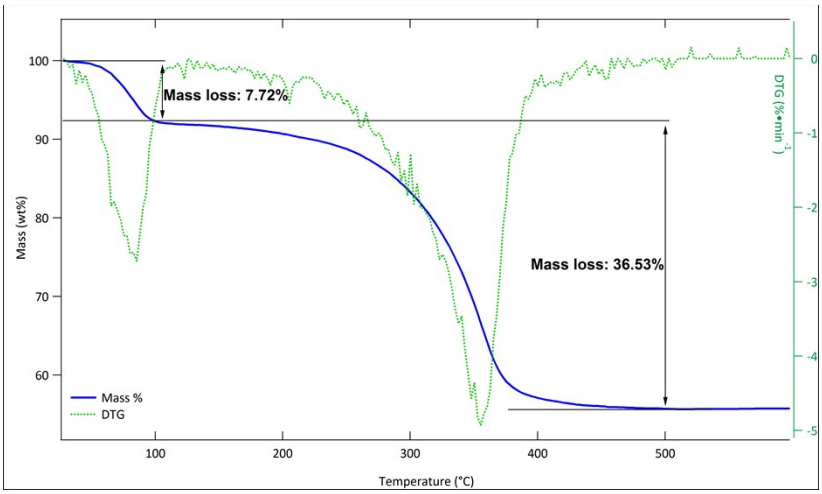


Fig. S4. TGA-DTG profile of TGA profile of CNT-40%LPEI.

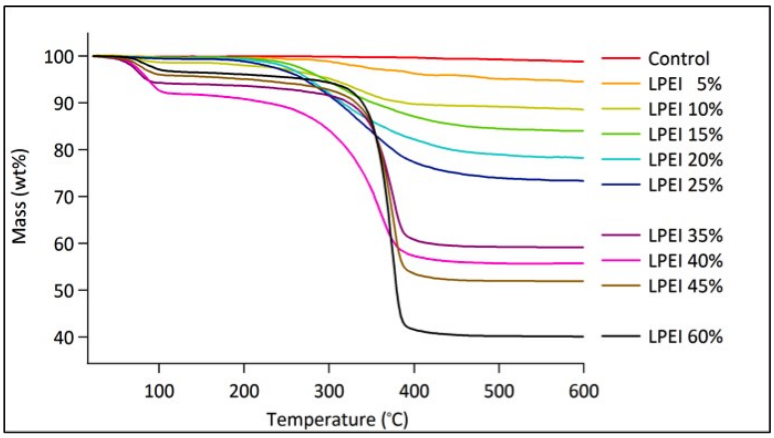


Fig. S5. TGA profile of CNT and CNT-LPEI with different PEI loadings.

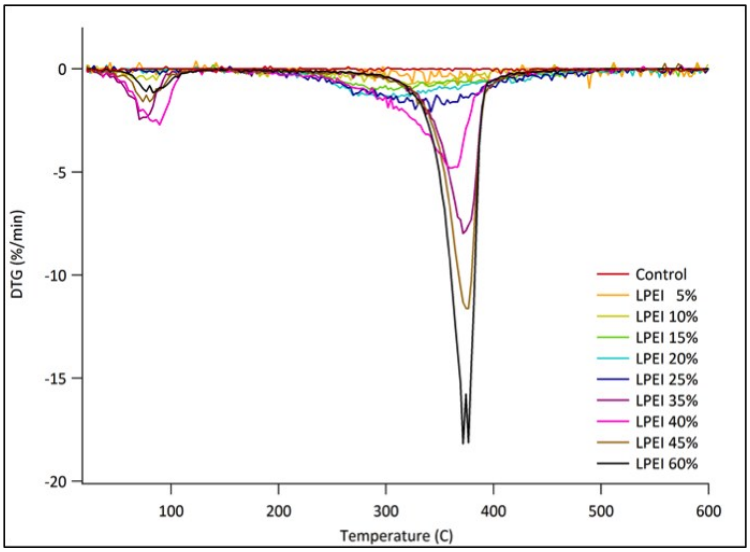


Fig. S6. DTG profile of CNT and CNT-LPEI with different PEI loadings.

Table S1 N_2 adsorption/desorption isotherms for surface area and pore volume of CNT, CNT-LPEI, CNT-BPEI and LPEI

Amine	Amine Loading (%)	Surface Area (m^2/g)	Pore Volume (cm^3/g)
CNT	0	123	0.555
CNT-BPEI	5	85	0.480
CNT-BPEI	10	76	0.442
CNT-BPEI	20	62	0.317
CNT-BPEI	25	42	0.280
CNT-BPEI	30	33	0.230
CNT-BPEI	35	27	0.209
CNT-BPEI	40	14	0.099
CNT-BPEI	45	3	0.013
CNT-LPEI	5	92	0.515
CNT-LPEI	10	60	0.396
CNT-LPEI	20	35	0.298
CNT-LPEI	25	34	0.215
CNT-LPEI	30	29	0.184
CNT-LPEI	35	27	0.163
CNT-LPEI	40	16	0.146
CNT-LPEI	45	5	0.022
LPEI	-	0.0036	0.000919

S4. CO_2 isotherm equation and data work up

CO_2 adsorption isotherms are often reported keeping the mass of materials constant. The breakthrough time and the area are not directly correlated to the CO_2 adsorption capacity of CNT-LPEI material in this study without taking into account the mass. For example, without correcting for mass in equation 1, the adsorption area of CNT-46%LPEI and CNT-60%LPEI are larger than CNT-40%LPEI. Maintaining a constant packing height (1.28 cm) is important to get relative and accurate CO_2 adsorption capacity between materials with different densities. Since LPEI is much heavier than CNT, in order to maintain the packing height, a higher mass of CNT-LPEI should be packed in the column compared to bare CNT or CNT with low PEI loading.

It is critical for the inlet and outlet flow rates to be similar. If they are different, then equation (1) cannot be used to calculate CO_2 adsorption because total flow rate (Q) is not constant. The outlet flow rate measured by a manual bubble flow meter can be and is often influenced by the packing height. For example as the packing height increases above 1.28 cm, the outlet flow rate decreases, which increases the breakthrough time and can cause an overestimation of CO_2 adsorption capacity. In this way, a large amount of material often causes higher total CO_2 adsorption. Keeping the height constant, as we have done, allows more accurate CO_2 adsorption capacity and doesn't require a correction for density or mass transfer effects. The mass of the materials at 1.28 cm and the net area of the uptake curves are shown in Table S2. After being normalized by mass, the CO_2 adsorption capacity of CNT-40%LPEI will be larger than CNT-46%LPEI and CNT-60%LPEI. This trend is in agreement to what others have reported.

Table S2 CO_2 adsorption net area based on CNT-LPEI mass with various PEI loadings

Material	Net area*	Mass of material (mg) at 1.28 cm
CNT	0.0069	93.2
CNT-5%LPEI	0.0177	123.2
CNT-10%LPEI	0.0260	131.3
CNT-15%LPEI	0.0620	211.2
CNT-20%LPEI	0.0787	205.1
CNT-25%LPEI	0.2144	226.1
CNT-35%LPEI	0.1298	168
CNT-40%LPEI	0.2466	229.7
CNT-45%LPEI	0.3412	394
CNT-60%LPEI	0.4076	478.4

* The area is calculated by $\int_0^t \frac{c_i - c_e}{1 - c_e} dt$ according to equation (1) and normalized by a control using only the glass reactor tube.