Electronic Supplementary Information (ESI)

Boosting rate capability of hard carbon with an ether-based electrolyte for sodium ion batteries

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Experimental section

1. Materials preparation

Hard carbon was prepared by the simple pyrolysis process of loofah sponges. The loofah sponges were carbonized under argon flow for 2 hours in the tube furnace at 1000°C and 1300°C, and the final products were marked as LS1000 and LS1300, respectively.

2. Materials characterization

The structure was characterized by X-ray diffraction (XRD, Rigaku D/Max Ⅲ diffractometer with Cu Kα radiation, λ = 1.5418 Å) and Raman spectroscopy (Renishaw inVia spectrometer, 514.5 nm Ar^+ laser). The morphology was analyzed through a field emission scanning electron microscope (FESEM, JEOL-JSM7500), high-resolution transmission electron microscope (HRTEM, FEI Tecnai, model G2F-20 field emission TEM) and selected area electron diffraction (SAED). The valence state of elements was detected by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical).

3. Electrochemical Tests

The working electrodes consisted of 75 wt% active material, 15 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF), which were dispersed in N-methyl-2-pyrrolidone (NMP) uniformly. The achieved slurry was pasted on Cu foil as the current collector and dried at 110 °C in a vacuum oven for 12 hours. The electrodes were punched out with diameters of 12 mm and mass loading of 1.0-1.5 mg cm^{-2}. In an Ar-filled glove box, the CR2025-type coin cells were assembled. The electrolyte was a solution of 1 mol L^{-1} $NaCF_3SO_3$ (NaOTf) in DEGDME and 1 mol L^{-1} NaClO4 (NaCO) in ethylene carbonate/dimethyl carbonate (EC/DEC, 1:1 in volume). Metallic sodium was selected as the counter electrode and glass fiber was used as the separator. The coin cells were cycled in the range of 0.01–2.5V on a LAND CT2001 tester at different rates. Cyclic voltammetric (CV) tests were tested on a CHI600A electrochemical workstation (Shanghai Chenhua) at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed on a Zahner-Elektrik IM6e electrochemical workstation by sweeping the frequency from 100 kHz to 10 mHz with an AC amplitude of 5 mV. The hall-cell of the LS1300 was performed 2cycles at 40 mA g^{-1} in different electrolytes before GITT. During the GITT tests, the cells were discharged/charged at 35 mA g^{-1} with current pulse duration of 0.5 h and interval time of 2 h. TEM-EDS was also performed. After the first cycle, the half-cells in different electrolytes were disassembled in the glovebox and washed with the related solvent, namely DMC and DEGDME, to remove excess sodium salt. The electrodes were then scraped to produce a fine powder and then placed on a TEM lacy carbon film supported on a copper grid. The TEM samples were loaded on a vacuum transfer holder and transferred to the TEM equipment to avoid any contamination from air or water.

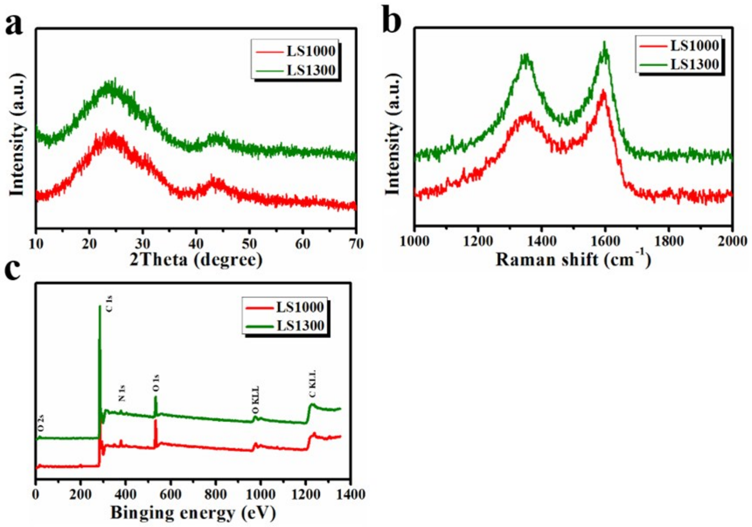

Fig. S1. Characterizations of LS100 and LS1300 carbonized at different temperatures. a) XRD patterns; b) Raman spectra; c) XPS.

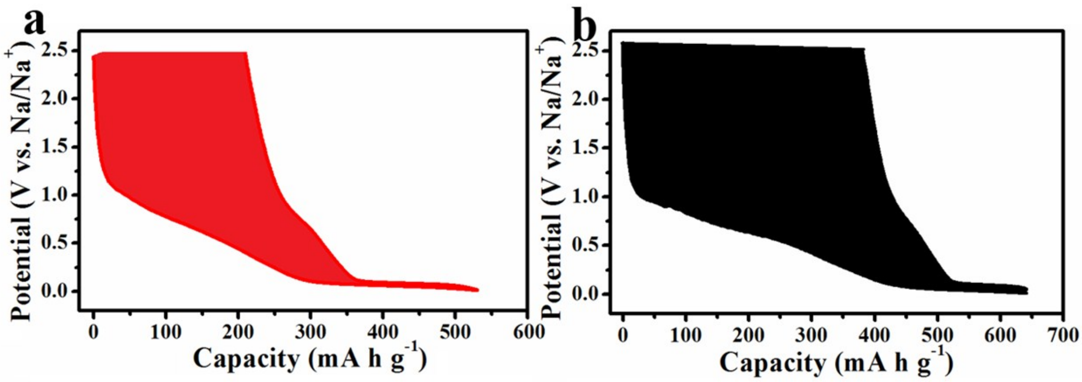

Fig. S2. The initial charge and discharge curves of LS1300 at 0.1 C in a) the ether-based electrolyte and b) the ester-based electrolyte.

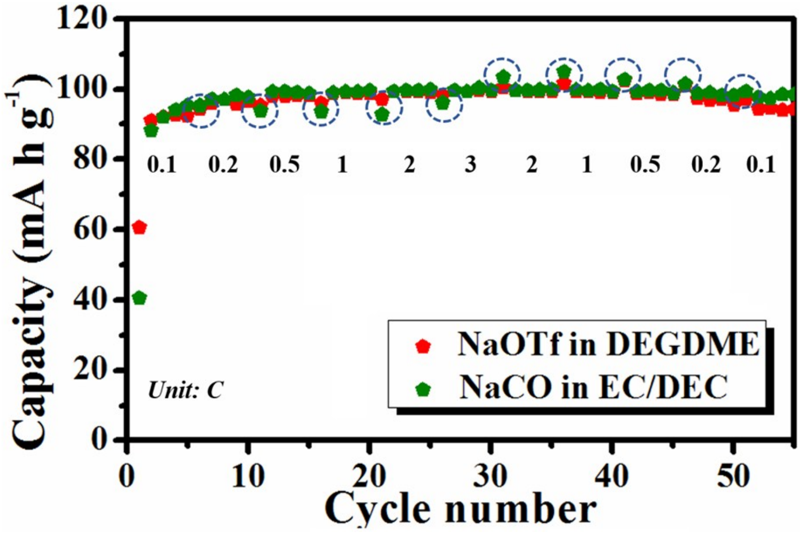

Fig. S3. Coulombic efficiency of LS1300 at various rates with different electrolytes.

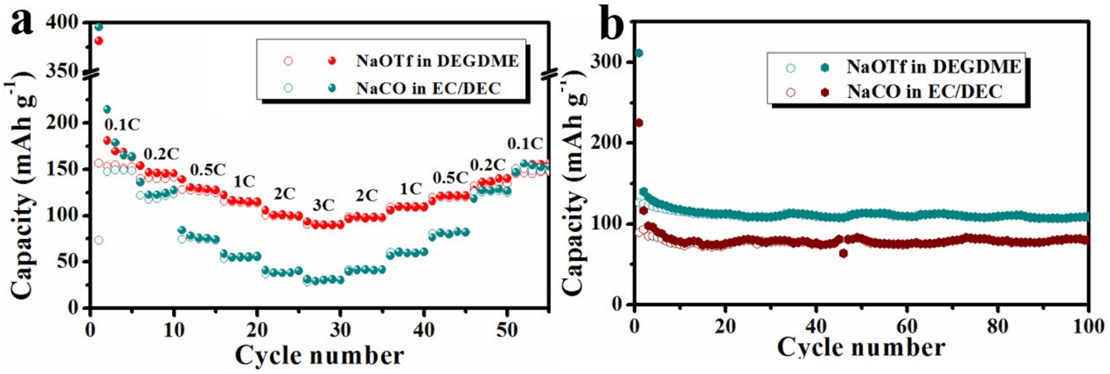

Fig. S4. Electrochemical measurements of LS1000 anodes in different electrolytes: (a) rate and (b) cycling performance at 0.5 C.

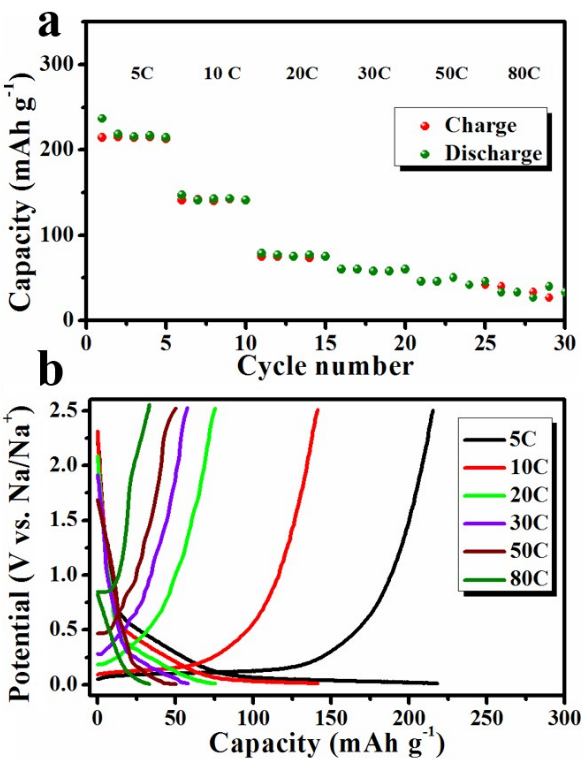

Fig. S5. a) The exceptional high-rate capability of LS1300 and b) corresponding charge/discharge curves at different rates in the ether-based electrolyte.

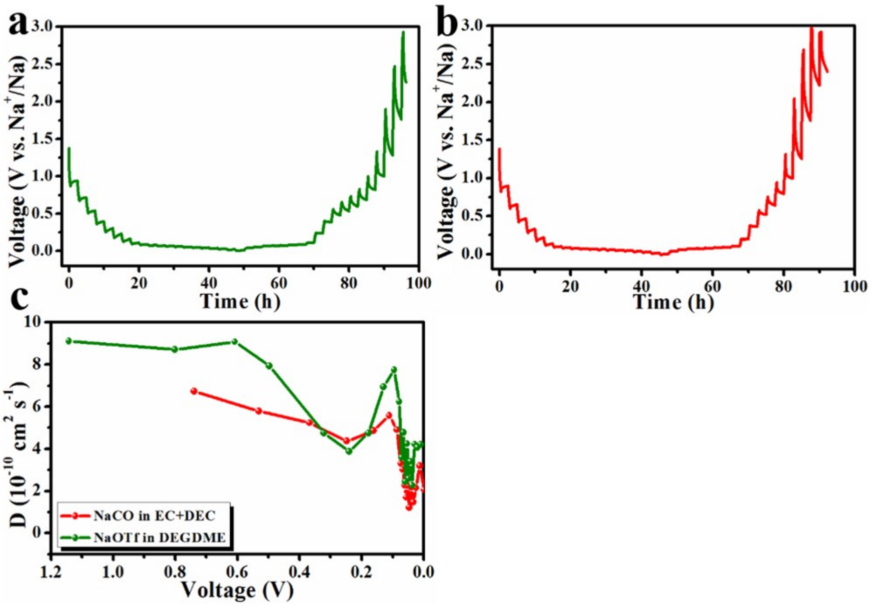

Fig. S6. GITT potential profiles of LS1300 in a) the ether-based electrolyte and b) the ester-based electrolyte during the third cycle; c) Na$^+$ apparent diffusion coefficients calculated from the GITT potential profiles for sodiation process.

D_{Na+} diffusion coefficient calculation

According to $$D_{GITT} = \frac{4}{\pi}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_S}{\tau\left({dE_\tau}/{d\sqrt{\tau}}\right)}\right)^2 \qquad \left(\tau \ll \frac{l}{D_{GITT}}\right)$$

If E vs. $\sqrt{\tau}$ shows straight-line behavior during the duration of the current pulse, then this equation can be transformed algebraically into.

$$D_{GITT} = \frac{4}{\pi\tau}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \qquad \left(\tau \ll \frac{l}{D_{GITT}}\right)$$

List of variables:

τ = current pulse time (sec).

m_B = mass of B in sample (g).

V_m = molar volume of B (cm^3/mol).

M_B = Molar Mass of B (g/mol).

S = Contact surface area (cm^2).

l = the thickness of electrode.

E_τ = cell voltage (V).

ΔE_s = the difference in the open circuit voltage measured at the end of the relaxation period for two successive steps (V).

Checking the units.

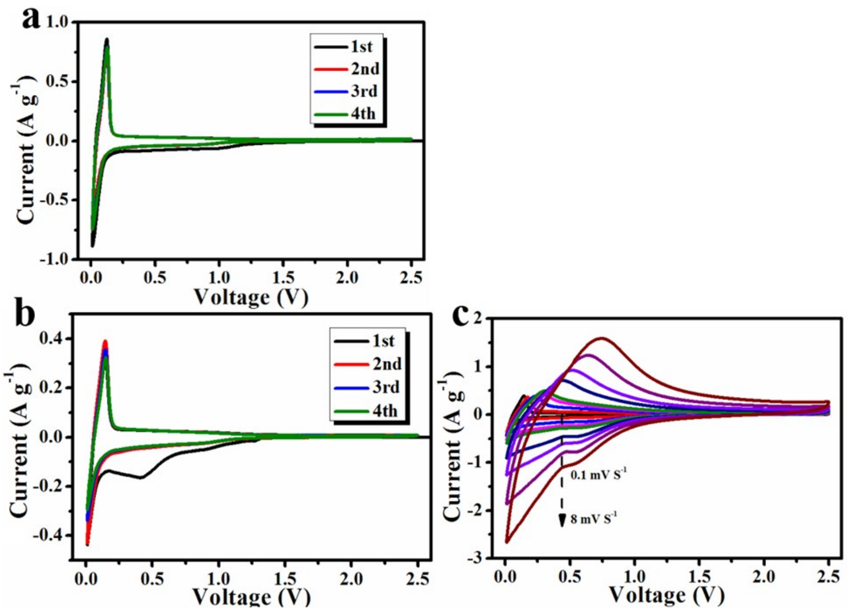

Fig. S7. CV curves at the scan rate of 0.1 mV s^{-1} of LS1300 in a) the ether-based electrolyte and b) the ester-based electrolyte; c) CV curves of LS1300 in the ester-based electrolyte at various sweep rates from 0.1 to 8 mV s^{-1} in the voltage range of 0.01-2.5V.

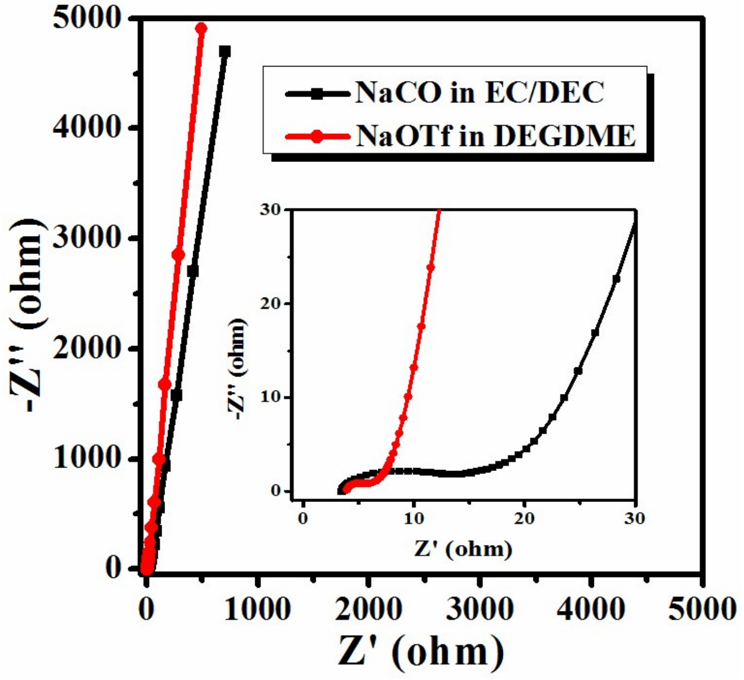

Fig. S8. Nyquist plots in symmetric cells (hard carbon//hard carbon) before cycles in different electrolytes.

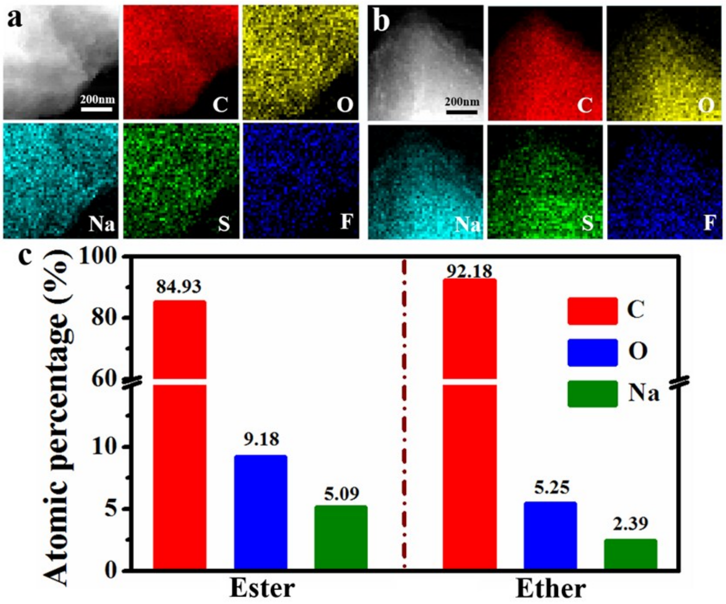

Fig. S9. Electron microscopy and elemental analysis of LS1300 electrodes cycled in a) the ester-based electrolyte and b) the ether-based electrolyte; STEM image and the corresponding EDS elemental mapping show the spatial distribution of C, O, Na, S, F. c) Atomic percentage comparison of different elements in LS1300 electrodes cycled in different electrolytes.