

Supporting Information

Super Stable Antimony-carbon Composite Anodes for Potassium-ion Batteries

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Experimental section

Materials and Synthesis:

Antimony chloride (340 mg) was first dissolved into 10 mL N, N-dimethylformamide (DMF). Then, polyacrylonitrile (PAN, 160 mg) was added to the solution followed by vigorous stirring overnight. The as-obtained mixture was used as the precursor for electrospray. The precursor solution was loaded into a 10 mL syringe tube and pumped through a flat-top stainless-steel needle (inner diameter: 203.2 μm). A pumping rate of 0.5 mL/hour, a voltage of 20 kV and a distance of 10 cm between the needle and the aluminum substrate were employed for the electrospray process. The as-prepared sample was loaded into a tube furnace, heated up to 250 $^{\circ}\text{C}$ with a heating rate of 5 $\text{min}/^{\circ}\text{C}$ in the air atmosphere, and kept at 250 $^{\circ}\text{C}$ for 30 mins. Then, the sample was heated up to 600 $^{\circ}\text{C}$ with a heating rate of 2 $^{\circ}\text{C}/\text{min}$ under H_2/N_2 (v:v=5:95) atmosphere and kept at 600 $^{\circ}\text{C}$ for 5 hours to obtain the desired Sb@CSN material.

Computational Method:

To study the electrochemical process during the K insertion into Sb at an atomic scale, first-principle computations based on density functional theory (DFT) ^{1, 2} are performed using the Vienna *Ab Initio* Simulation Package (VASP). ³ The Projector Augmented Wave (PAW) ⁴ method with an energy cut-off of 520 eV is used to describe the ion-electron interaction on a well-converged k-point mesh. The Perdew-Burke-Ernzerhof (PBE) functional in the Generalized Gradient Approximation (GGA) ⁵ is employed to calculate the exchange-correlation energy. The equilibrium voltage plateaus are computed by Nernst equation using the calculated DFT energies of all relevant equilibrium phases in K-Sb phase diagram from the Materials Project. ⁶ The geometry optimizations are performed using the conjugated gradient method, and the convergence threshold is set to be 10^{-5} eV in energy and 0.01 eV/Å in force. Visualization of the structures is made by using VESTA software. ⁷

Structural Characterization:

The Sb@CSN material was characterized by X-ray diffraction (XRD, Bruker Smart 1000 using a Cu K α line radiation source), thermogravimetry-differential scanning calorimetry (CAHN TG 2131, under Air with a heating rate of 5°C/min), Raman spectra (with 514.5 nm laser source), scanning electron microscopy (SEM, Hitachi SU-70 field emission scanning), high-resolution transmission electron microscopy (HRTEM, 2100F field emission), X-ray photoelectron spectroscopy (XPS, monochromatized ESCALAB 250 with Al K α source radiation, with an Ar⁺ sputtering gun). The electrolyte ignition and combustion experiment were recorded by high-speed digital camera with a Vision Research Phantom v 12.1 digital camera, and the frame rate of 1,000 frames per second with a resolution of 640 × 480 pixel. A small piece of glass fiber membrane was soaked with about 0.5 mL electrolyte and fixed by an alligator clip, followed by immediate ignition with a butane lighter.

Electrolytes Preparation:

The salts of potassium trifluoromethanesulfonimide (KTFSI) and potassium hexafluorophosphate (KPF₆) was purchased from TCI and used as received. The solvents of Ethylene Carbonate (EC) and Diethyl Carbonate (DEC) were purchased from Sigma-Aldrich and used without any purification. The different electrolytes are prepared in Ar-filled glovebox as follows: a certain molar of salt dissolving into the mixed solvent of EC+DEC (V: V=1: 1) to obtain different electrolytes: 4M KTFSI/EC+DEC electrolyte (abbreviated as “4M KTFSI”), 1M

KTFSI/EC+DEC electrolyte (abbreviated as “1M KTFSI”), and 1M KPF₆/EC+DEC electrolyte (abbreviated as “1M KPF₆”).

Coin cells preparation:

The Sb@CSN composite, conductive carbon (from SAFT) and sodium alginate with a mass ratio of 8:1:1 were mixed in certain amount of H₂O solvent to form homogeneous slurry by stirring for 2 hours. The slurry was coated onto a thin Cu foil and dried at 90 °C for 10 h in vacuum. The coin cells (CR2032) were assembled in the Ar-filled glove box with the as-prepared Sb@CSN composite as the working electrode, pure potassium metal foil as the counter electrode, polypropylene microporous (PP, Celgard) film as the separator.

Electrochemical Measurements:

The galvanostatic charge/discharge tests were performed with Arbin Battery instrument (BT2000, Arbin Instruments, USA) at a voltage range of 0.01-2.0 V at room temperature. The galvanostatic intermittent titrations (GITT) were also tested after 10 cycle’s charge/discharge activation cycles on the Arbin station by alternating the current density with 100 mA/g for 20 min and rest intervals for 2h. Cyclic voltammetry (CV) measurements were performed on Gamry instrument (Reference 3000) with a scan rate of 0.1 mV/s in the range of 0.01 to 2.0 V. Electrochemical impedance spectroscopy (EIS) were also tested on the Gamry instrument with a frequency range of 10⁵ to 10⁻² Hz under the AC signal amplitude of 5 mV.

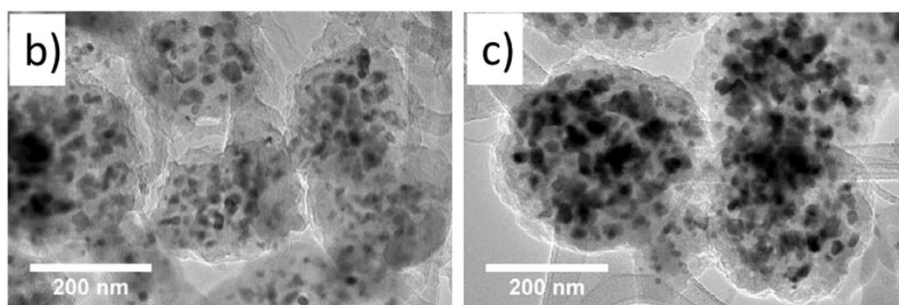
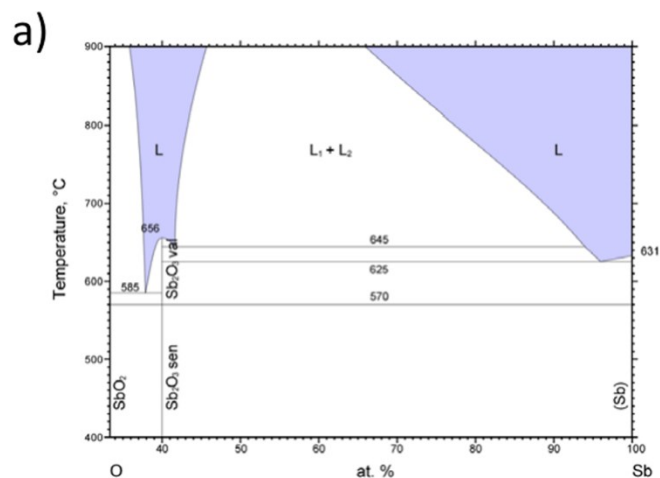


Figure S1. a) Oxygen-antimony binary phase diagram⁸; b-c) TEM images of Sb nanoparticles in associated carbon sphere network.

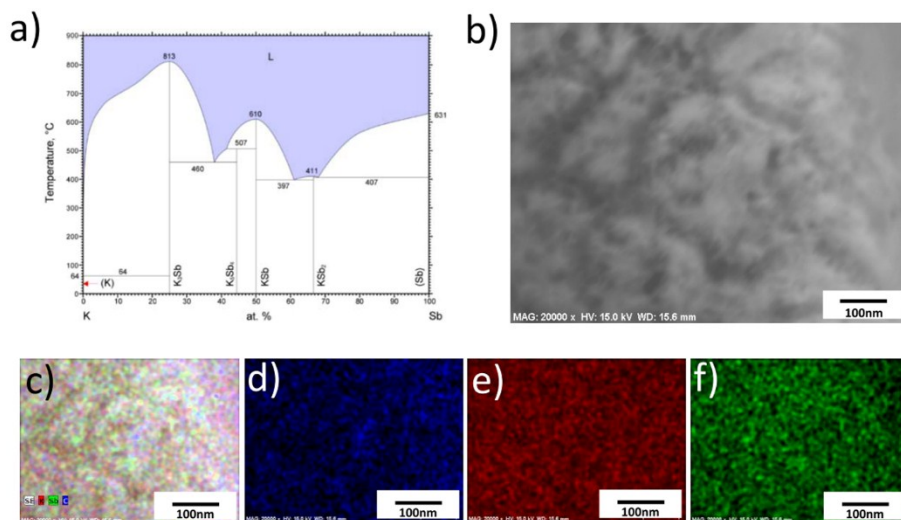


Figure S2. a) Potassium-antimony binary phase diagram; b) SEM image and c-f) the corresponding EDS elemental mapping of Sb@CSN electrode at discharge cut-off voltage of 0.01 V in 4M KTFSI electrolyte.

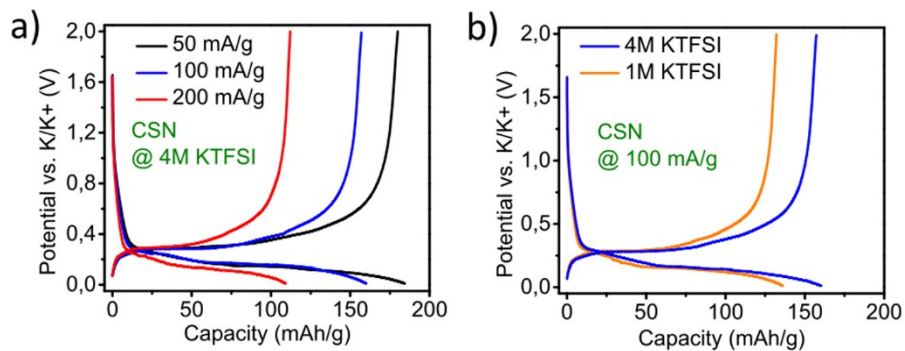


Figure S3. Charge/discharge curves for CSN material a) in 4M KTFSI electrolyte with different current densities, b) in different electrolytes.

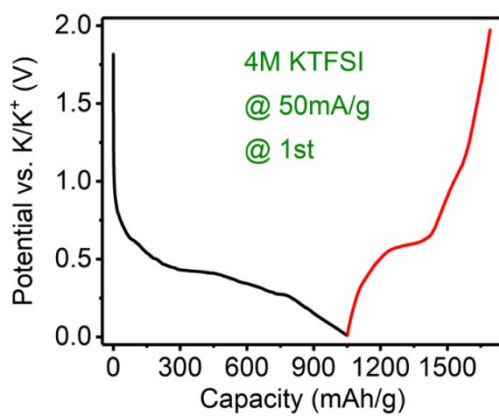


Figure S4. the 1st charge/discharge voltage profile for Sb@CSN electrode at 50 mA/g in 4M KTFSI electrolyte.

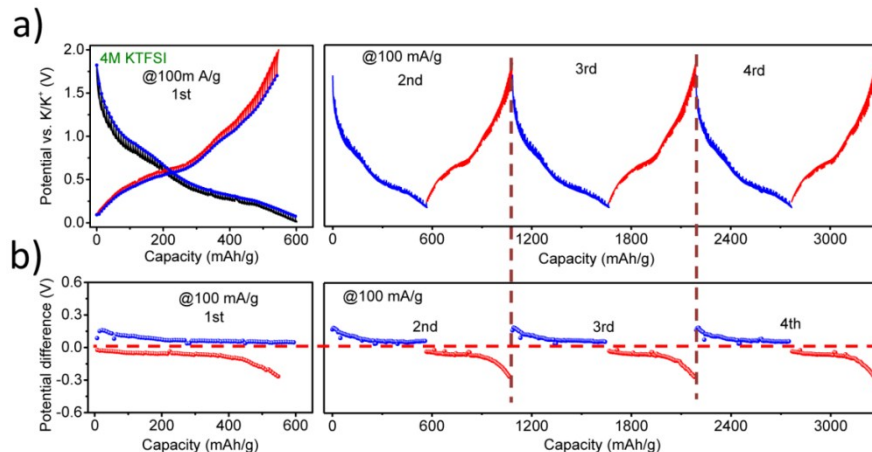


Figure S5. a) four successive GITT curves after 10 activation cycles; b) the potential difference curves for the successive GITT curves in 4M KTFSI electrolyte (Potential difference= rest end potential - rest initial potential).

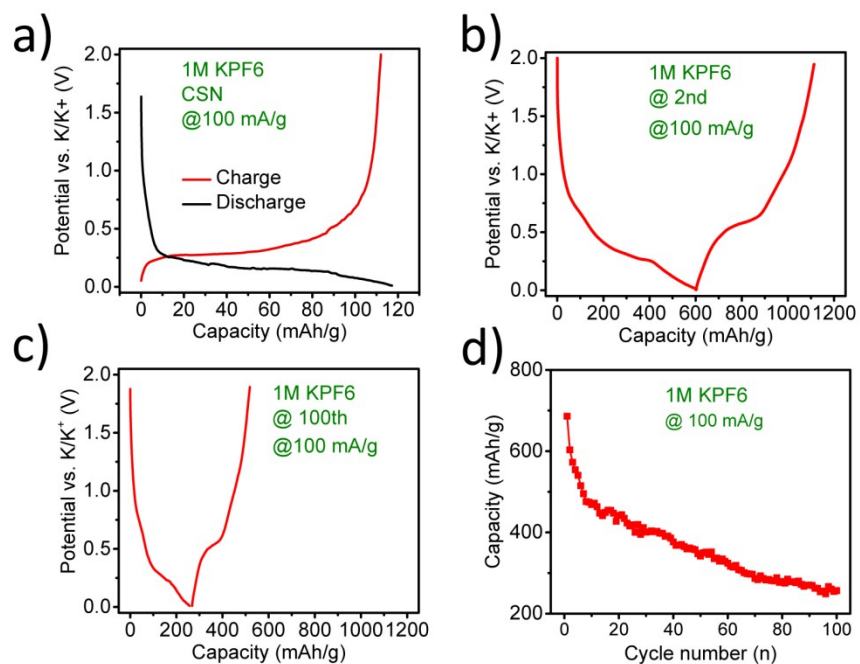


Figure S6. Electrochemical performance in 1M KPF₆ electrolyte: a) charge/discharge curves for CSN material; charge/discharge curves for Sb@CSN anode at b) 2nd and c) 50th cycling; d) its corresponding cycling performance.

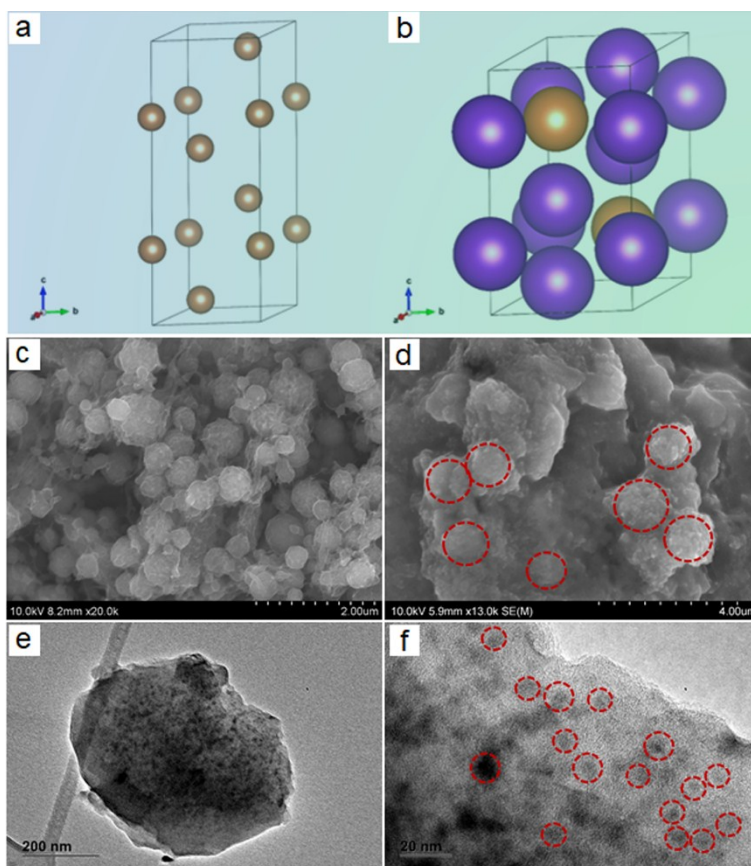


Figure S7. a, b) Crystal structures of a) Sb (space group: $R3m[166]$) and b) K_3Sb (space group: $P63/mmc[194]$); c, d) SEM images of c) fresh prepared Sb@CSN and d) cycled Sb@CSN; e, f) TEM images of cycled Sb@CSN.

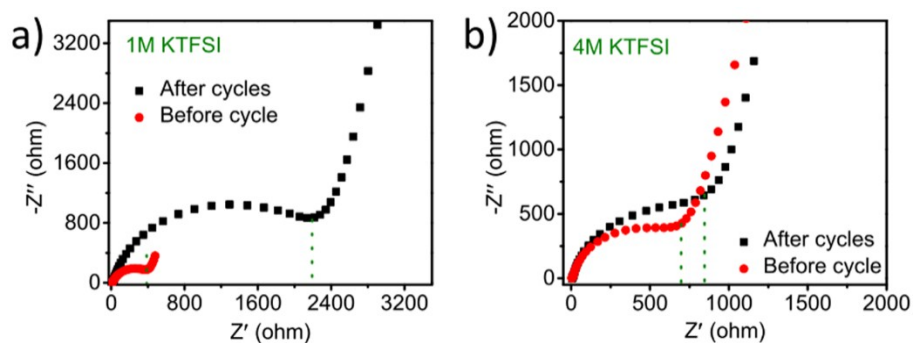


Figure S8. EIS curves before and after 100 cycling at 100 mA/g in a) 1M KTFSI and b) 4M KTFSI electrolyte.

Table S1. A comparison summary of potassium storage performances for the most common anodes materials in the previous reports.

Samples	Current density (mA/g)	Cycle number	Capacity (mAh/g)	Reference
Graphene	100	10	280	9
Sn/C	150	15	25	10
Sb@C	200	15	461	11
Sn/C	25	30	150	12
Graphite	28	50	244	13
Graphite	140	50	139	14
Soft C	228	50	222	14
Graphene	50	50	474	15
Bi/RGO	50	50	290	12
Sn ₄ P ₃ /C	50	50	307	16
Sb/C	35	50	250	17
Sb/C	50	50	470	12
Co ₃ O ₄ -Fe ₂ O ₃	50	50	220	18
K ₂ Ti ₈ O ₁₇	20	50	110	19
Sb@RGO	100	60	368	20
Hard C	28	100	216	21
Bi microparticle	400	100	392	22
Sb@CSN	100	100	551	This work
RGO	10	175	150	23
Hard-soft C	56	200	186	24
MoS ₂	20	200	65	25
Sb@CSN	200	220	504	This work
MoSe ₂ /C	100	300	258	26
CNFs	279	1900	170	27

Table S2. Atomic percentage concentrations of different elements with increasing etching time for the SEI layers on Sb@CSN electrode formed in 1M KTFSI and 4M KTFSI electrolytes.

Electrolytes	Etching times	C(at.%)	K(at.%)	F(at.%)	S(at.%)	N(at.%)	O(at.%)	Sb(at.%)
1M KTFSI	0s	14.3	64.2	1.47	0.21	0	19.8	0
	150s	10.5	71.3	1.67	0.18	0	16.3	0
	300s	8.71	75.3	1.84	0.15	0	13.9	0
	900s	9.62	75.3	1.55	0.14	0.05	13.2	0.11
	1800s	10.5	74.4	1.44	0.1	0.25	13	0.36
	3600s	11	73.5	1.32	0.11	0.39	13	0.81
4M KTFSI	0s	8.67	65.99	1.89	1.86	0.95	20.63	0
	150s	6.18	72.44	2.69	1.67	0.41	16.6	0
	300s	5.93	73.19	2.98	1.63	0.3	15.97	0
	900s	6.13	74.43	3.39	1.42	0.33	14.12	0.18
	1800s	7.56	74.22	3.02	1.13	0.36	13.18	0.53
	3600s	10.72	72.18	2.41	0.92	0.43	12.42	0.92

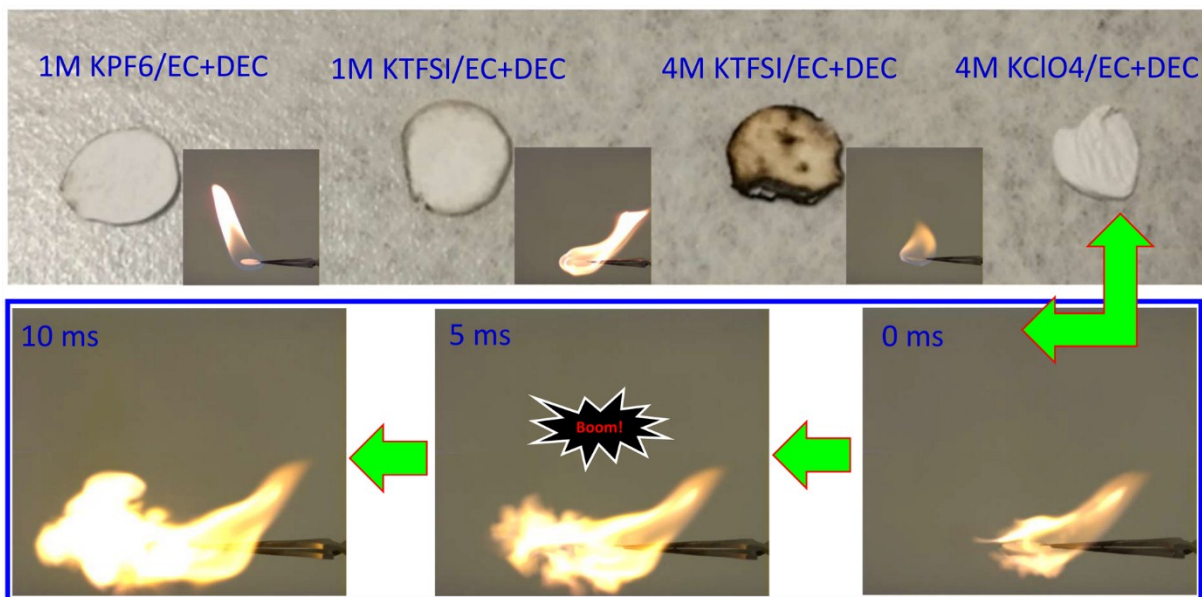


Figure S9. Ignition and combustion experiments for different electrolytes used in PIBs.

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