

Chemical Reduction of a Diimide Based Porous Polymer for Selective Uptake of Carbon Dioxide Versus Methane

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General information

Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received unless otherwise noted. N,N'-dimethylformamide (DMF) used for chemical reduction was purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA).

Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA851e. Samples placed in alumina pans were heated from 25°C to 700°C at 10°C/minute under N₂ flow.

Inductively coupled plasma (ICP) spectroscopy was conducted on a Varian model ICP spectrometer that is equipped to cover the spectral range from 175 to 785 nm. Samples (3-5 mg) were digested in 3:1 H₂SO₄:H₂O₂ and heated at 120°C until the solution became clear and colorless and no further vapor was produced. An aliquot of this concentrated acid solution was diluted to 5.0% in DI H₂O and analyzed for Li (610.365 nm) content.

Low-pressure adsorption isotherms were measured with an Autosorb 1-MP from Quantachrome Instruments. Ultra-high purity grade nitrogen and carbon dioxide were used for all adsorption measurements. Nitrogen isotherms were carried out in a liquid nitrogen bath (77K). Carbon dioxide isotherms were measured in an ethylene glycol/water bath held at 273K using a refrigerant circulator.

For high-pressure isotherms a home-built volumetric-type apparatus was used to measure the adsorption equilibria of CO₂ and CH₄ in **4**, **5** and **6** at 298 K and 0-18 atm.¹ The void volume of the system was determined by using He gas. CO₂ (99.9%) and CH₄ (99%) were obtained from Airgas Inc. (Radnor, PA). Prior to analysis, gases were passed through molecular sieves to remove residual moisture. Equilibrium pressures were measured with an MKS Baratron transducer 627B (accuracy ±0.12%). Adsorbate was

dosed into the system incrementally, and equilibrium was assumed when no further change in pressure was observed (within 0.01 kPa). Ideal adsorbed solution theory calculations were done using previously published method and parameters.¹

Chemical Reduction

As synthesized polymer **3** was made using previously published method.² Thermal activation of **3** was done under 10^{-5} torr dynamic vacuum at 100°C for 2 hours then 160°C for 24 hours. The activated sample was then taken into an argon atmosphere glove box. To make the reductant solution, first a small piece of lithium metal (3.2mm wire in mineral oil) was cut and rinsed in dry THF to remove mineral oil. Any black oxide was scraped off and a measured amount cut off (1.2mg for **5**; 2.4mg for **6**).

Caution: Lithium metal is extremely reactive with water and potentially reactive with nitrogen! All manipulations with lithium metal were undertaken in an argon atmosphere glove box.

The piece of lithium was stirred vigorously for 1 hr in 15ml dry DMF. To a measured amount of activated **4** (100mg) the reductant solution was added and allowed to react (10min for **5** and 15min for **6**). The solution changes from clear to a deep green color and the powder changes from a pale orange color to a dark purple (see figure S1). The powder is filtered on a fine frit and rinsed with 3x5ml fresh DMF. The reduced samples **5** and **6** are air sensitive and will oxidize if exposed to air. Oxidation is accompanied with a color change back to pale orange. Samples are sealed under argon and again activated under vacuum at 160°C for 24 hours to remove all DMF before adsorption measurements are taken.

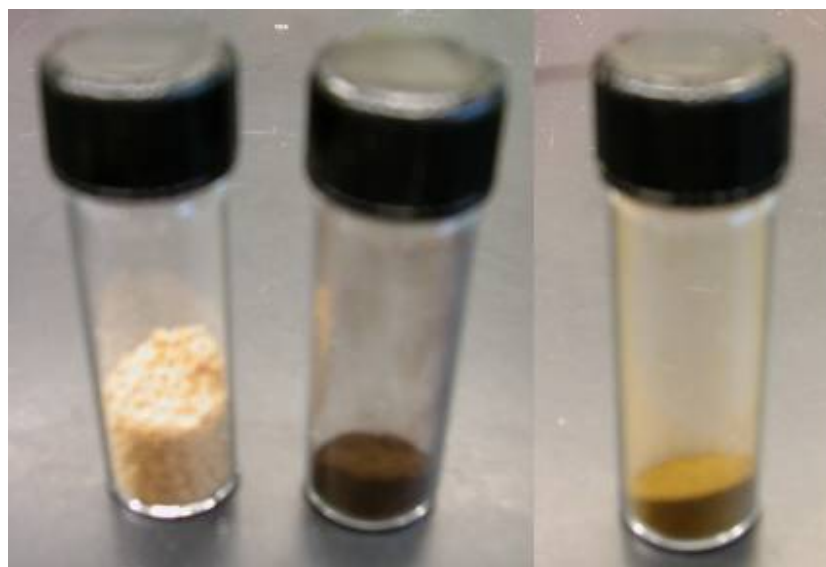


Figure S1. Photographs of as synthesized polymer (left) and lithium reduced polymer (middle). Polymer returns to orange neutral color upon exposure to air for 5 minutes (right).

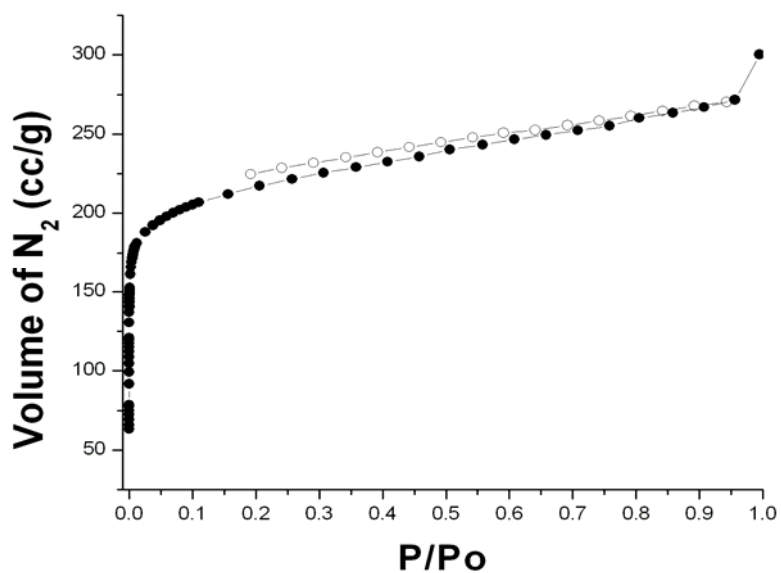


Figure S2. Nitrogen adsorption measurement for **4**. Nitrogen measurements for samples **5** and **6** showed no nitrogen uptake. Filled symbols adsorption, open symbols desorption.

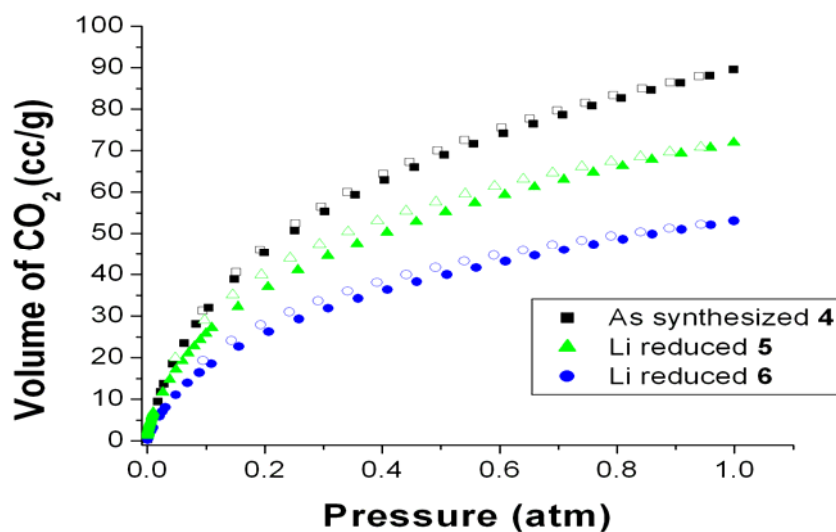


Figure S3. Low pressure (up to 1atm) carbon dioxide isotherms for as synthesized sample **4** and lithium metal reduced **5**(Li_{0.35}) and **6**(Li_{0.55}) at 273K. Filled symbols adsorption, open symbols desorption.

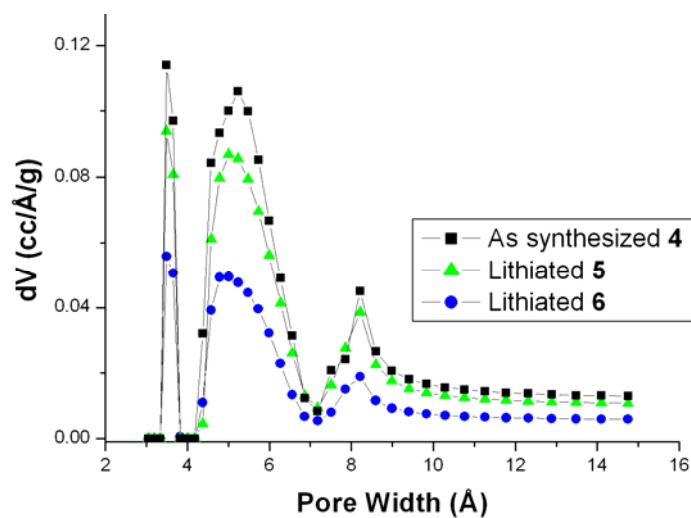


Figure S4. Non-local density functional theory (NLDFT) calculated pore size distribution for as synthesized sample **4** and lithium metal reduced **5**(Li_{0.35}) and **6**(Li_{0.55}). Distribution calculated using the NLDFT CO₂ kernel at 273K based on a *slit-pore model* in the AS1WIN software package from Quantachrome Instruments.

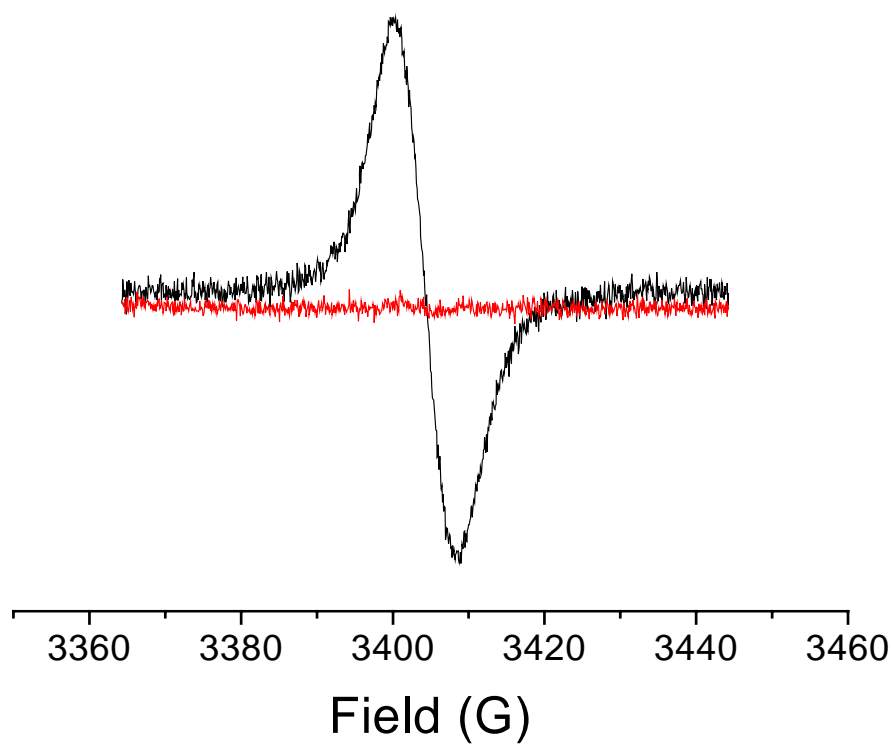


Figure S5. Solid-state room temperature CW-EPR spectra of as synthesized **4** (red) and lithium reduced **6** (black). Microwave power was 2 mW with a frequency modulation depth of 100 KHz.

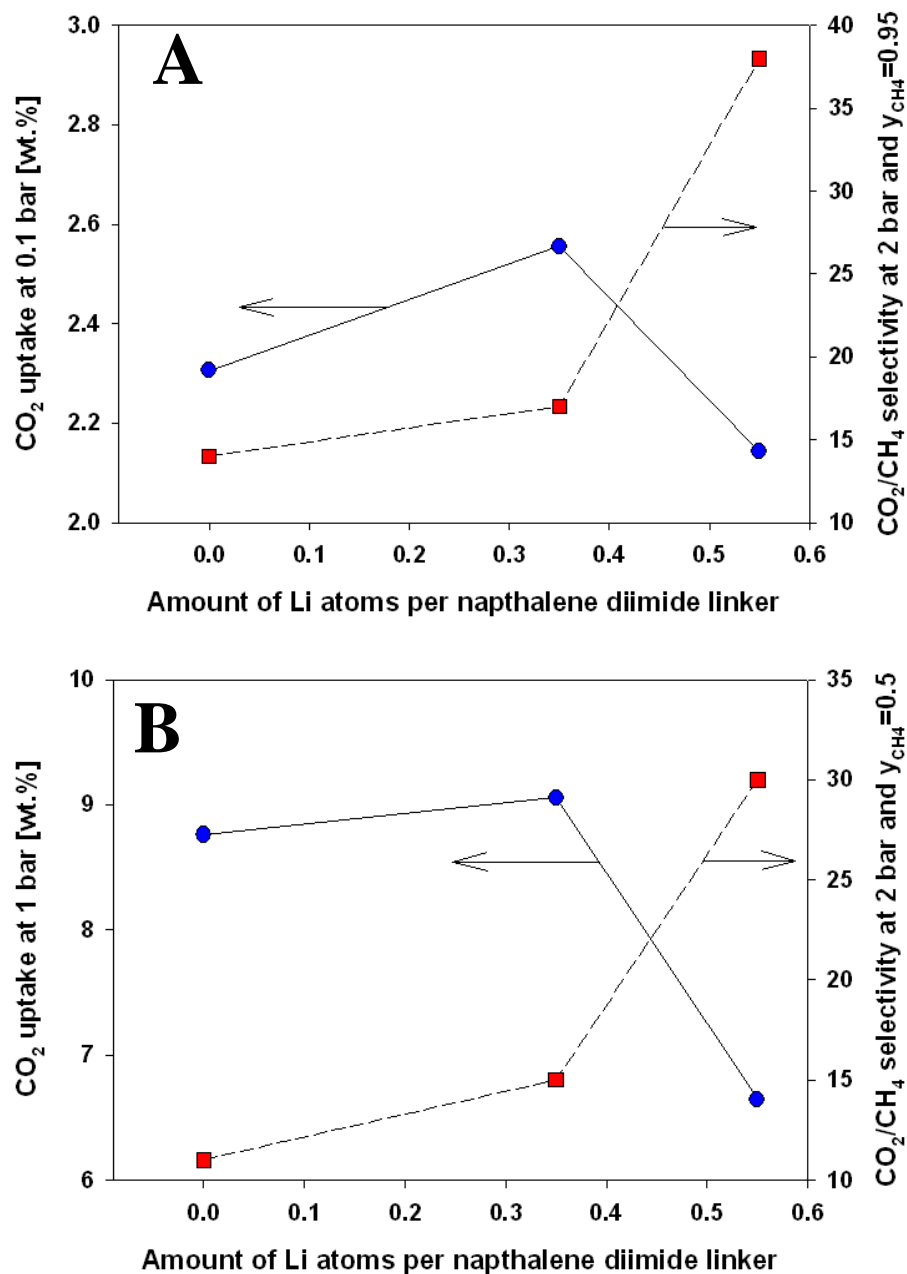


Figure S6. (A) Normalized graph showing the number of Li ions per naphthalene linker versus CO₂ uptake at 0.1 bar and versus CO₂/CH₄ selectivity at 2 bar and $y_{\text{CH}_4} = 0.95$ (standard natural gas conditions). (B) Normalized graph showing the number of Li ions per naphthalene linker versus CO₂ uptake at 1.0 bar and versus CO₂/CH₄ selectivity at 2

bar and $y_{\text{CH}_4} = 0.5$ (standard flue-gas conditions). (uptakes were measured and selectivities were calculated)

¹ Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp and R. Q. Snurr, *Langmuir*, 2008, **24**, 8592-8598.

² O. K. Farha, A. M. Spokoyny, B. G. Hauser, Y.-S. Bae, S. E. Brown, R. Q. Snurr, C. A. Mirkin and J. T. Hupp, *Chem. Mater.*, 2009, **21**, 3033-3035.