

Supplementary Information

Long Cycle Life Microporous Spherical Carbon Anodes for Sodium-ion Batteries Derived from Furfuryl Alcohol

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Experimental

In order to synthesize carbon spheres, an emulsion polymerization approach was adapted.¹ In a typical synthesis, 12 g of surfactant (Pluronic F-127, Sigma- Aldrich) was added into a solvent mixture comprised of 40 mL ethanol and 12 mL water. Then, 2.8 g of HCl (initiator, 36.5 wt%, Sigma Aldrich) and 6 g of furfuryl alcohol (98% purity, Sigma Aldrich) were added together to the solution. Slow polymerization of furfuryl alcohol continued for 12 hours. The soft polymeric spheres were hardened by adding 35 cc of 5M sulfuric acid and the temperature was increased to 90 °C. The concentrated acid and heat induce a high degree of cross-linking within the polymer structure which subsequently hardens the spheres' surface. The brown polymeric residue was washed and centrifuged with excess amount of distilled water. The polymer spheres were dried in an oven at 90-100 °C, overnight. Final end-product carbon spheres were obtained by carbonization of polymeric particles in a tube furnace at 800 °C for 5 hours under argon flow.

The electrode was made up of 80% active microporous carbon sphere particles, 10% super P (TIMCAL) and 10% PVDF binder (Kureha, KF-9130). 2032 coin cells were assembled against Na metal in an argon filled glove box with 0.1 ppm oxygen level. 1 M NaPF₆ in

EC:EMC (3:7 by weight) was used as electrolyte and a monolithic glass fiber was used as the separator. The electrochemical performance was tested with a MACCOR Series 4000 electrochemical cycler. Constant galvanostatic charge-discharge currents were applied to the battery between 5mV and 2 V voltage cutoffs. Current densities were varied from 20 mA g⁻¹ to 1000 mA g⁻¹, and are indicated as such in the cycling figures in the paper. Note that the electrode loading was a nominal 3.5-4.0 mg/cm², certainly a very practical and viable electrode loading for large scale coating on commercial coaters.

The surface morphology and the size of the microporous carbon particles were observed by a field-emission scanning electron microscope (FEI Nova NanoSEM 630). BET surface area of dried microporous carbon particles was calculated based on the nitrogen adsorption isotherms conducted using a micromeritics porosity analyzer (ASAP 2020). Pore size distribution was obtained by gravimetric adsorption measurement performed at different temperature ranges using methyl chloride.² XRD measurement was carried out with a Bruker D2 diffractometer (CuK_α radiation at $\lambda=1.54 \text{ \AA}$). Raman spectroscopy measurement was conducted by WITec Confocal Raman instrument at 488 nm wavelength. ²³Na MAS solid-state NMR experiments were performed at 224.758 MHz, on a Varian 850 MHz spectrometer (19.96 Tesla superconducting magnet) using a 4 mm MAS probe operating at 15 kHz spinning speed at Pacific Northwest National Laboratory (PNNL). Samples were prepared in an inert argon atmosphere after rinsing cycled electrodes with propylene carbonate solvent. The NMR spectra were referenced to 1 M NaCl at 0 ppm and single pulse experiments were performed with a pulse width of 1.5 μ s and a recycle delay of 5 s. The ²³Na MAS NMR was measured after cycling the sphere carbon for 1000 cycles, and left at 50% SOC (state-of-charge). The cell was dismantled, the electrode recovered, rinsed with PC and dried prior to measurement. The result is shown in Figure S1.

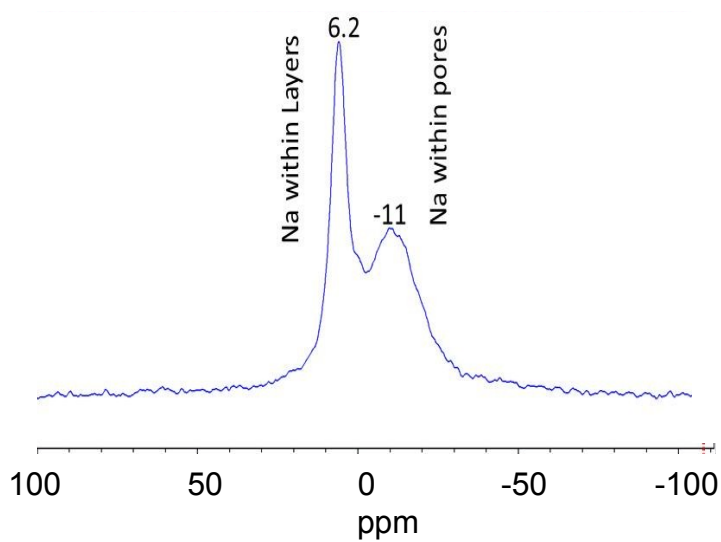


Figure S1. ^{23}Na MAS NMR of spherical carbon in 50% SOC sodiated state after 1000 charge-discharge cycles @ 1C rate between 5 mV and 2.0 V vs. Na.

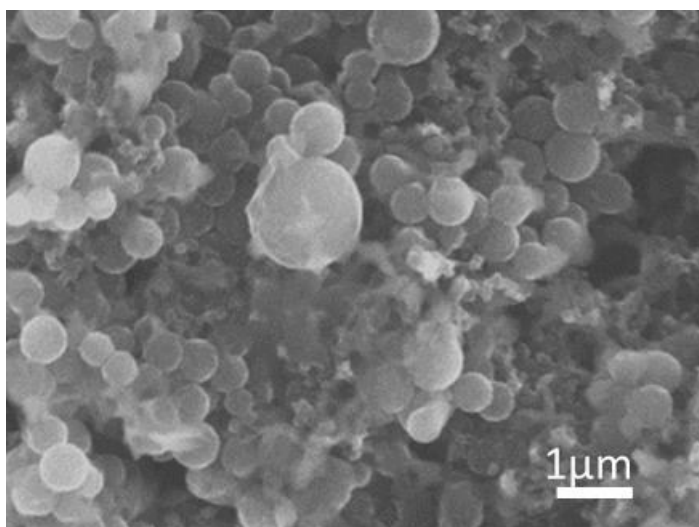


Figure S2. SEM of a sphere hard carbon electrode after 20 cycles that was extracted out of a dismantled coin cell. The cell was opened in the discharged state; the electrode washed with PC and dried in the argon glovebox. Note the smooth homogeneous SEI coverage and the consistent sphere shape has been maintained through cycling.

The **Table S1** shows an electrochemical cycling comparison of various carbonaceous materials previously reported from the literature and tested in sodium-ion batteries.

Table S1. Comparisons of electrochemical performance of hard carbon materials as anodes in sodium ion batteries.

Carbon material	Cycle Number	Capacity (mAhg ⁻¹)	Current density (mA g ⁻¹)	Reference
Carbon from peat moss plant material	210	203	500	[3]
Hollow carbon nanowires	400	251	50	[4]
Carbon from wood fiber cellulose	200	196	100	[5]
N-doped porous carbon nanosheet	260	155	50	[6]
N-doped porous carbon fibers	100	170	100	[7]
Hard carbon derived from furfuryl alcohol	1000	115	200	this work

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