Electronic Supplementary Information

Hierarchical nickel nanowire@NiCo2S4 nanowhiskers composite arrays with test-tube-brush-like structure for high-performance supercapacitors

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Fabrication of NNA@$NiCo_2S_4$ with different mass loadings

The synthesis of NNA@$NiCo_2S_4$ follows a two-step hydrothermal method. Typically, 0.25 g $Co(NO_3)_2 \cdot 6H_2O$, 0.12 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.09 g urea were dissolved in 60 mL deionized water to form a transparent pink solution followed by immersing a piece of NNA (2 cm × 2 cm) into the solution. This solution containing NNA was then transferred to a 100 mL Teflon-lined stainless steel autoclave and aged at 120°C for 10 hours. After the first hydrothermal step, the NNA deposited with nickel cobalt carbonate hydroxide precursor (NNA@precursor) sample was taken out and rinsed with ethanol and deionized water for several times and then dried at 60°C for 12 hours. In the second step of the hydrothermal reaction, the NNA@precursor samples were immersed in an aqueous solution containing 0.01 M thioacetamide (TAA) and transferred to a 100 mL Teflon-lined stainless steel autoclave and kept at 180°C for 5h. Later on, the samples were taken out and rinsed with ethanol and deionized water for several times, followed by drying process at 60°C for 12 hours. The mass loading of NNA@$NiCo_2S_4$ was controlled by simply changing the concentration of the solution during the first hydrothermal process. The concentrations of the solutions are given in Table S1. The scanning electron microscope (SEM) images of the NNA@NiCo2S4 with different mass loadings are shown in Figure S3.

Fabrication of nickel foam@$NiCo_2S_4$ (NFNCS) and carbon clothes@$NiCo_2S_4$ (CCNCS)

The fabrication of NFNCS and CCNCS follows a two-step hydrothermal method. Typically, 1.00 g $Co(NO_3)_2 \cdot 6H_2O$, 0.5 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.36 g urea were dissolved in 60 mL deionized water to form a transparent pink solution followed by

immersing a piece of nickel foam (NF) or carbon clothes (CC) (2 cm × 2 cm) into the solution. The solution containing NF or CC was then transferred to a 100 mL Teflon-lined stainless steel autoclave and aged at 120°C for 10 hours. Then the NF or CC coated with nickel cobalt carbonate hydroxide precursor was taken out and rinsed with ethanol and deionized water for several times and then dried at 60°C for 12 hours. In the second step of the hydrothermal reaction, the NF@precursor or CC@precursor samples were immersed in 0.01 M thioacetamide (TAA) solution and transferred to a 100 mL Teflon-lined stainless steel autoclave and kept at 180°C for 5h. Later on, the samples were taken out and rinsed with ethanol and deionized water for several times, followed by drying process at 60°C for 12 hours.

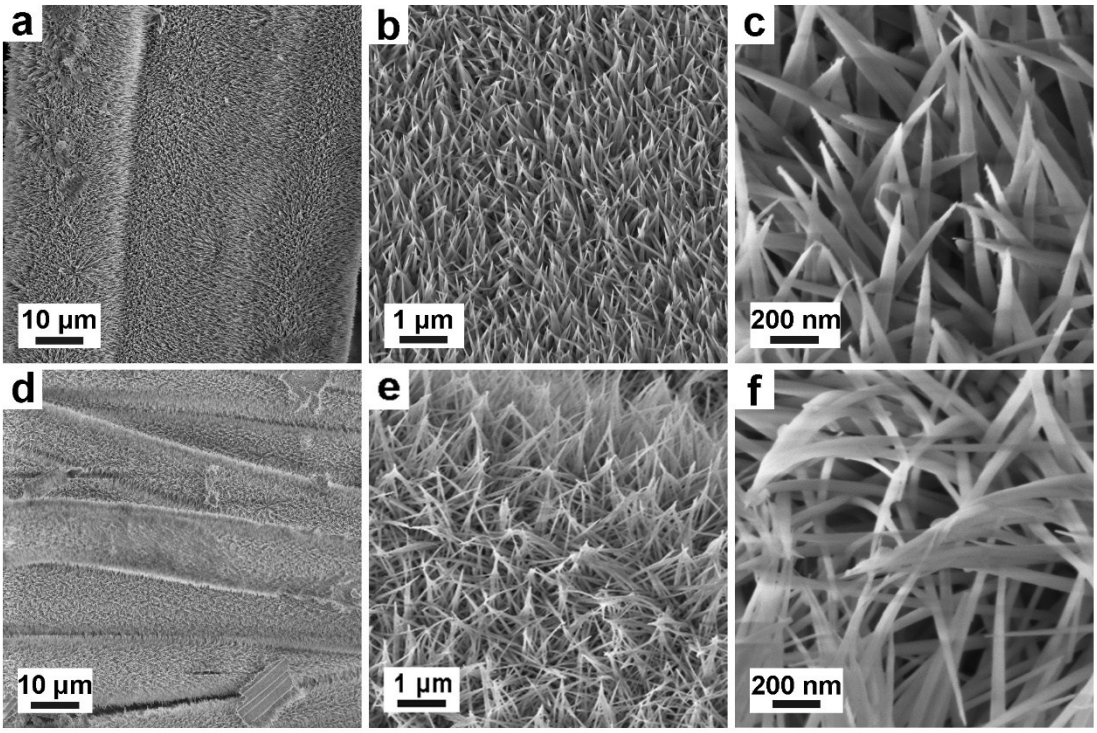

Figure S1. a)-c) SEM images of the nickel foam@$NiCo_2S_4$ (NFNCS) composite materials at different magnifications. d)-f) SEM images of the carbon clothes@$NiCo_2S_4$ (CCNCS) composite materials at different magnifications.

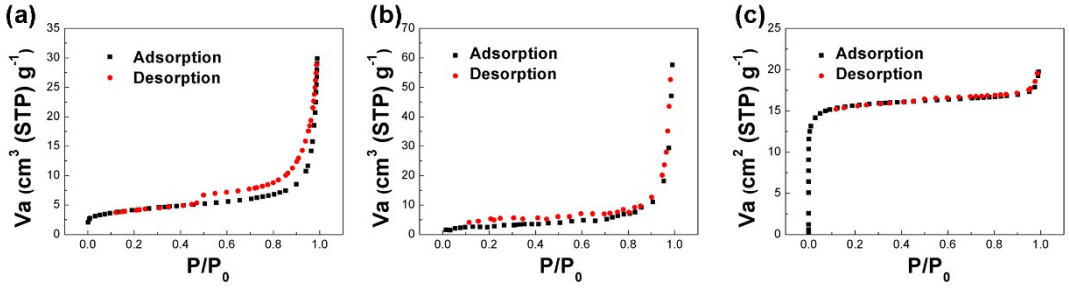

Figure S2. Nitrogen adsorption/desorption isotherms for: a) NFNCS. b) CCNCS. c) NNANCS. The specific surface areas of NFNCS, CCNCS, and NNANCS are calculated to be 14.90, 11,84 and 61.30 $m^2 g^{-1}$, respectively.

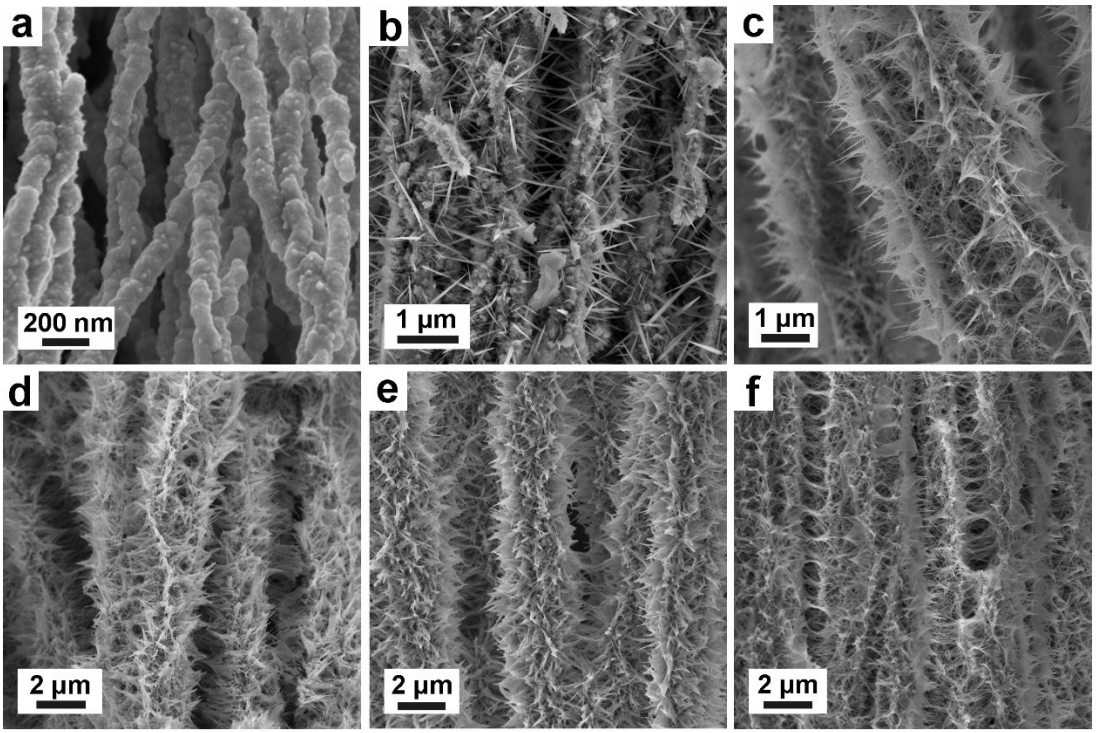

Figure S3. SEM images of: a) bare nickel nanowire arrays and (b-f) NNA@$NiCo_2S_4$ obtained by treating with b) solution 1, c) solution 2, d) solution 3, e) solution 4, and f) solution 5.

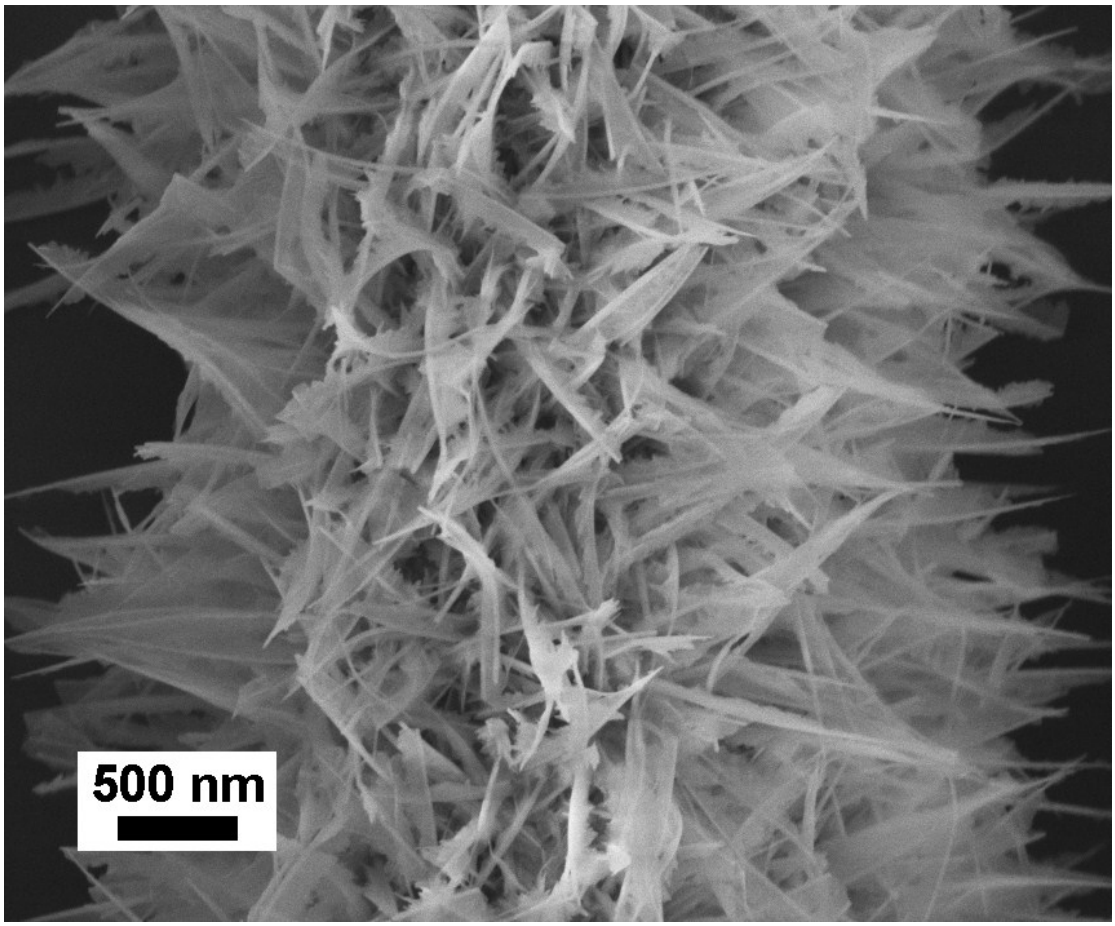

Figure S4. SEM image of the NNA@$NiCo_2S_4$ electrode after repeated charging/discharging at 5 A g^{-1} for 20,000 cycles.

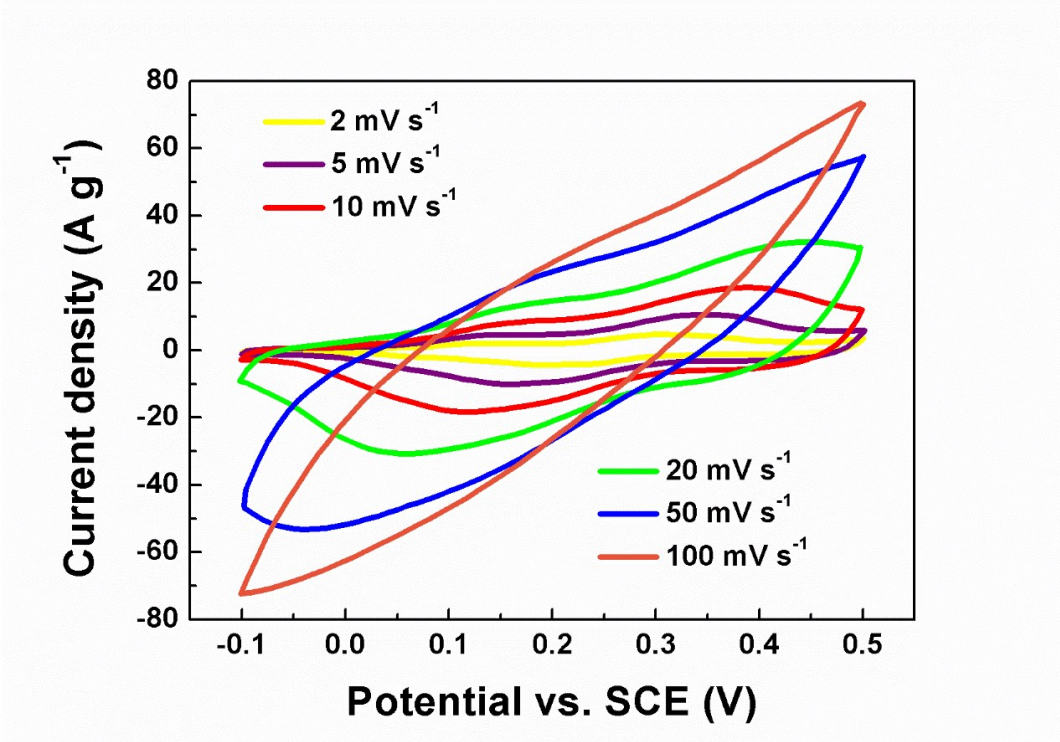

Figure S5. Cyclic voltammetry curves of the NNA@$NiCo_2S_4$ with a mass loading of 10.57 mg cm^{-2} at various scan rates.

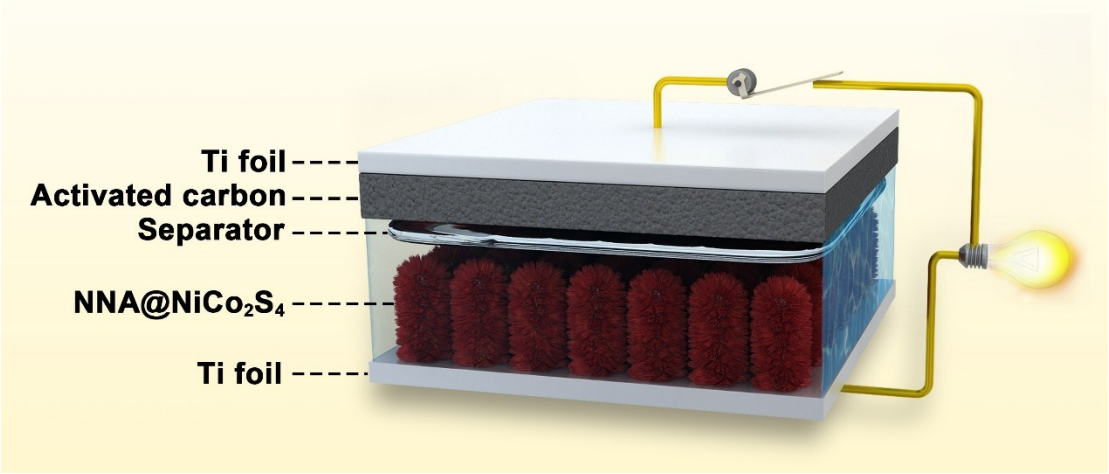

Figure S6. Schematic illustration of the asymmetric supercapacitor

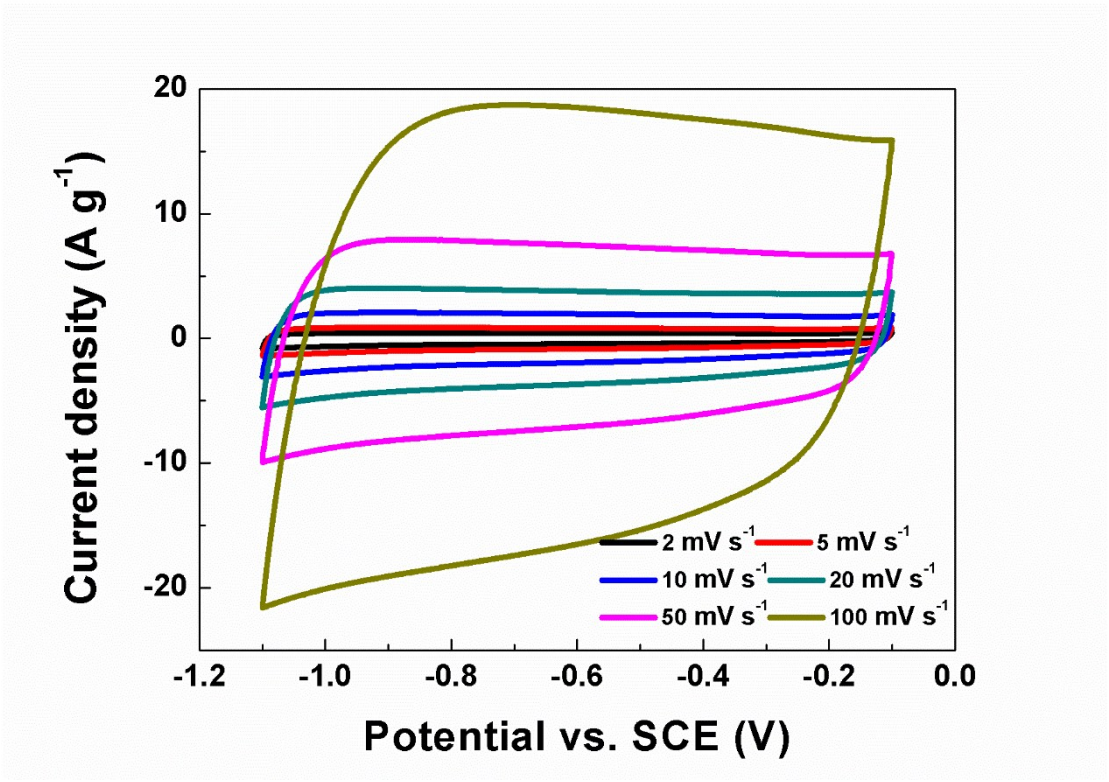

Figure S7. Cyclic voltammetry curves of the activated carbon electrode at various scan rates.

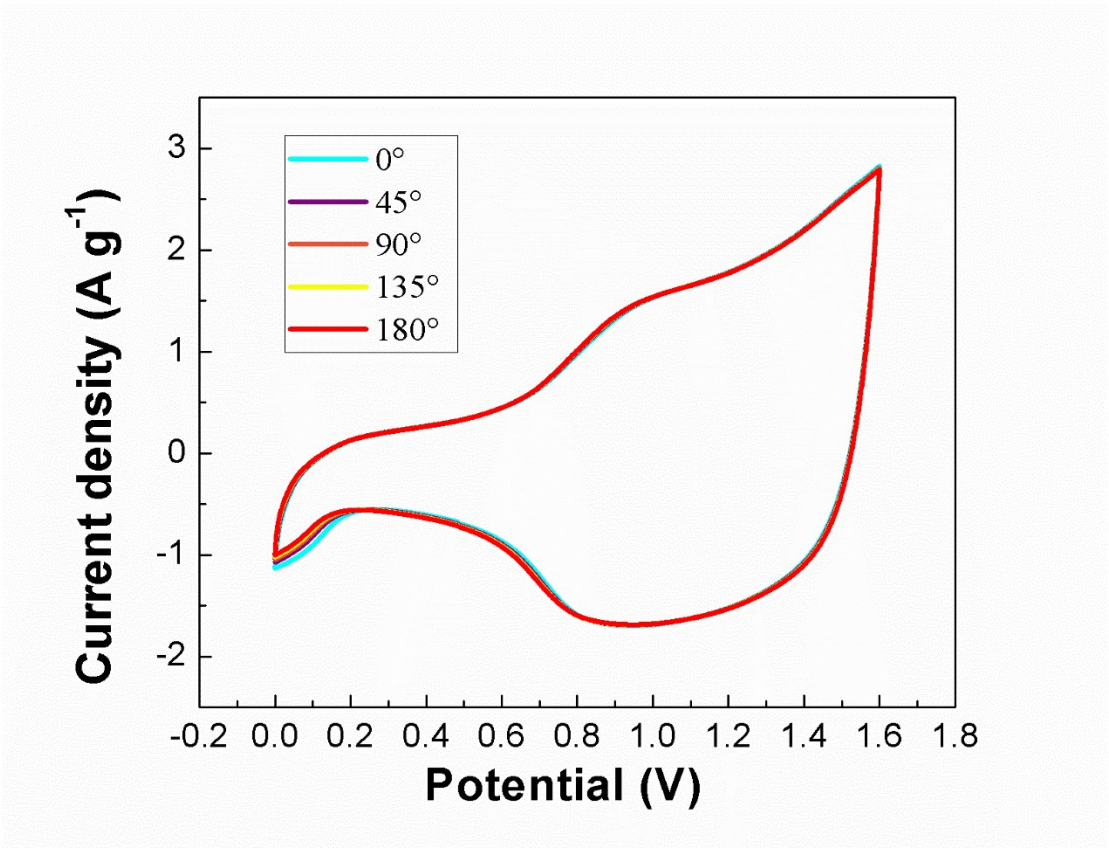

Figure S8. Cyclic voltammetry curves of the aymmetric supercapacitor under different bending angles at the scan rate of 5 mV/s.

Table S1. The mass loadings of NNA@$NiCo_2S_4$ and NNA@precursors obtained from different concentrations of solutions in the first hydrothermal step.

Solution	Masses of solutes in 60 mL water (g)			Mass loading of precursor (mg)	Mass loading of $NiCo_2S_4$ (mg)
	$Co(NO_3)_2$	$Ni(NO_3)_2$	Urea		
1	0.25	0.12	0.09	0.85	0.81
2	0.50	0.25	.018	2.47	2.36
3	1.00	0.50	0.36	4.21	4.03
4	2.00	1.00	0.72	7.18	6.82
5	3.00	1.50	1.08	11.03	10.57

Table S2. Electrochemical performances of Ni-Co sulfide electrodes from recent reports.

Ref	Capacitance at current density	Rate retention	Cycling stability	Energy density at Power density
This work	1,523 F/g at 1 A/g	61.8% from 1~40 A g	92.4% after 20000 cycles	47.29 W h kg^{-1} at 793.5 W kg^{-1}
1	1351 F/g at 1 A/g	58.6% from 1~10 A/g	80.1% after 5,000 cycles	42.55 W h kg^{-1} at 458.8 W kg^{-1}
2	1440 F/g at 3 A/g	75.1% from 2~50 A/g	91.7% after 5000 cycles	28.3 W h kg^{-1} at 245 W kg^{-1}
3	1036 F/g at 1 A/g	68.1% from 1~20 A/g	78.6% after 10000 cycles	22.9 W h kg^{-1} at 10208 W kg^{-1}
4	1492 F/g at 1 A/g	96% from 1~50 A/g	90% after 8000 cycles	43.3 W h kg^{-1} at 800 W kg^{-1}
5	1016 F/g at 2 A/g	79% from 2~20 A/g	87% after 10000 cycles	42.7 W h kg^{-1} at 1583 W kg^{-1}
6	1437 F/g at 1 A/g	61.7% from 1~30 A/g	92.1% after 5000 cycles	39.5 W h kg^{-1} at 1778 W kg^{-1}
7	14.39 F/cm^2 at 5 A/cm^2	66.7% from 5~30 A/cm^2	92% after 5000 cycles	16.6 W h kg^{-1} at 2348 W kg^{-1}
8	1154 F/g at 1 A/g	62.3% from 1~20 A/g	107% after 8000 cycles	17.3 W h kg^{-1} at 1A/g
9	1231 F/g at 2 A/g	71.2% from 2~20 A/g	90.4% after 2000 cycles	45.5 W h kg^{-1} at 512 W kg^{-1}
10	895.2 F/g at 1 A/g	65.4% from 1~20 A/g	85.7% after 1,500 cycles	---
11	1048 F/g at 3 A/g	50.1% from 3~10 A/g	75.9% after 5,000 cycles	---
12	1777 F/g at 1 A/g	40.5% from 1~20 A/g	83% after 3,000 cycles	---
13	1149 F/g at 1 A/g	66.2% from 1~50 A/g	91.4% after 5,000 cycles	---

Reference:

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