Electronic Supplementary Information

$Na_2FeP_2O_7$ as a positive electrode material for rechargeable aqueous sodium-ion batteries

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Experimental

Synthesis

$Na_2FeP_2O_7/C$ was synthesized using a simple solid-state reaction. Stoichiometric amounts of $Fe(NO_3)_3$ was first dissolved in de-ionized water and heated at 80-100 ^{o}C. Then, glycine was added to the solution during stirring, and nitric acid was added to adjust to pH to 1-2. After that, Na_2CO_3 and $NH_4H_2PO_4$ were added to the mixture under continuous stirring and heating until the mixtures were dried as powders. Lastly, the collected powders were heated at 600 ^{o}C for 10 hours under a N_2/H_2 (5 %) atmosphere.

Characterization

The crystal structure of the as-synthesized powders was confirmed based on synchrotron radiation powder X-ray diffraction (SPXRD) data collected at room temperature from the 9B-HRPD beamline of the Pohang Accelerator Laboratory (PAL) in Korea with a wavelength of $\lambda = 1.5474$ Å. The diffraction patterns were acquired over an angular range of $10° \leq 2\theta \leq 130°$ at a step width of 0.01° using a six multi-detector system. Rietveld refinement analysis of the SPXRD patterns was conducted using the GSAS program[1] with the EXPGUI.[2] A pseudo-Voigt function was used to fit the line shape of the diffraction peaks. The following parameters were refined in the final runs: the unit cell parameter, scale factor, displacement shift, pseudo-Voigt function corrected for asymmetry parameters, positional coordinates, and isotropic thermal factors.

The morphology of the particles was characterized using scanning electron microscopy (FE-SEM, Philips, XL-30), and the carbon contents of the samples were measured using an element analyzer (Thermo Scientific, Flash 2000 series). The atomic ratios of Na, Fe, and P of the synthetic powders were determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Thermo Scientific, iCAP 6300 Duo). *Ex-situ* XRD measurements were performed using an X-ray diffractometer (Rigaku, D/Max-2500) with a Cu X-ray source ($\lambda = 1.5418$ Å) at room temperature.

The oxidation states of iron in $Na_2FeP_2O_7/C$ were investigated using X-ray absorption near-edge structure (XANES) analysis at the 7D-XAFS beamline of the PAL. The electrodes for the XANES analysis were prepared by casting the $Na_2FeP_2O_7/C$ slurry on carbon paper (Toray, TGP-H-090) as a current collector. The XANES spectra were collected in the transmission mode at room temperature. Fe K-edge energy calibration was performed using

Fe metal foil as a reference, and a reference spectrum was simultaneously recorded for the *in-situ* spectrum. Analysis of the obtained XAS data was conducted using the program Athena.[3]

Electrochemical testing

The electrode for the electrochemical tests was fabricated using $Na_2FeP_2O_7$/C, carbon black (Super-P, Timcal), poly(vinylidene fluoride) (Aldrich) and dopamine hydrochloride (Sigma) in a weight ratio of 75:17:5:3 on a stainless steel foil. The loading of $Na_2FeP_2O_7$/C was approximately 1-2 mg cm^{-2}. A beaker-type cell was assembled to characterize the $Na_2FeP_2O_7$/C electrode in both nonaqueous and aqueous electrolytes. To test the $Na_2FeP_2O_7$/C in organic solvents, Na metal was used as the counter and reference electrode in an Ar-filled glove box ($[H_2O]$ and $[O_2] < 1$ ppm), and the nonaqueous electrolyte was 1 M $NaClO_4$ in propylene carbonate (PC). A saturated calomel electrode (SCE, 0.241 V vs. SHE), a large size of activated carbon on a stainless steel foil and a 1 M Na_2SO_4 aqueous solution (pH ~7) were used as the reference, counter electrode and electrolyte, respectively, for the aqueous electrolyte tests. Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were performed using a VMP3 potentiostat (Bio-Logic). The scan rate for CV was 1 mV s^{-1}, and the galvanostatic tests were performed using a 1 C-rate based on 97 mAh g^{-1}, the theoretical capacity of $Na_2FeP_2O_7$. All the measurements were conducted at ambient temperature.

Atom	x	y	Z	Occupancy	Multiplicity	Uiso*100
Fe1	0.7196(5)	0.3952(4)	0.2188(3)	1.0	2	1.44(9)
Fe2	0.6465(5)	0.0050(4)	0.2598(3)	1.0	2	0.84(7)
P1	0.5808(9)	0.2044(6)	0.4552(5)	1.0	2	1.73(6)
P2	0.1183(9)	0.0518(7)	0.3078(6)	1.0	2	1.73(6)
P3	0.0791(9)	0.3267(7)	0.7888(6)	1.0	2	1.73(6)
P4	0.2953(8)	0.6844(6)	0.0358(5)	1.0	2	1.73(6)
Na1	0.0146(16)	0.3100(11)	0.4701(9)	1.0	2	8.00(18)
Na2	0.4255(14)	0.6161(11)	0.3477(8)	1.0	2	8.00(18)
Na3	0.2082(15)	0.3418(11)	0.0917(10)	1.0	2	8.00(18)
Na4	0.5	0	0	0.3333	1	8.00(18)
Na5	0.338(3)	0.097(3)	-0.026(3)	0.5	2	8.00(18)
Na6	0.432(6)	-0.053(4)	0.087(3)	0.3333	2	8.00(18)
O1	0.0266(16)	0.2158(13)	0.2909(10)	1	2	1.95(9)
O2	0.6719(17)	0.3590(14)	0.4246(11)	1	2	1.95(9)
O3	0.3200(16)	0.0365(13)	0.2207(10)	1	2	1.95(9)
O4	0.1444(16)	0.4337(12)	0.8422(9)	1	2	1.95(9)
O5	0.7937(15)	0.0554(13)	0.5242(10)	1	2	1.95(9)
O6	0.2838(17)	0.1760(13)	0.7923(11)	1	2	1.95(9)
O7	-0.0048(17)	0.0487(12)	0.6937(9)	1	2	1.95(9)
O8	0.8422(15)	0.3807(12)	0.0485(10)	1	2	1.95(9)
O9	0.4453(16)	0.5496(11)	0.1428(10)	1	2	1.95(9)
O10	0.5990(16)	0.1798(12)	0.0464(10)	1	2	1.95(9)
O11	0.3820(16)	0.1842(11)	0.5359(9)	1	2	1.95(9)
O12	0.5737(16)	0.1827(12)	0.3157(10)	1	2	1.95(9)
O13	0.0922(16)	0.7696(11)	0.0910(10)	1	2	1.95(9)
O14	0.0282(16)	0.5930(12)	0.3522(10)	1	2	1.95(9)

Table S1. Atomic coordinates, site occupancies, and isotropic displacement (Å^2) for $Na_2FeP_2O_7$/C obtained by Rietveld refinement of the synchrotron powder XRD data.

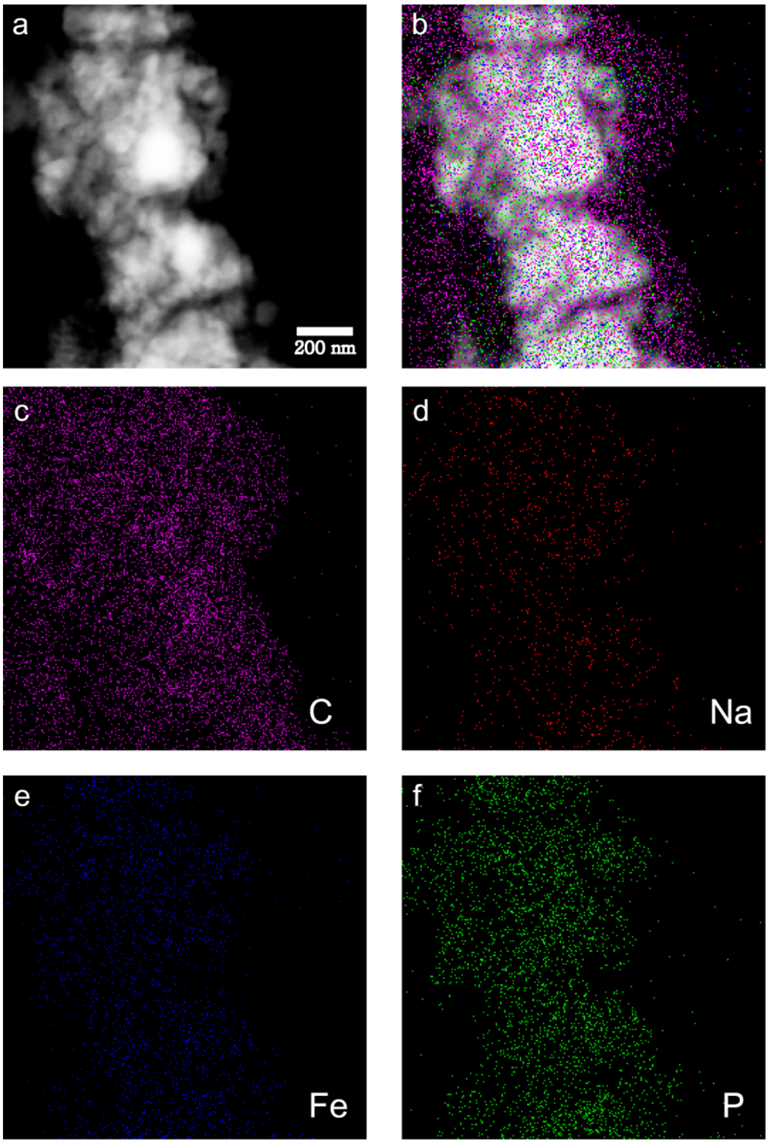

Fig. S1. (a) An STEM image of the as-synthesized $Na_2FeP_2O_7$/C. (b) EDS elemental mappings of (c) carbon (d) sodium (e) iron and (f) phosphorus.

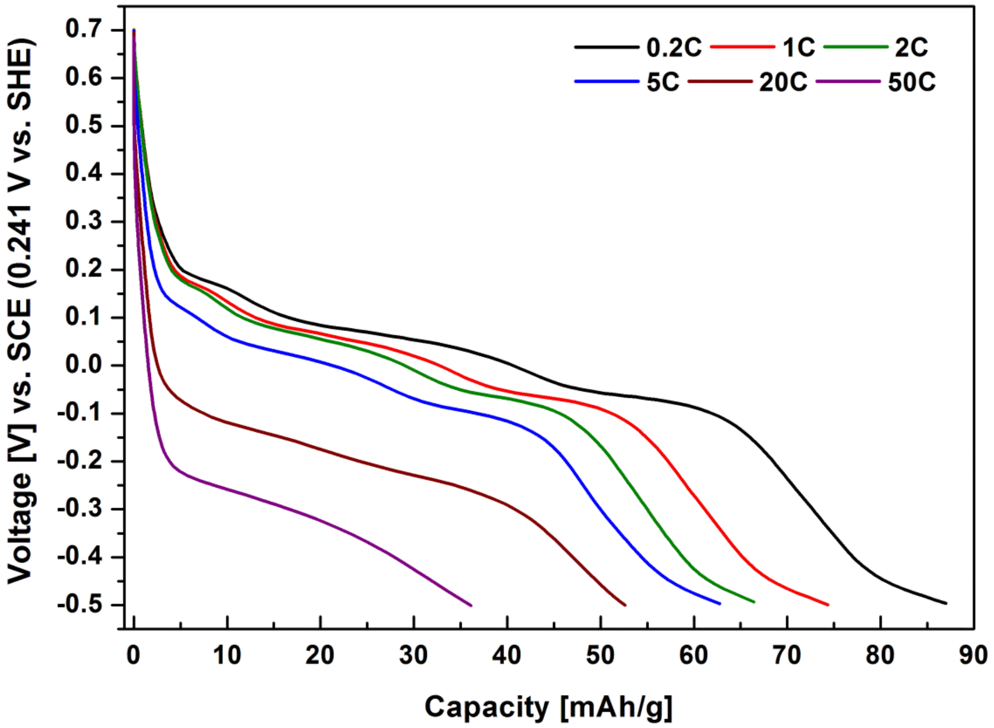

Fig. S2. The galvanostatic discharge profiles for $Na_2FeP_2O_7$/C at different C-rates in aqueous electrolytes (1 M Na_2SO_4). The charge rate was fixed at 1 C and the tested voltage range was from 0.7 V to -0.5 V vs. SCE.

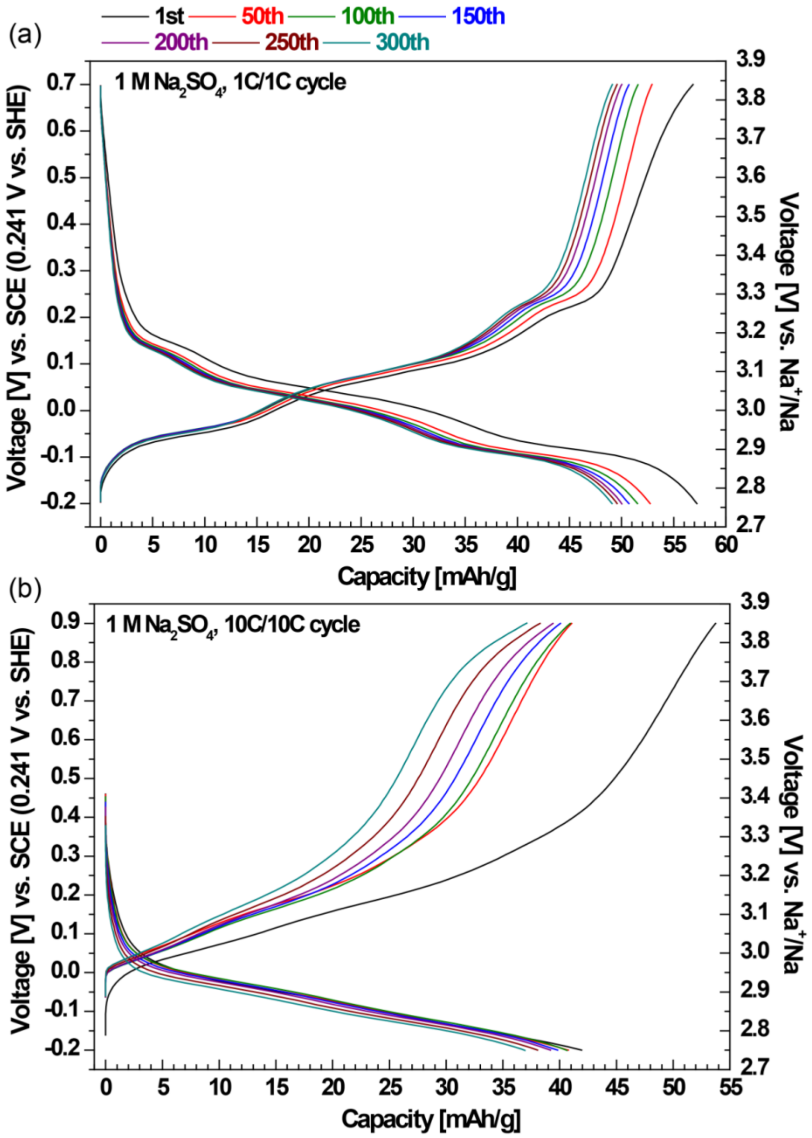

Fig. S3. The galvanostatic charge/discharge curves of the (a) 1C/1C cycle and (b) 10C/10C cycle in aqueous electrolytes (1 M Na_2SO_4).

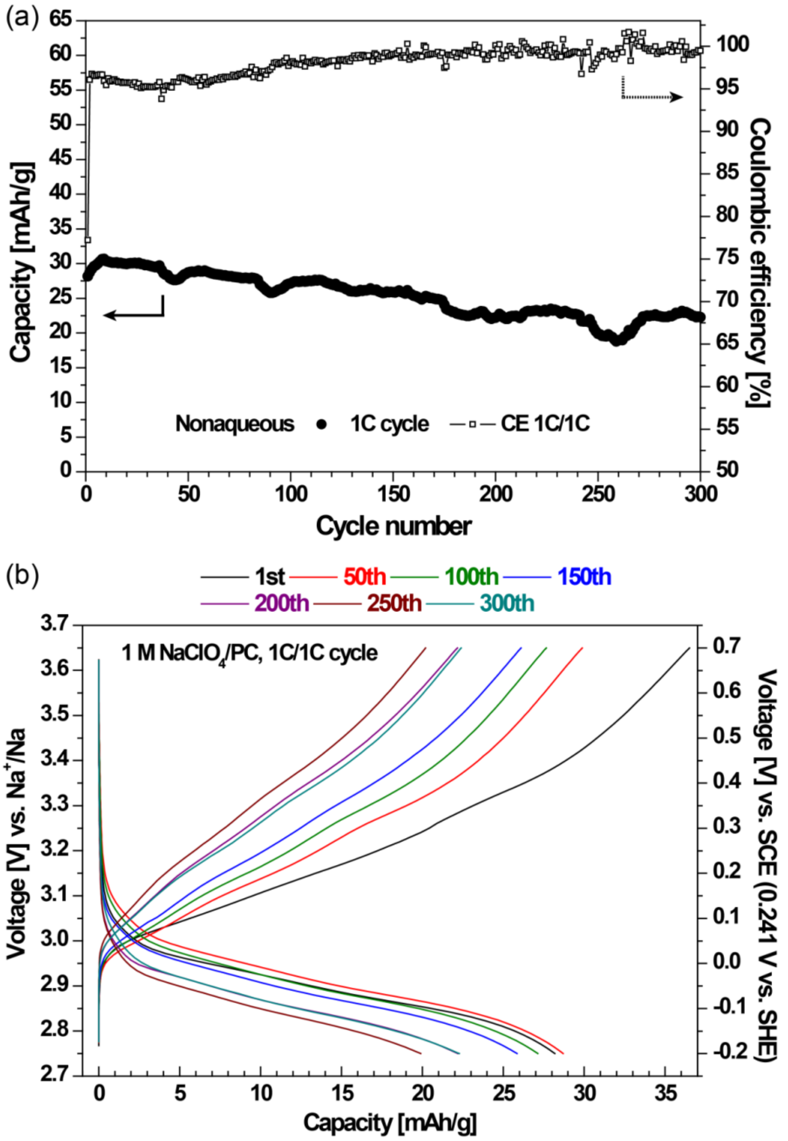

Fig. S4. (a) Capacity retention and (b) the galvanostatic charge/discharge curves of the 1C/1C cycle between 2.75 and 3.65 V vs. Na in nonaqueous electrolytes (1 M $NaClO_4$/PC).

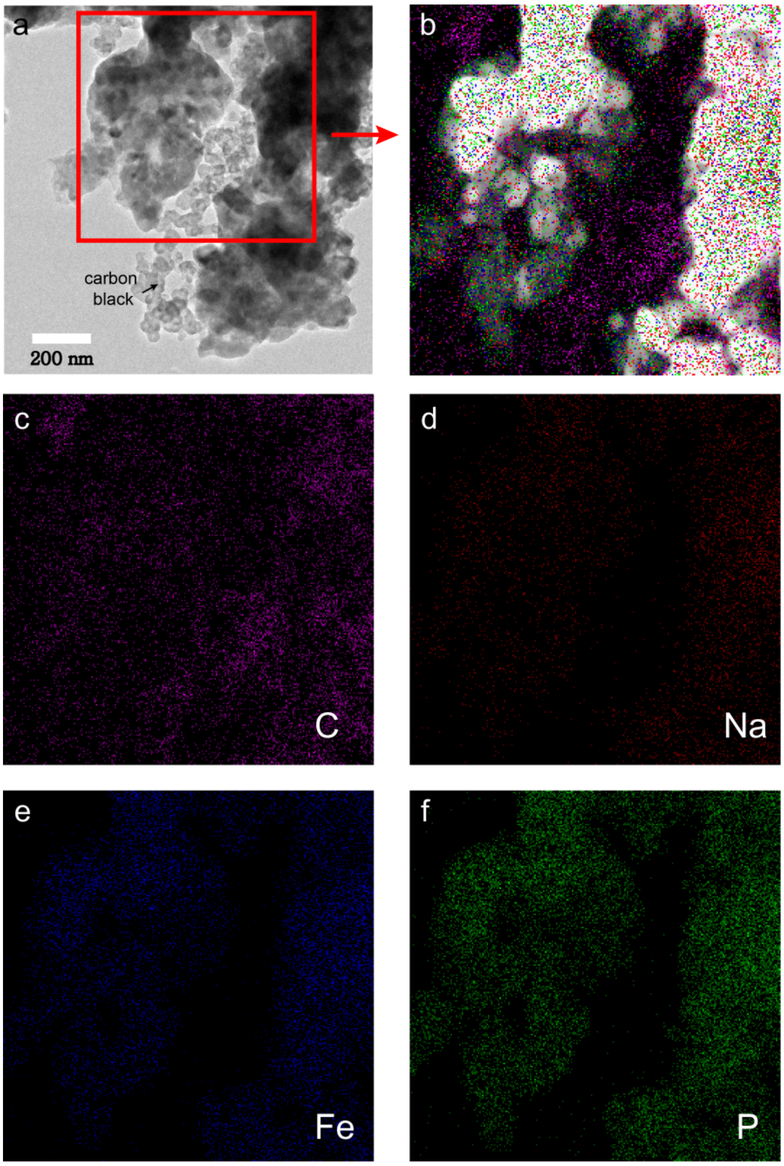

Fig. S5. (a) A TEM image, (b) EDS elemental mappings of (c) carbon (d) sodium (e) iron and (f) phosphorus of the $Na_2FeP_2O_7$/C after 300 cycles in aqueous electrolytes.

References

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2. B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210.

3. B. Ravel and M. Newville, *J. Synchrotron Rad.*, 2005, **12**, 537.