Supplementary material

A new method of synthesis of high performance $Na_2FeM(SO_4)_3$ M=Fe, Mn, Ni alluaudites for low cost Na-ion full cells

Anna Plewa, Andrzej Kulka, Emil Hanc, Wojciech Zając, Jianguo Sun, Li Lu, Janina Molenda

Table S1. Crystal data and refinement parameters for X-ray diffraction data.

Chemical formula	$Na_2Fe_2(SO_4)_3$
Crystal system, space group	Monoclinic, C2/c
Temperature	25 °C
Lattice parameters [Å]	a= 12.71; b= 12.84; c= 6.54
α, β, γ [°]	90; 115.61; 90
Unit cell volume [Å^3]	962.32
Rp	2.62%
χ^2	3.11

Table S2. Fractional atomic coordinates and isotropic displacement parameters for X-ray diffraction.

	x	y	z	Occ.	Uiso	Mult.
Na1	0.0	0.7677(9)	0.25	1.0	0.0170	4
Na2	0.0	0.0	0.0	0.744(1)	0.0241	4
Na3	0.0	0.4803(4)	0.25	0.315(3)	0.0253	4
Fe1	0.7278(2)	0.1564(2)	0.1434(5)	0.999(3)	0.0065	8
S1	0.0	0.2237(6)	0.25	1.0	0.0214	4
S2	0.7621(5)	0.5994(4)	0.8696(10)	1.0	0.0171	8
O1	0.0748(7)	0.8572(7)	0.7059(17)	1.0	0.0218	8
O2	0.4485(8)	0.2131(9)	0.5412(17)	1.0	0.03	8
O3	0.7768(10)	0.6703(7)	0.6962(18)	1.0	0.0419	8
O4	0.3388(7)	0.9927(11)	0.3752(16)	1.0	0.0214	8
O5	0.3675(8)	0.5838(9)	0.6771(20)	1.0	0.0711	8
O6	0.3315(7)	0.1588(8)	0.0839(17)	1.0	0.0131	8

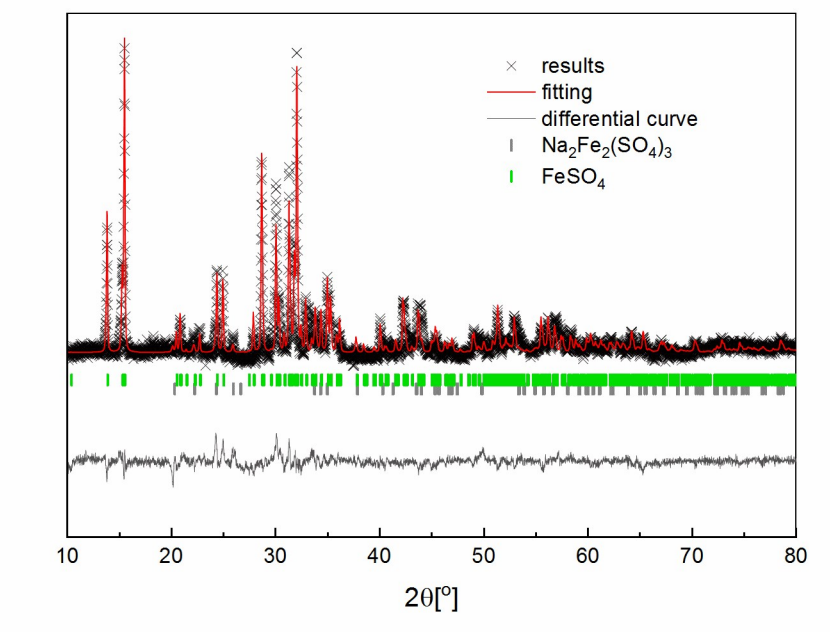

Fig. S1. Refined XRD patterns for $Na_2Fe_2(SO_4)_3$/C.

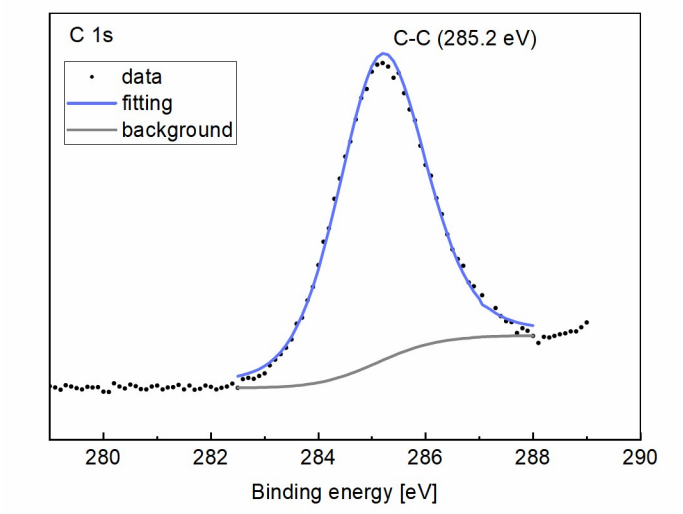

Fig. S2. XPS spectrum for $Na_2Fe_2(SO_4)_3$/C sample (15 wt.% glucose, 25 mol.% CH_3COONa)

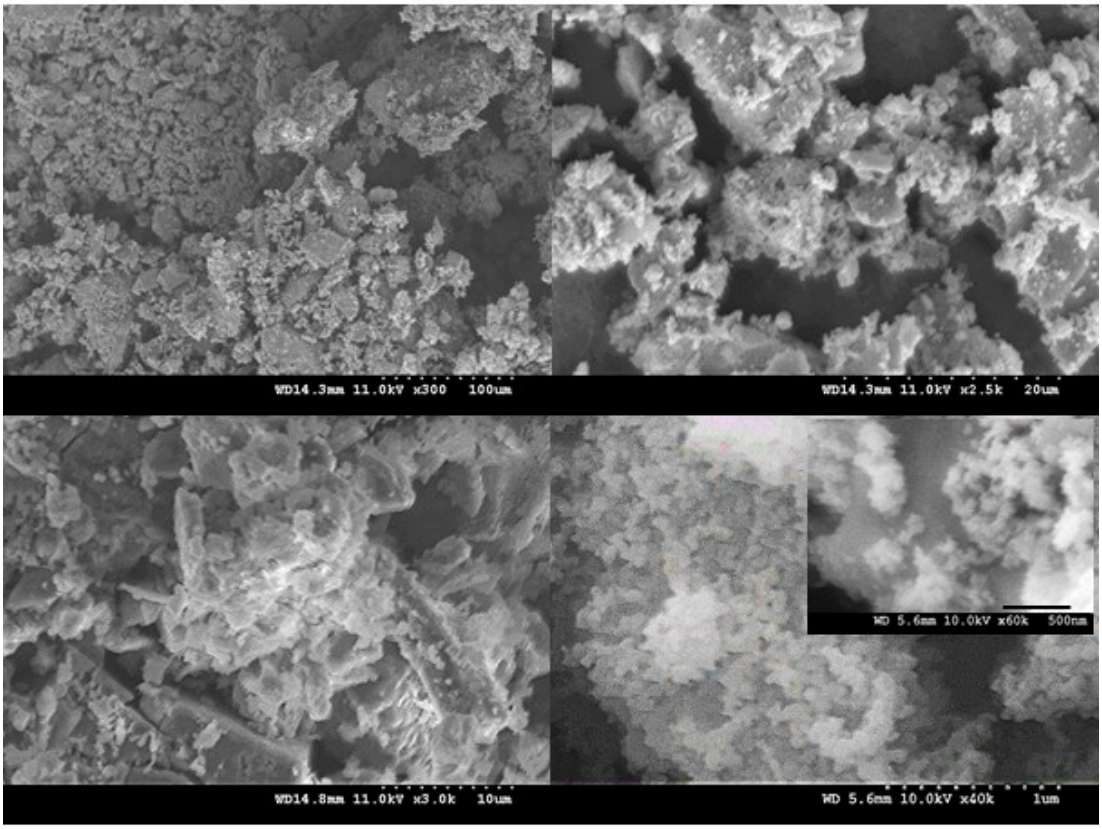

Fig. S3. SEM images of $Na_2FeMn(SO_4)_3$/C.

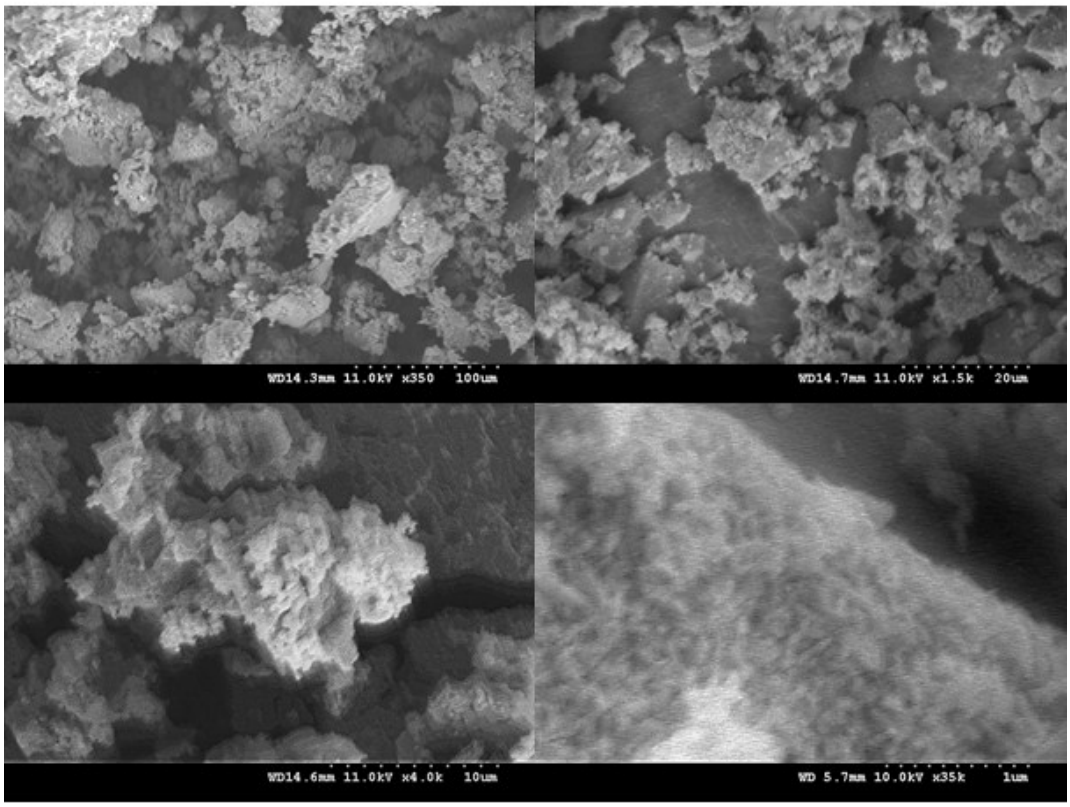

Fig. S4. SEM images of $Na_2Fe_2(SO_4)_3$/C.

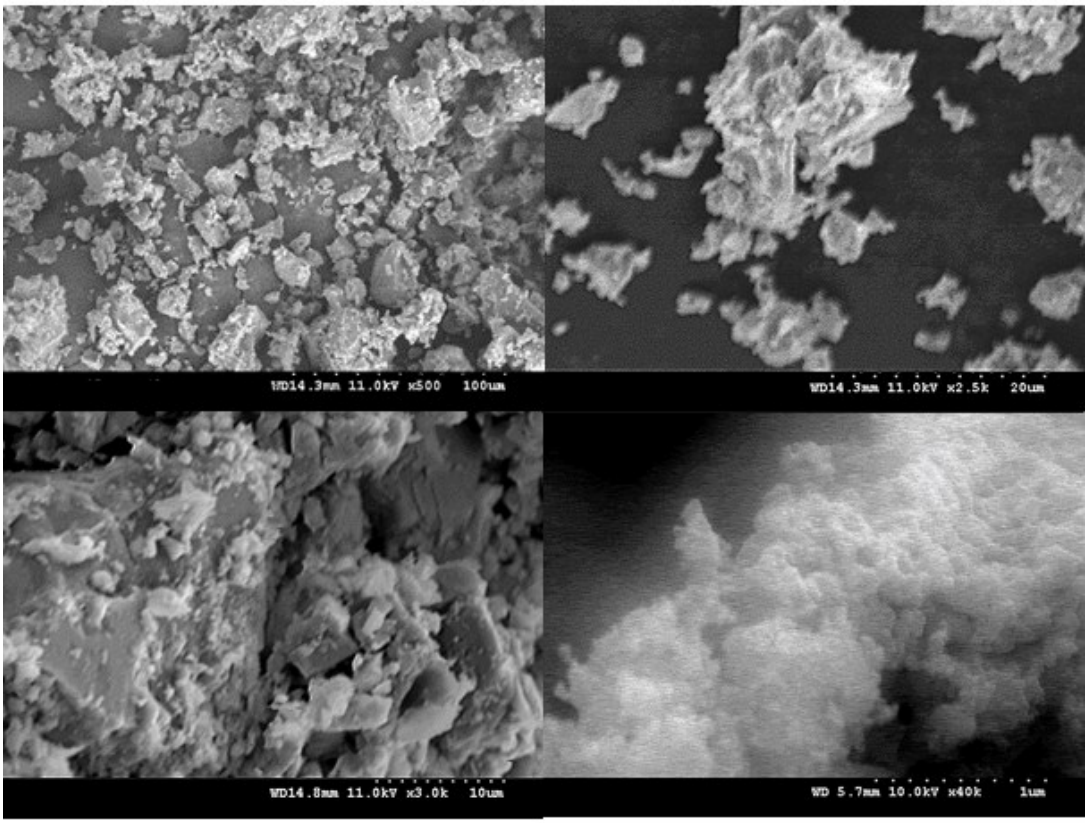

Fig. S5. SEM images of $Na_2FeNi(SO_4)_3/C$.

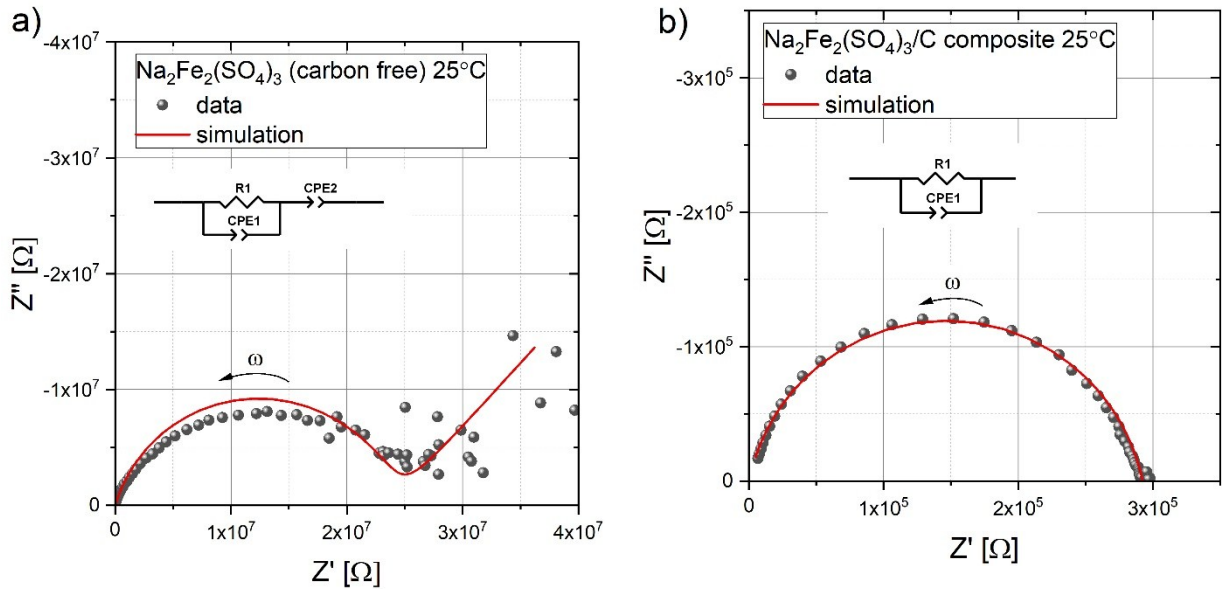

Fig. S6. Impedance spectra of (a) carbon free $Na_2Fe_2(SO_4)_3$ and (b) $Na_2Fe_2(SO_4)_3$/C composite measured at 25°C. Before measurement gold electrodes were sputtered on flat surfaces of disk shape pellets in order to ensure good contact between the sample and frequency response analyzer as well as to form Na-ion blocking electrodes.

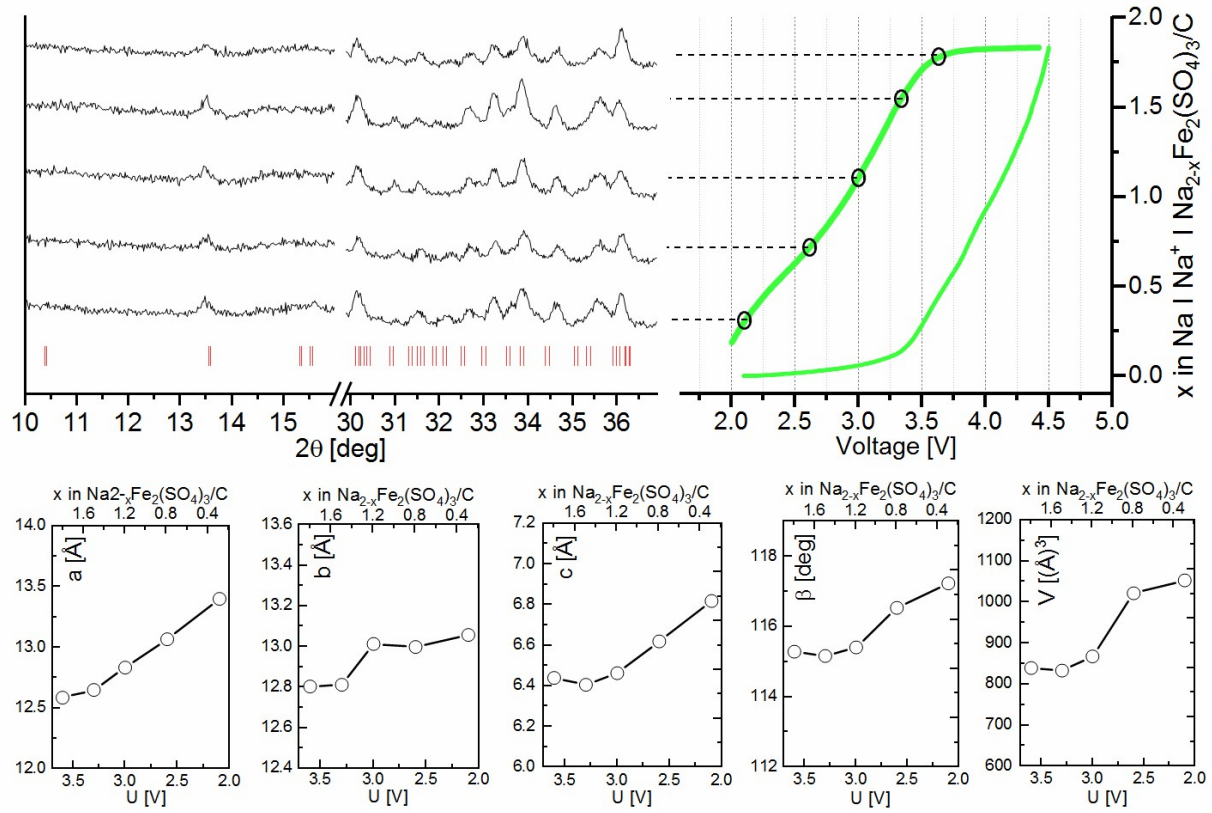

Fig. S7. *Ex-situ* XRD measurements during the first discharging (current at C/10) measured for $Na_2Fe_2(SO_4)_3$/C and change in lattice parameters. For the refinements, the amount of Na was fixed to be those calculated by the electrochemical reaction and relation of lattice parameters were prepared using this values. During cycling Na I Na^+ I $Na_{2-x}Fe_2(SO_4)_3$ alluaudite material uses 1.7 sodium mole which is 85% of sodium content in stoichiometric alluaudite.

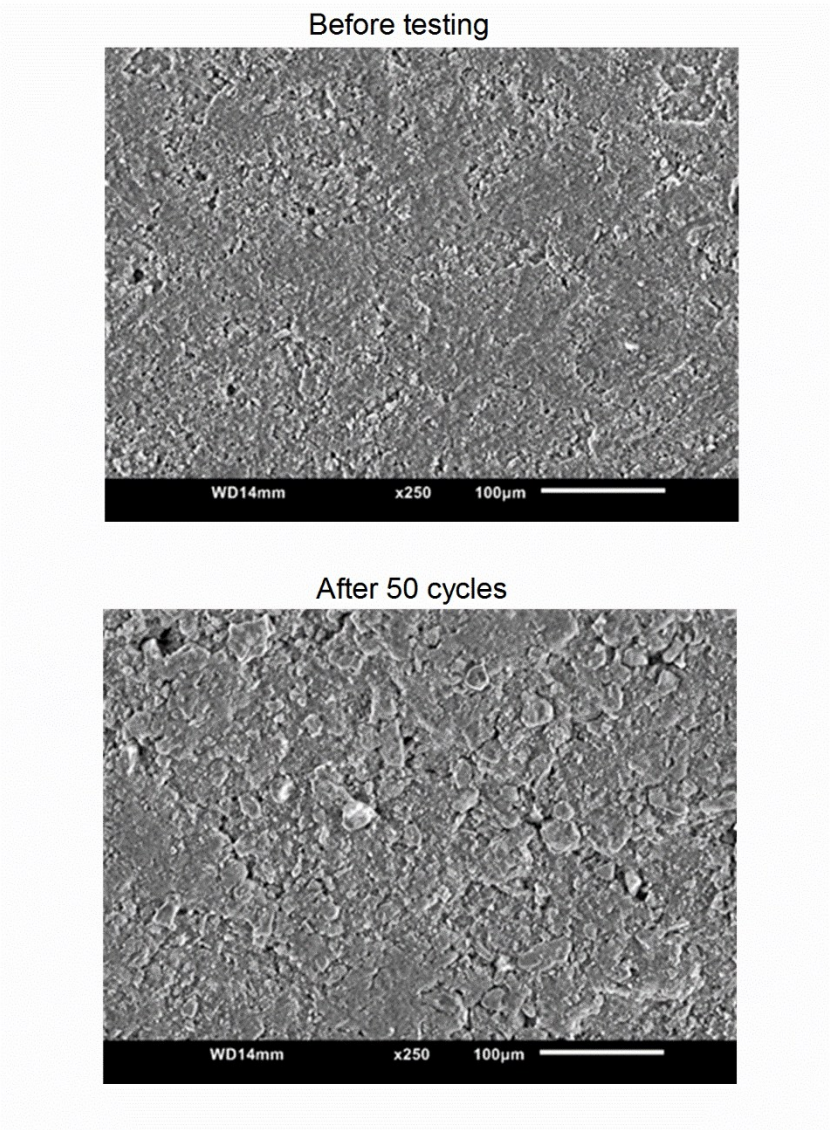

Fig. S8. SEM images of $Na_2Fe_2(SO_4)_3$/C cathode layers before testing and after 50 cycles (C/10).

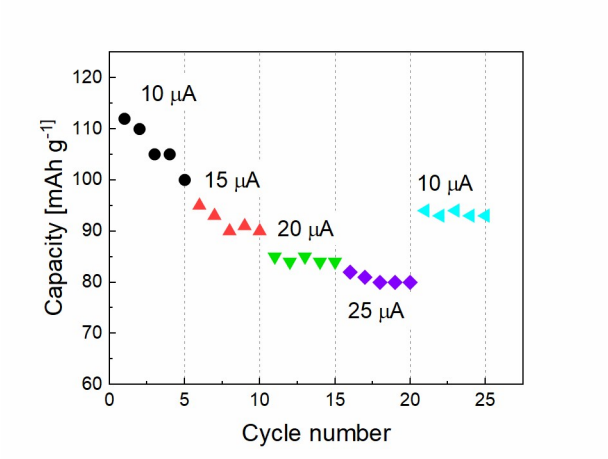

Fig. S9. Rate capability plot for Na I Na^+ I $Na_2Fe_2(SO_4)_3$/C.

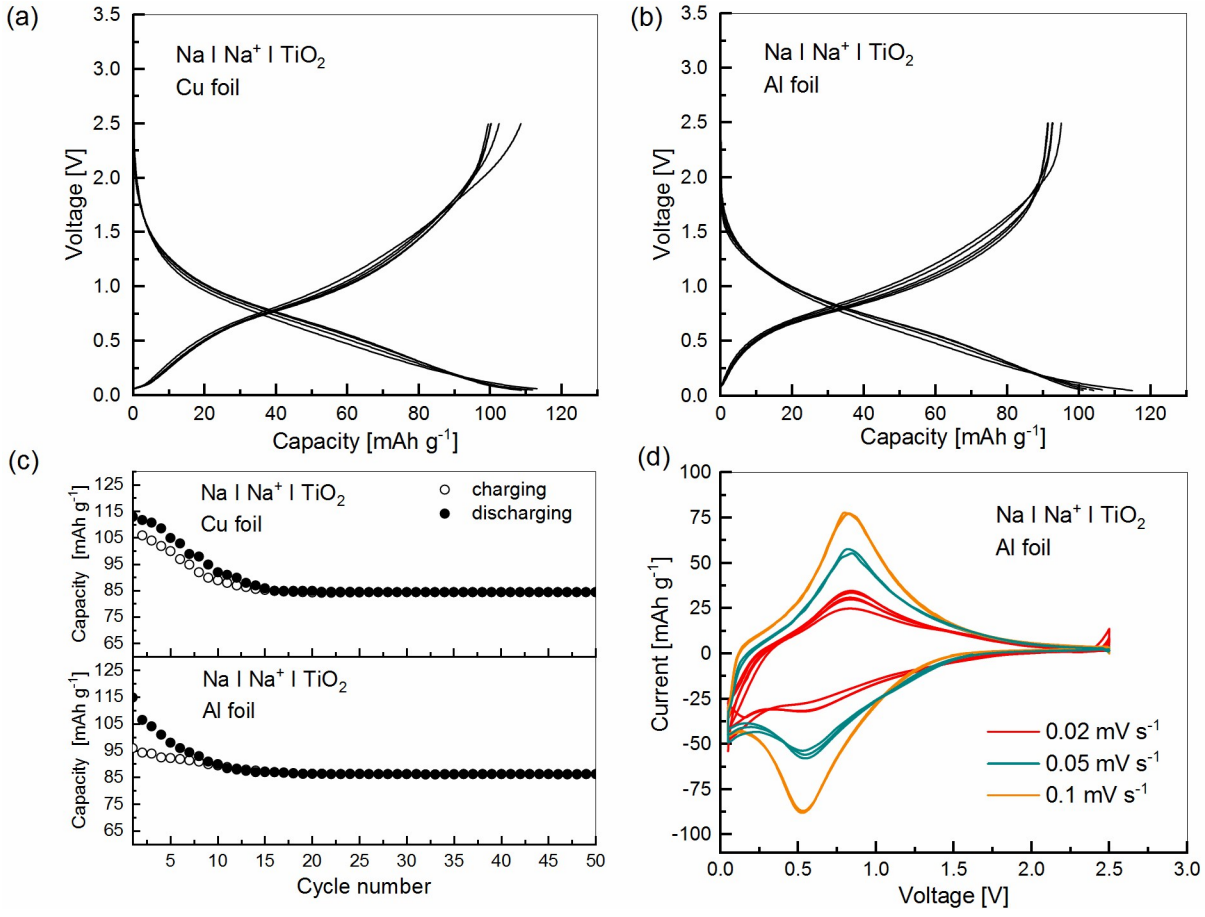

Fig. S10. Charge/discharge curves Na | Na^+ | TiO_2 (C/10) using (a) Cu foil and (b) Al foil as the current collector, (c) change of capacity during 50 cycles and (d) voltammetric curves.