Supporting Information

Stable and Fast Na-ion Storage of Recovery Carbon from Spent Carbon Cathode of Aluminum Electrolysis

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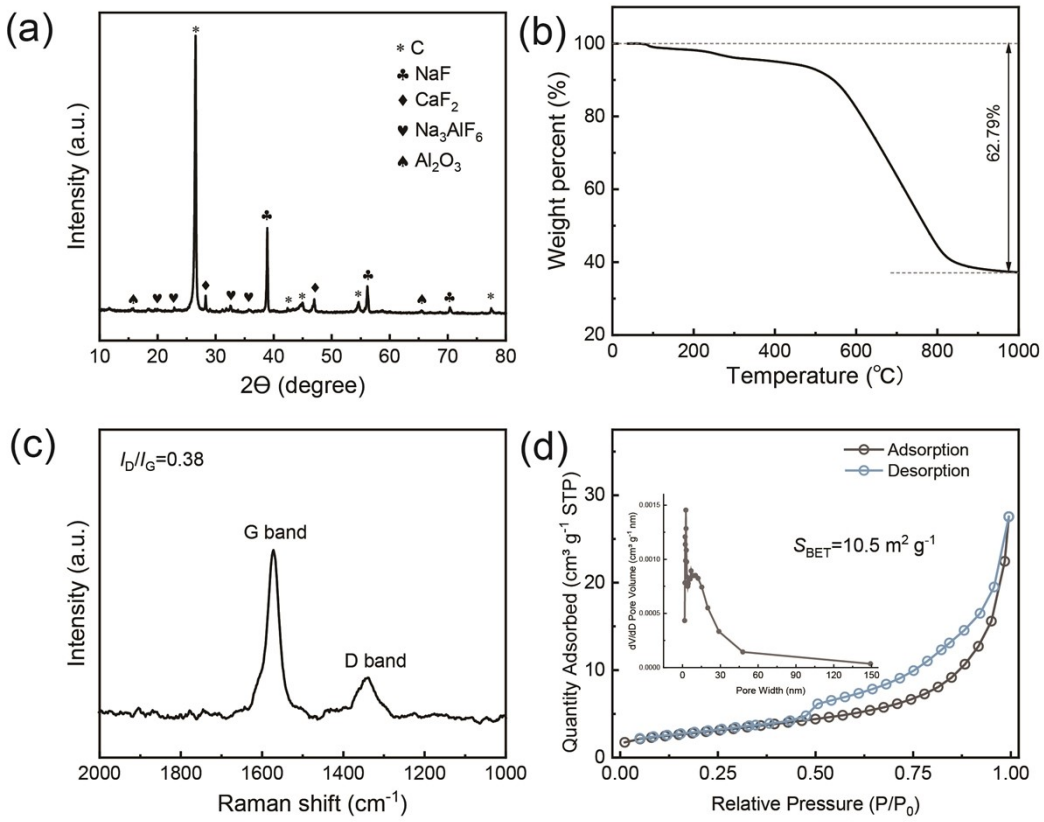

Figure S1. The physical properties of spent carbon cathode. (a) XRD pattern. (b) Raman pattern with deconvolved peaks of D1 and G peak. (c) TG test to identify the carbon content. (d) N_2 adsorption-desorption isotherm and BJH desorption pore size distribution.

For SCC, the diffraction peaks observed in XRD pattern can be indexed to carbon (PDF #89-8487) and the impurities (NaF, CaF_2, Na_3AlF_6, Al_2O_3). The content of carbon is examined by TG test in oxygen atmosphere. The curve indicates that there is 62.79 wt. % carbon in SCC, the remaining is inorganic impurities. And the Raman spectra is used to study the degree of graphitization. The intensity (peak area) ratio (I_D/I_G) of D band (~1350 cm^{-1}, disordered structure) and G band (~1575 cm^{-1}, graphite) is 0.38, meaning that the carbon mainly has ordered structure and high degree of graphitization. The nitrogen adsorption-desorption isotherms reveal that SCC has specific surface area of 10.5 m^2 g^{-1} and mesopores characteristic in the style of type-IV adsorption-desorption

curve with the H3 hysteretic loop ($p/p_0 \approx$ 0.5-1.0), based on Brunauer-Emmett-Teller (BET) analysis. And the pore size distribution (based on Barrett-Joyner-Halenda (BJH) model) indicates that SCC mainly has mesopores, mostly with 2.7 nm width, and slightly macropores (>100 nm).

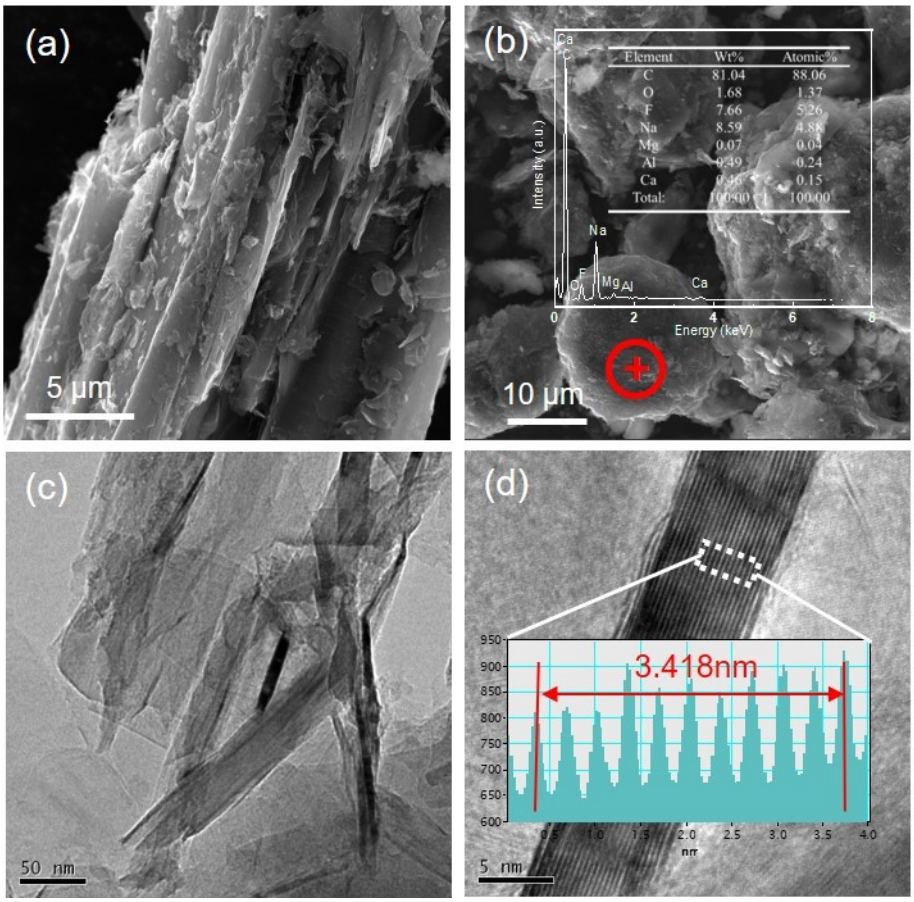

Figure S2. The morphology of spent carbon cathode. (a-b) SEM images at different magnifications, and the elements content from EDS spot scanning are inserted in (b). (c-d) TEM and HRTEM images.

The morphology and elements composition of the SCC are checked by SEM. The SCC mainly composed of flake structure. The elements composition checked by EDS spot scanning shows that C, O, F, Na, Mg, Al, Ca can be detected, among them, the F and metal element attributing to unremoved impurities. Moreover, the TEM images shows

that SCC has nanosheets structure, with 3.418 Å lattice interlayer of the graphite-like structure.

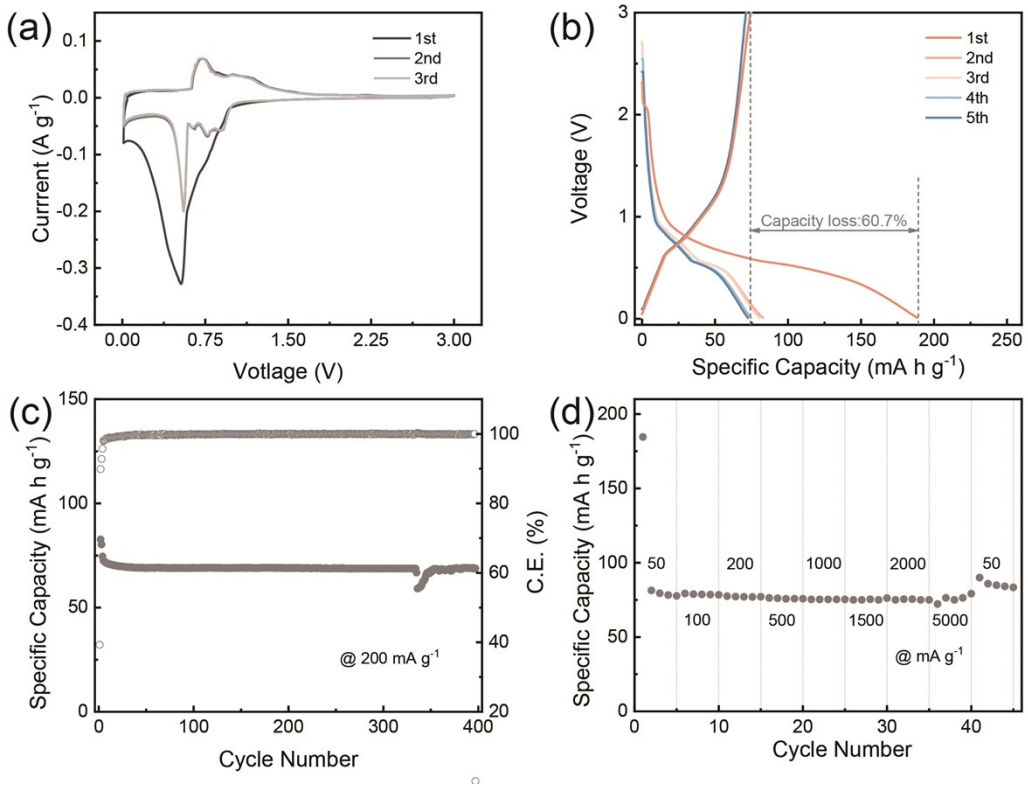

Figure S3. The electrochemical performance of spent carbon cathode anode. (a) CV curves of first three cycles at 0.1 mV s^{-1} at 0.01~3.00 V *vs*. Na/Na^+. (b) The charge-discharge curves for the first five cycles. (c) Cycling performance under 200 mA g^{-1} for 400 cycles. (d) Rate performance.

The kinetics and electrochemical performance of SCC when used as anode for NIB are studied. In the first three cycles of CV, the distinct oxidation and reduction peaks in 0.4-1.5 V represent the formation of Na-graphite intercalation compounds (Na-GIC). However, the capacity loss in the first cycle is huge, up to 60.7%. This is the decomposition of electrolyte and the formation of solid electrolyte interface (SEI) at the anode/electrolyte interface. The long-term stability is tested under 200 mA g^{-1}, giving ~75 mA h g^{-1} for 400 cycles, and nearly 100 % coulombic efficiency all the time.

What's more, in the rate capability test from under 50 mA g^{-1} to 5000 mA g^{-1}, the capacity does not show obvious decline.

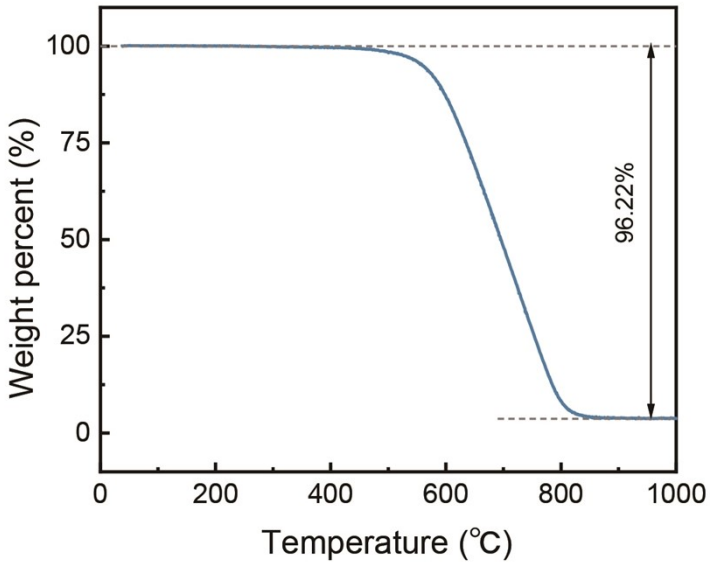

Figure S4. TG test to identify the carbon content.

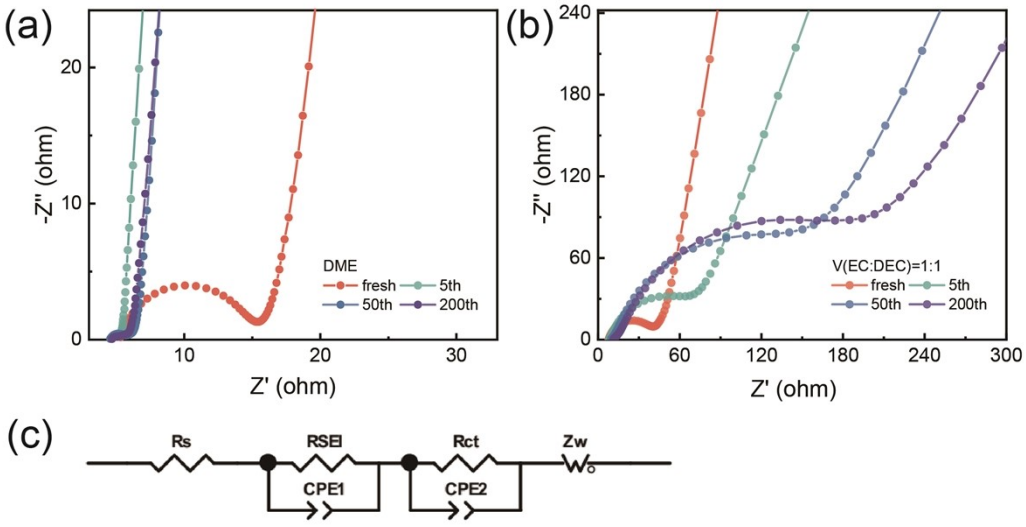

Figure S5. The Nyquist plot of RC in (a) DME and (b) V(EC:DEC)=1:1 electrolytes in the first 200 th cycles and (c) the equivalent circuit.

Table S1. Elemental analysis results (wt.%) of SCC and RC.

Sample	C	S	Ca	O	K	Na	F	Si	Al	Fe	Others
SCC	63.04	0.30	3.89	2.90	1.02	10.32	9.77	0.42	6.30	1.43	0.61
RC	90.29	1.98	1.64	1.36	1.10	0.78	0.78	0.72	0.61	0.37	0.36

Table S2. Equivalent circuit fitting results of Nyquist plot.

Electrolyte	Cycles	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
DME	Fresh	5.48	1.167	7.47
	5th	4.81	0.06	0.50
	50th	4.63	0.44	0.53
	200th	4.70	0.23	1.30
V(EC:DEC)=1:1	Fresh	7.54	23.46	0.72
	5th	8.00	21.28	40.83

	50th	9.17	107.20	49.99
	200th	10.66	134.70	94.95