Electronic Supplementary Information (ESI)

High Capacity Na-storage and Superior Cyclability of Nanocomposite Sb/C Anode for Na-ion Batteries

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Experimental details

Preparation of Sb/ C nanocomposite: The Sb/ C nanocomposite was prepared by direct ball milling of commercial Sb powders (99.3% purity, 100 mesh) and Super P carbon (TIMCAL Graphite & Carbon) in an optimized mass ratio of 7:3. The weight ratio of milling balls to reagent powders was selected to be 20:1. The milling vial was filled with Ar and set in a shaking miller (QM-3A, Nanjing, China). The rotation speed of the miller was set to 1200 rpm and the billing time was fixed to 10 h.

Characterizations: The crystalline structure of the active powder was characterized by powder X-ray diffractometry (XRD) on a Shimadzu XRD-6000 diffractometer with CuKa source. The morphological view of the powder was observed by Scanning Electron Microscopy (Sirion 2000, FEI) and Transmission Electron Microscopy (JEM-2010HT and JEM-2010FEF).

Electrochemical Measurements: The electrochemical measurement of the Sb/C nanocomposite as anode-active materials was examined by 2032 type coin cells. The working electrode was made by spreading an electrode slurry of 80 wt % active material, 10 wt% CMC binder and 10 wt% Super P on copper foil substrate. The mass loading of the active material within the film was about 3 mg cm^{-2}. The mass loading of the active material in our film electrode was about 3 mg cm-2 and the area of the Sb/C electrode for 2032 type coin cells was restricted to be ～1.13 cm$^{2.}$ Then the electrode film was dried in 80 °C oven for overnight. A sodium disk was served as the counter and reference electrode. The electrolyte used in this work was 1.0 mol/L $NaPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) solution with or without addition of 5% fluoroethylene carbonate (FEC). All the cells were assembled in a glove box with water/oxygen content lower than 1ppm and tested at room temperature. The galvanostatic charge/discharge test was conducted on LAND cycler (Wuhan Kingnuo Electronic Co., China). Cyclic voltammetric measurements were carried out with coin cell at a scan rate of 0.1 mV/s using a CHI 600c electrochemical workstation (ChenHua Instruments Co., China). Electrochemical impedance spectra were recorded by the Impedance Measuring Unit (IM 6e, Zahner) with oscillation amplitude of 5 mV at the frequency range from 100 m Hz to 100 kHz.

1. Electrochemical sodium insertion/extraction capacities of Super P carbon

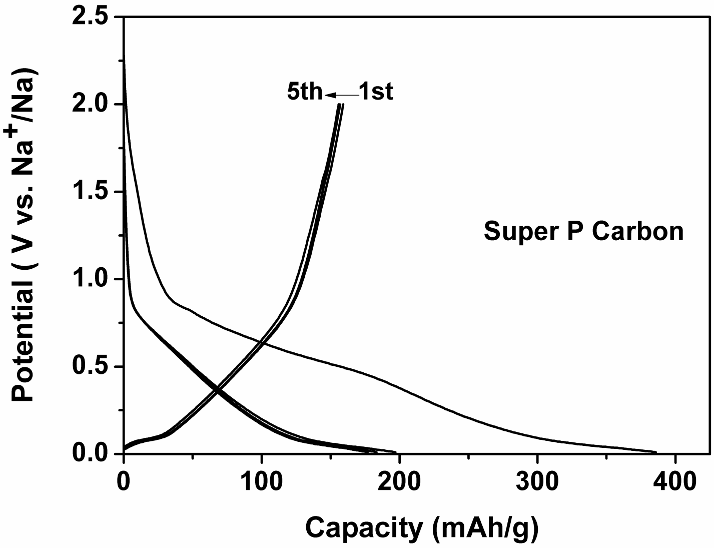

Figure S1. Charge-discharge curves of the Super P carbon at a cycling current of 100 mA/g.

The first charge and discharge capacity of the super P carbon are 386 and 152 mAh/g, corresponding to an initial columbic efficiency of 40%. Considering that the carbon content in the Sb/C composite is 30% by weight, the super P would contribute a part of reversible capacity ca. 46 mAh/g (152 mAh/g × 30%) and initial irreversible capacity of 70 mAh/g. In order to analyze clearly the electrochemical utilization of electroactive Sb component, we expressed all the capacity values of the Sb/C composite on the basis of the mass of Sb.

2. XRD patterns of the Sb/C anode charged and discharged at different depths.

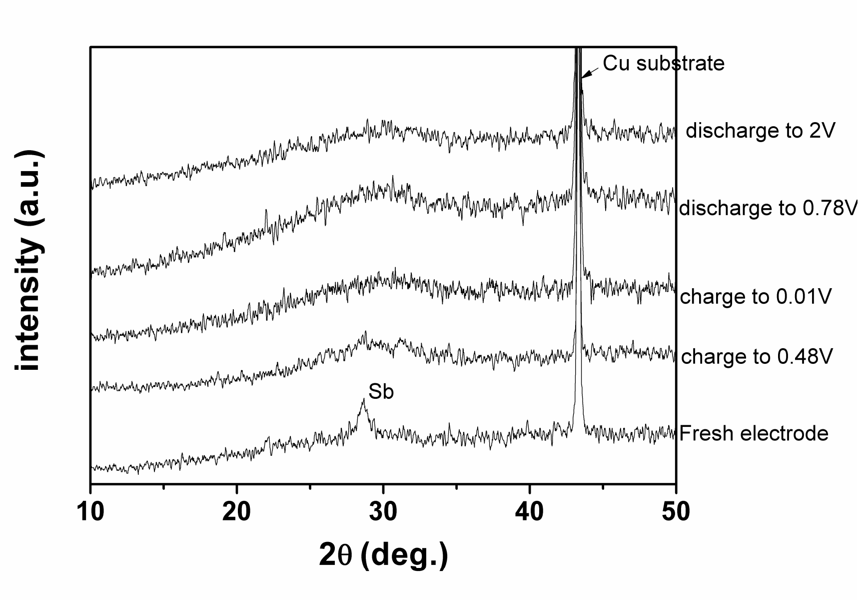

Figure S2. XRD patterns of the Sb/C nanocomposite in different depths of charge and discharge at the first cycle.

As revealed in the XRD analysis above, the Sb/C composite lost its crystallinity, since the first charge (Na-insertion), to show a featureless XRD pattern throughout following charge and discharge cycles. This could be attributed to a rapid amorphization and the subsequent apparent solid solution behavior of the electrode material.

3. Electrochemical sodium insertion/extraction propeties of metallic Sb

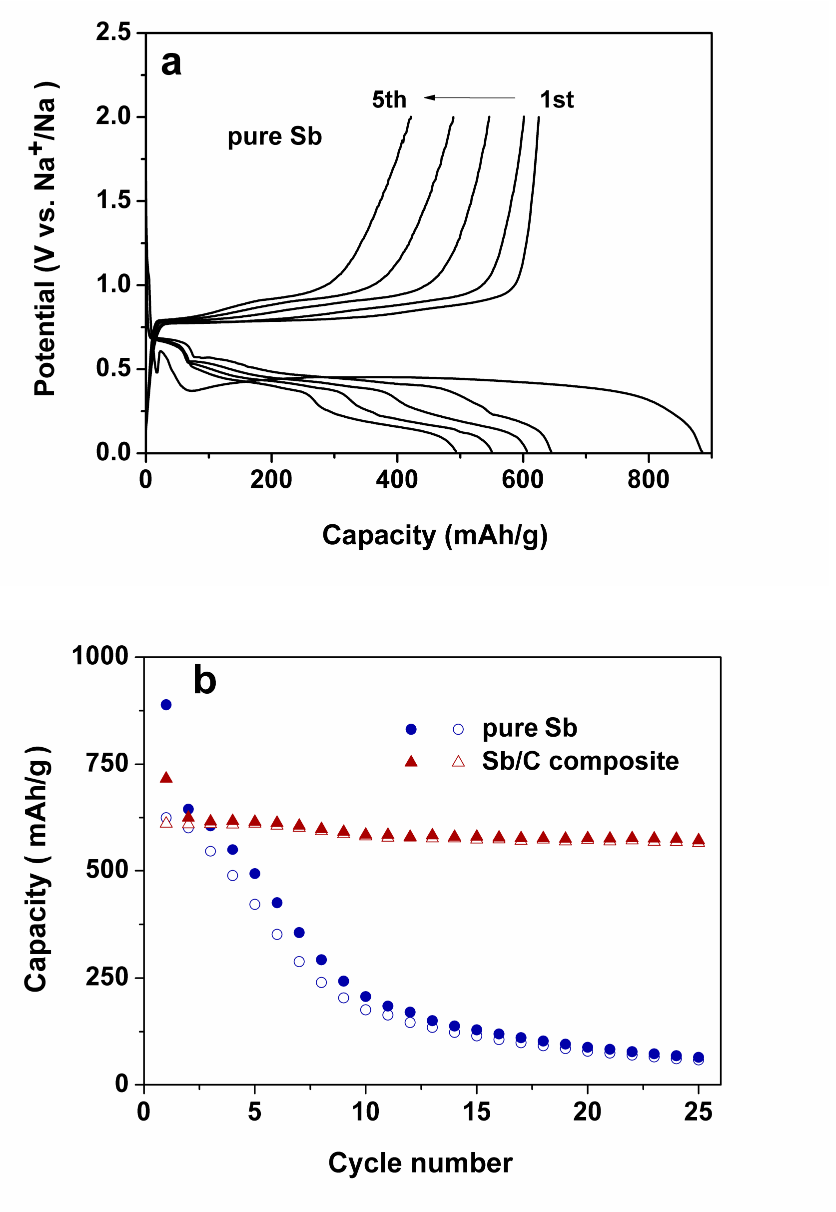

Figure S3. a. Charge-discharge curves of the metallic Sb powder at a cycling current of 100 mA/g. b. A comparision of the cycling capacities of the metallic Sb and the Sb/C nanocomposite electrode at a current rate of 100 mA/g;

4. EIS analysis of the Sb/C electrode cycled in the electrolytes with and without addition of 5% FEC additive.

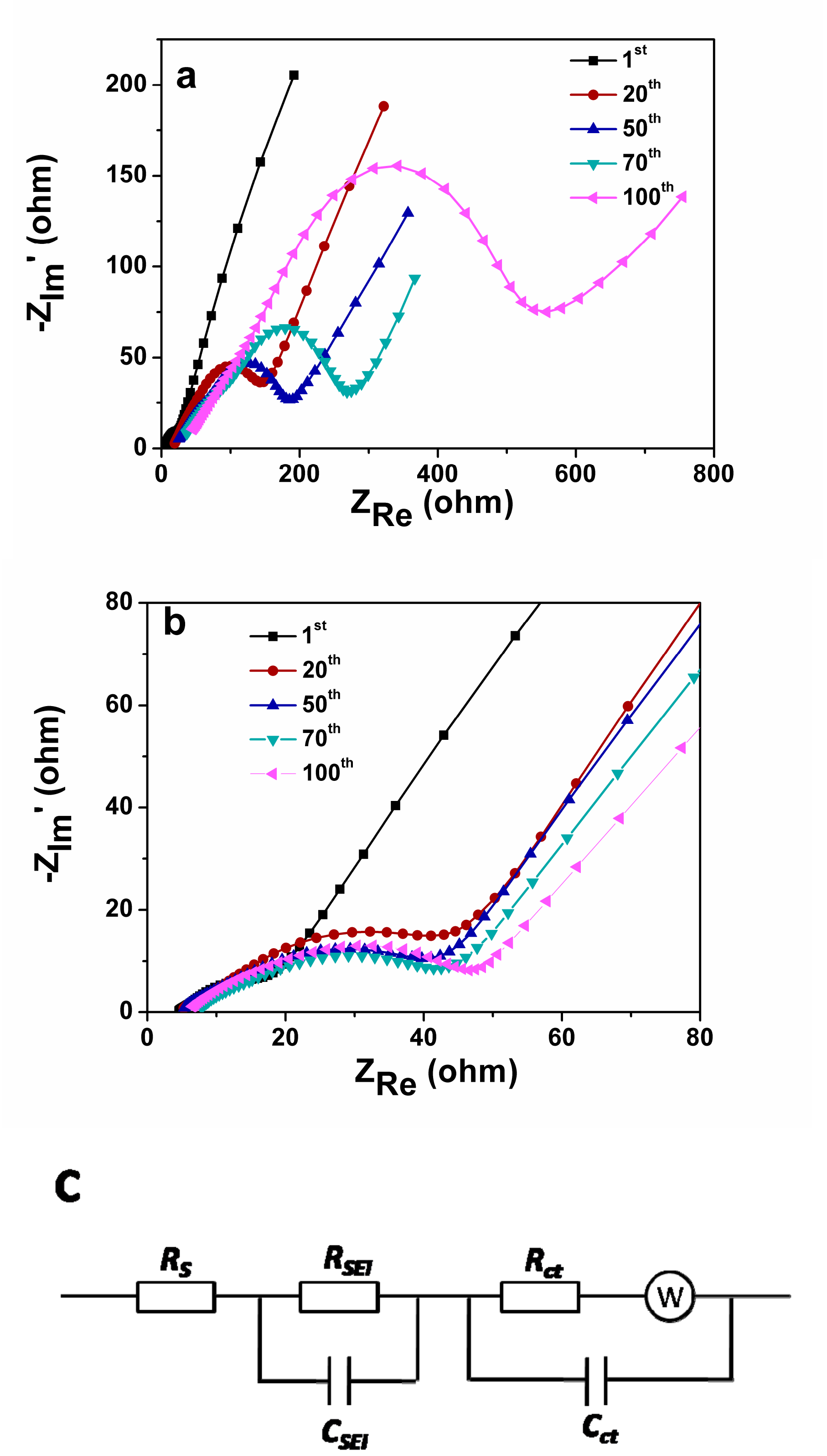

Figure S4. Electrochemical impedance spectra (EIS) of the Sb/C electrode at selected cycles from 1st, 20th,50th, 70th, to 100th in 1.0 mol/L $NaPF_6$ + EC-DEC electrolyte: a. with no FEC; b. with 5% FEC additive; c. Equivalent circuit for the EIS spectra.

5. The changes of the the SEI film resistance (R_{SEI}) and the charge transfer resistance (R_{ct}) of the Sb/C electrodes with cycles, measured in the 1.0 mol/L $NaPF_6$ + EC-DEC electrolyte with and with addition of 5% FEC additive

Table S1. Simulation results of the EIS spectra using the equivalent circuit shown in Figure S3c.

cycle	FEC-free		5% FEC-additive	
	R_{SEI}	Rct	R_{SEI}	Rct
1st cycle	7.7	12.7	5.756	8.79
10th cycle	108.7	100	23.64	16.82
20th cycle	68.67	49.68	21.58	22.05
30th cycle	85.36	53.38	25.79	15.4
40th cycle	78.9	44.37	24.4	17.39
50th cycle	127.3	134.9	23.67	15.6
60th cycle	166.5	101.4	28.81	22.45
70th cycle	184.7	58.47	21.85	13.52
80th cycle	174.9	74.54	23.42	14.39
90th cycle	200.6	115.6	23.22	15.46
100th cycle	392.8	165.8	29.34	13.51