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## **Supporting Information**

## Hierarchical porous nitrogen-rich carbon monoliths *via* icetemplating: high capacity and high-rate performance as lithium-ion battery anode materials

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	Total Intrusion Volume (cm³/g)	Total Pore Area (m²/g)	Average Pore Diameter (4V/A) (μm)
PAN50	8.01	3.56	9.0
CPAN50	1.13	0.82	5.6

Table S1. Characterization data for the PAN50 and CPAN50 samples by Hg intrusion porosimetry

Table S2. Summary of the conductivity and elemental content of the carbonized PAN monoliths

PAN concentration (mg cm <sup>-3</sup> )	Conductivity (Scm <sup>-1</sup> )	C (%)	Н (%)	N (%)	O (%) (inferred)
25	1.53×10 <sup>-3</sup>	72.0	1.04	16.4	10.56
50	2.03×10 <sup>-2</sup>	74.9	1.31	15.7	8.09
100	3.06×10 <sup>-2</sup>	70.9	1.05	16.7	11.35
150	4.29×10 <sup>-2</sup>	73.2	0.84	17.3	8.66
200	5.73×10 <sup>-2</sup>	75.9	0.77	16.0	8.03

Template	Carbon precursor	C <sub>irr</sub> (mAh g <sup>-1</sup> )	C <sub>rev</sub> (mAh g <sup>-1</sup> )	C <sub>rev</sub> after N cycles (mAh g <sup>-1</sup> )	N cycles	Ref.
Silica monolith	Mesophase pitch	680	900	500	40	[1]
Silica SBA-15	Sucrose	2000	1100	800	20	[2]
Silica particles & PS spheres	Furfurylalcohol	671	903	799	80	[3]
SBA-15	Furfurylalcohol	N/A	714	583	80	[3]
Inverse silica opal	Benzene (CVD)	N/A	326	320	60	[4]
PMMA	Recorcinol Formaldehyde	400	300	150	150	[5]
Ice crystals	Polyacrylonitrile	450	702	570	50	This work

**Table S3.** Comparison of reversible ( $C_{rev}$ ) and irreversible ( $C_{irr}$ ) capacity values of a number of templated porous carbons described in the literature.

**Table S4.** Comparison of some of the best high-rate performance carbon-based anode materials described in the literature

Description	C <sub>rev</sub> at current density X (mAh g <sup>-1</sup> )	Current density X (A g <sup>-1</sup> )	Ref.
Carbon templated by silica and PS spheres	750	1	[3]
Nitrogen-doped pristine graphene	250	10	[6]
Boron-doped pristine graphene	300	10	[6]
N-rich porous carbon derived from protein	210	4	[7]
N-doped activated carbon nanofiber web	320	10	[8]
N-doped carbon spheres (<100nm)	200	3	[9]
CPAN50	320	1	This work
CPAN50 - Melamine & graphene doped	300	10	This work



Figure S1. Schematic representation of the 'home-made' pyrolysis setup.



Figure S2. SEM images of PAN monoliths prepared from the relatively low concentrations of a) & b) 1 mg cm<sup>-3</sup>, c) 2.5 mg cm<sup>-3</sup> and d) 10 mg cm<sup>-3</sup>



Figure S3. Schematic representation of the oxidative annealing (crosslinking) process of PAN.



Figure S4. Comparison of the specific capacity values of the porous carbons prepared at different initial PAN/DMSO concentrations, over 10 charge/discharge cycles.



Figure S5. SEM images of the silicon nanoparticle-carbon composite prepared by icetemplating started from a suspension of silicon nanoparticles in a PAN in DMSO solution. The PAN concentration was 50 mg cm<sup>-3</sup> and the ratio of silicon nanoparticles to PAN was 1:1.



Figure S6. a) XRD patterns of a PAN-Sn(OAc)<sub>2</sub> composite before and after carbonization at 550 °C. The appearance of the associated (110), (101) and (200) diffraction peaks indicates the conversion of Sn(OAc)<sub>2</sub> to SnO<sub>2</sub>. The concentration of PAN was 50 mg cm<sup>-3</sup> and the ratio of PAN to Sn(OAc)<sub>2</sub> was 1:1. b) SEM images of the carbon-SnO<sub>2</sub> composites.

## References

1. Y. S. Hu, P. Adelhelm, B. M. Smarsly, S. Hore, M. Antonietti and J. Maier, *Advanced Functional Materials*, 2007, **17**, 1873-1878.

2. H. Zhou, S. Zhu, M. Hibino, I. Honma and M. Ichihara, *Advanced Materials*, 2003, **15**, 2107-2111.

3. B. Fang, M.-S. Kim, J. H. Kim, S. Lim and J.-S. Yu, *Journal of Materials Chemistry*, 2010, **20**, 10253-10259.

4. F. Su, X. S. Zhao, Y. Wang, J. Zeng, Z. Zhou and J. Y. Lee, *The Journal of Physical Chemistry B*, 2005, **109**, 20200-20206.

5. K. T. Lee, J. C. Lytle, N. S. Ergang, S. M. Oh and A. Stein, *Advanced Functional Materials*, 2005, **15**, 547-556.

6. Z.-S. Wu, W. Ren, L. Xu, F. Li and H.-M. Cheng, *ACS Nano*, 2011, **5**, 5463-5471.

7. Z. Li, Z. Xu, X. Tan, H. Wang, C. M. B. Holt, T. Stephenson, B. C. Olsen and D. Mitlin, *Energy & Environmental Science*, 2013, **6**, 871-878.

8. L. Qie, W.-M. Chen, Z.-H. Wang, Q.-G. Shao, X. Li, L.-X. Yuan, X.-L. Hu, W.-X. Zhang and Y.-H. Huang, *Advanced Materials*, 2012, **24**, 2047-2050.

9. Y. Wang, F. Su, C. D. Wood, J. Y. Lee and X. S. Zhao, *Industrial & Engineering Chemistry Research*, 2008, **47**, 2294-2300.