Supporting Information Available

Hollow Carbon Nanowires as High-performance Anode Material for Sodium-ion Batteries

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Experimental Section

Material Preparation*:* The hollow polyaniline nanowire precursor was synthesized using a one-step, self-assembly approach. First, 10 mmol of aniline and 2.5 mmol of DL-tartaric acid (99%, Aldrich) were vigorously stirred in 50 mL of deionized water at room temperature for 0.5 h. The mixture then was cooled in an ice-water bath for 0.5 h. After cooling, 50 mL of oxidant aqueous solution containing 10 mmol of ammonium persulfate (APS, 98%, Sigma-Aldrich), which had been cooled in advance in an

ice-water bath, was poured into the previously prepared mixture. The polymerization reaction took place under ice-water bath condition for a period of 12 h. The resulting solid product was washed with de-ionized water several times and then dried overnight at 50 ^{o}C. Finally, the precursor was calcinated at 1150 ^{o}C for 6 h in nitrogen to obtain the targeting product, as called hollow carbon nanowires (HCNWs).

Structural Characterization: SEM, TEM, and high-resolution transmission electron spectroscopy (HRTEM) experiments were performed on a FEI Helios Nanolab, dual-beam, focused, ion beam/scanning electron microscope (FIB/SEM) and a JEOL-2010 high-resolution electron microscope, respectively. XRD measurements were carried out on a Philips Xpert X-ray diffractometer using Cu Kα radiation at λ = 1.54 Å. Nitrogen adsorption/desorption isotherms for surface area and pore analysis were measured with a Quantachrome, autosorb, automated, gas sorption system.

Simulation: To calculate the equilibrium distance between the graphite layers in the presence of Li and Na ion we have determined the balance of attractive van der Waals forces between graphite layers and the interactions between the Na or Li ion and the graphite sheets. It has been shown theoretically[1] that van der Waals force per unit area between two graphite layers can be expressed as:

$f = -\frac{A}{r^4}$, where the constant $A \approx 0.40$ eV Å.

On the other hand the DFT simulations suggest that the equilibrium distance for Li and Na ion adsorption onto graphite surface is 1.63 and 2.42 Å, respectively, with the corresponding adsorption energies equal to 1.68 and 0.69 eV.[2] On the basis of these data and the Badger's rule for the bond force constants we have calculated the interaction energy function for Li and Na ion with graphite surface. We use the Morse form for potential energy, $E(r) = E_{ad}\left(1 - e^{-a(r-r_{eq})}\right)^2$, where $a = \sqrt{\frac{k}{2E_{ad}}}$, E_{ad} is the adsorption energy and r_{eq} is the equilibrium distance.

The bond force constant k is determined using the empirical Badger's rule,[3] which was extensively tested with quantum mechanical simulations.[4] According to this rule $k = A\left(r_{eq} - B\right)^{-3}$ with constant A = 1.86 eV Å, and constant B depends on the interacting atom row numbers in the periodic table. The values of B = 0.68 Å and 0.74 Å were used for the interactions of Li and Na ion with graphite, respectively.[5]

Electrochemical measurements: The HCNWs anode was prepared by mixing 80wt% HCNW powder, 10wt% Super P carbon black, and 10wt% polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) to form slurry. Then, the electrode slurry was pasted on the Cu foil. Electrochemical tests were performed with 2035 coin cells with Na metal as counter and reference electrodes. The electrolyte was 1 M $NaClO_4$ dissolved in a mixture of EC and EMC (1:1 by wt.), and the separator was a microporous membrane (Celgard 2135). The cells were assembled in an argon-filled glovebox. The galvanostatic charge-discharge tests were conducted at a voltage interval of 0-1.2 V with a BT-2000 Arbin Battery Testing System. CV measurements were carried out at a scan rate of 0.1 mV s^{-1} using a SI 1287 electrochemical interface (Solartron).

Reference:

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2. F. Valencia, A. H. Romero, F. Ancilotto and P. L. Silvestrelli, *J. Phys. Chem. B*, 2006, **110**, 14832-14841.
3. R. M. Badger, *J. Chem. Phys.*, 1934, **2**, 128.
4. J. Cioslowski, G. H. Liu and R. A. M. Castro, *Chem. Phys. Lett.*, 2000, **331**, 497-501.
5. D. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 1961, **35**, 458-&.

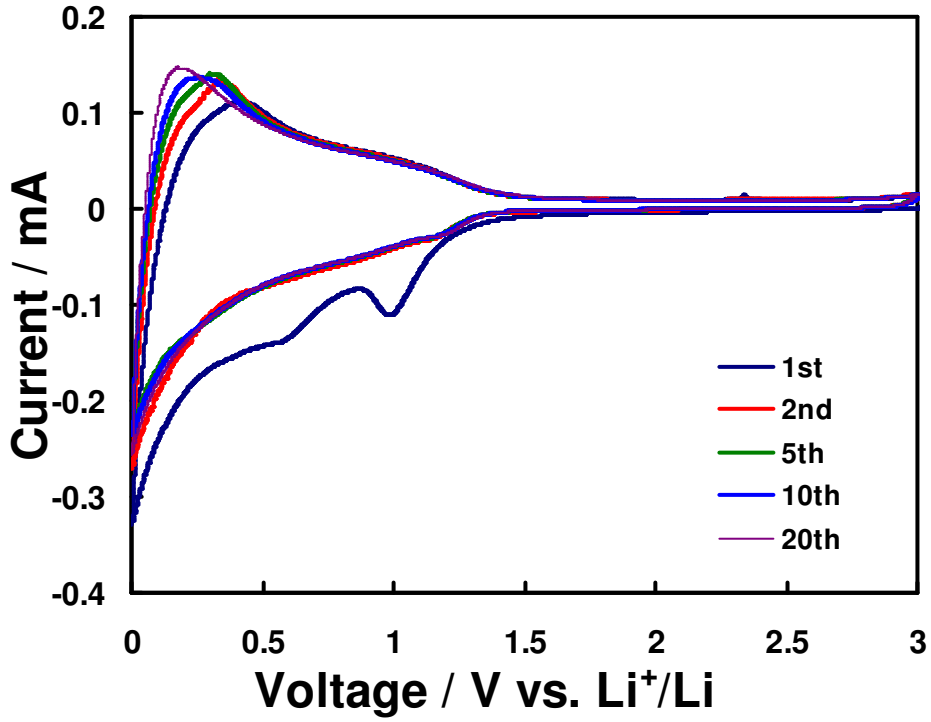

Figure S1 CV curves of the HCNWs electrode between 0 and 2.5 V at a potential sweep rate of 0.1 mV s^{-1} in 1 M $LiPF_6$/EC:EMC electrolyte for Lithium-ion battery.

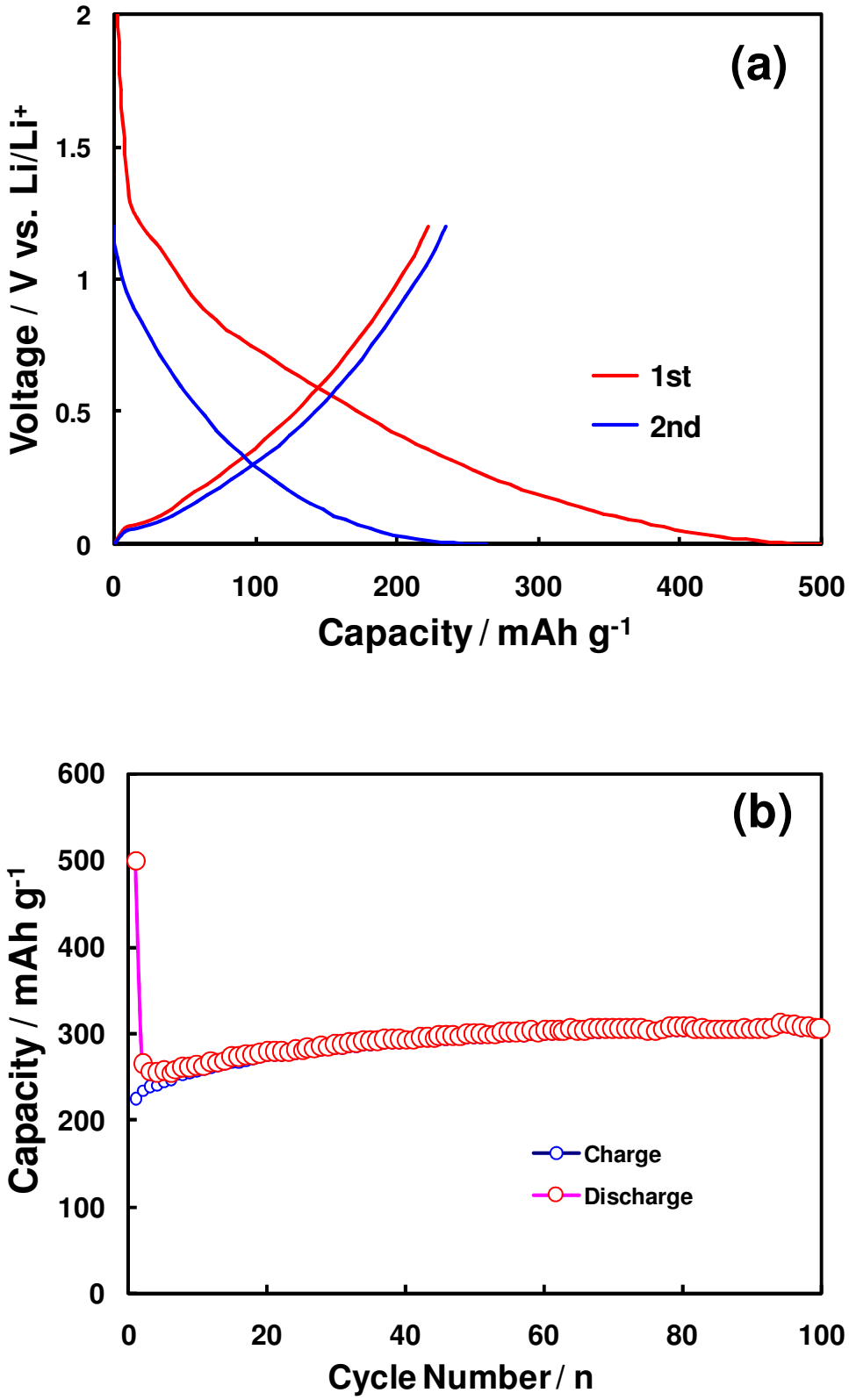

Figure S2 Electrochemical characterization of the HCNWs electrode in 1M $LiPF_6$/EC:EMC electrolyte for Lithium-ion battery. (a) First two charge/discharge profiles of the HCNWs electrode between 0 and 1.2 V at a current density of 50 mA g^{-1}. (b) Cycle performance of the HCNWs electrode at a current density of 50 mA g^{-1}.

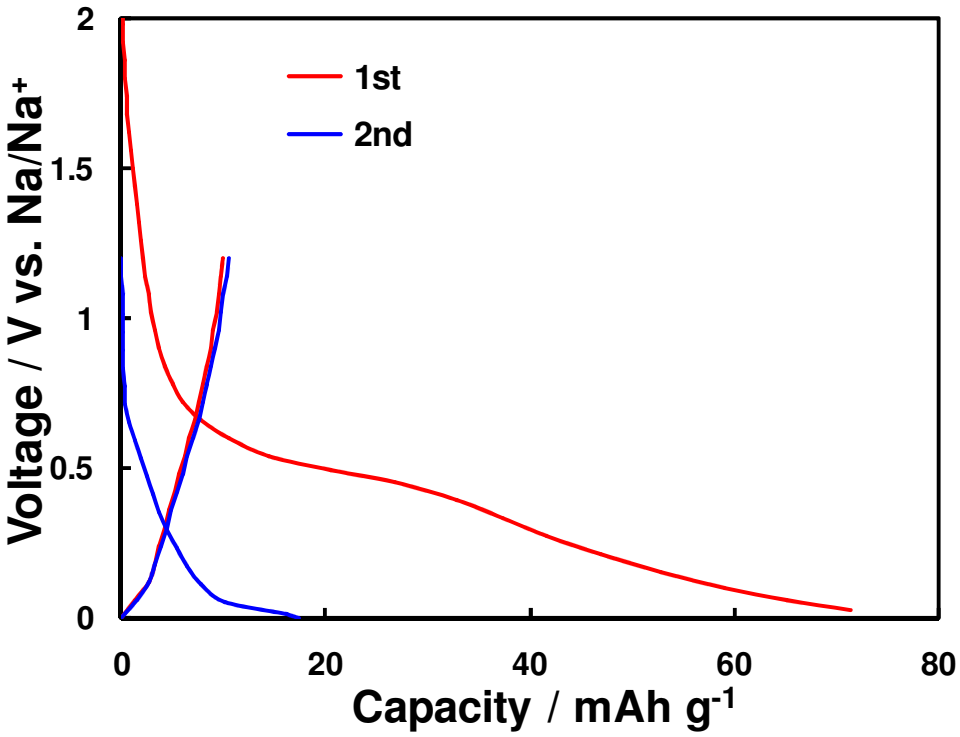

Figure S3 First two charge/discharge profiles of the graphite electrode between 0 and 1.2 V at a current density of 50 mA g^{-1} in 1M $NaClO_4$/EC:EMC electrolyte.