Sodium Zinc Hexacyanoferrate with a Well-defined Open Framework as a Positive Electrode for Sodium Ion Batteries

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Electronic Supplementary Information

Section A. Experimental details

A.1. Material preparation

$Na_2Zn_3[Fe(CN)_6]_2{\cdot}xH_2O$ was synthesized by a simple precipitation method as previously described.[1, 2] Briefly, two precursors in aqueous media were mixed for the reaction at 100 °C for 2 h. 40 mL of 0.1 M sodium hexacyanoferrate(II) ($Na_4Fe(CN)_6{\cdot}10H_2O$, Sigma-Aldrich) was dropwisely added to 60 mL of 0.1 M zinc nitrate ($Zn(NO_3)_2{\cdot}xH_2O$, Sigma-Aldrich). After the reaction was completed, white slurry was formed. Finally, the precipitate was washed with de-ionized water several times using centrifugation (3600 rpm, 10 min) and then dried at 40 °C for 2 days. Finally, the precipitates were dehydrated by heating at 95 °C for 24 h in a vacuum oven.

A.2. Characterization

The crystal structures of the synthesized samples were charactrerized by using X-Ray Diffraction (XRD) (Rigaku, D/MAX-2500, Tokyo, Japan) equipped with Cu Kα radiation operating at 40 kV/40 mA. Lattice parameters were determined by XRD pattern processing using Divol. Scanning electron microscopy (SEM) images were collected by a field-emission (FE) SEM (Philips, XL30 FEG, Eindhoven, Netherlands, 20 kV). Fourier Transform Infrared (FT-IR) spectra (Alpha FT-IR spectrometer, Brucker, Germany, ATR spectrum mode, 375-4000 cm^{-1}) were also obtained to detect cyanide ligands in NZH. Atomic ratios of metals and water in NZH were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, POLY SCAN 61 E, ELTRA ONH 2000).

A.3. Electrochemical Measurements

The electrode films were prepared using the doctor-blade technique. A slurry in which NZH (70 wt.%), super-P (20 wt.%), and poly(vinylidene fluoride) (10 wt.%) were dissolved in N-methyl-2-pyrrolidone (NMP) was cast onto aluminum foil. The cast film was dried in a vacuum oven at 95 °C for 24 h. Electrochemical tests were examined by preparing 2032 coin-type half-cells in which Na metal disks were used as both counter and reference electrodes. Poly(propylene) separator (PP2400, Celgard) and 1 M $NaClO_4$ in propylene carbonate (PC, Panax Etec Co., Ltd., Korea) were used as separator and electrolyte, respectively. In order to see the electrolyte effects on the capacity retention, additional electrolytes of 1 M $NaClO_4$ and 1 M $NaPF_6$ in ethylene carbonate (EC), dimethyl carbonate (DMC) mixture (1:1 volumetric ratio, Panax Etec Co., Ltd., Korea) were tested. The cells were assembled in an argon-filled glove box. Galvanostatic measurements were carried out in the potential range of 2.0-4.0 V (vs. Na^+/Na) using a WBCS 3000 battery tester (Wonatech Co., Korea) at room temperature.

Section B. FT-IR spectroscopic characterization

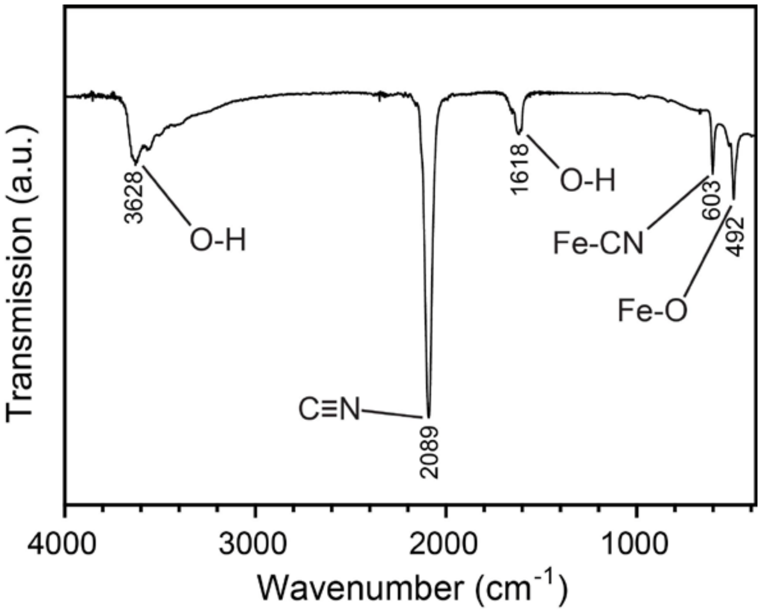

Fig. S1. An FT-IR spectrum of the as-prepared NZH.

An FT-IR spectrum also supports the formation of the designated compound. The presence of cyanide ligands is verified by the absorption peaks at 603 and 2089 cm^{-1} that correspond to the Fe-CN bending mode and cyanide stretching mode, respectively.[3] Furthermore, the absorption peaks at 3628 cm^{-1} and 1618cm^{-1} are ascribed to the stretching mode of OH, indicating the presence of water molecules in the framework.[4, 5]

Section C. *Ex-situ* XRD experiment

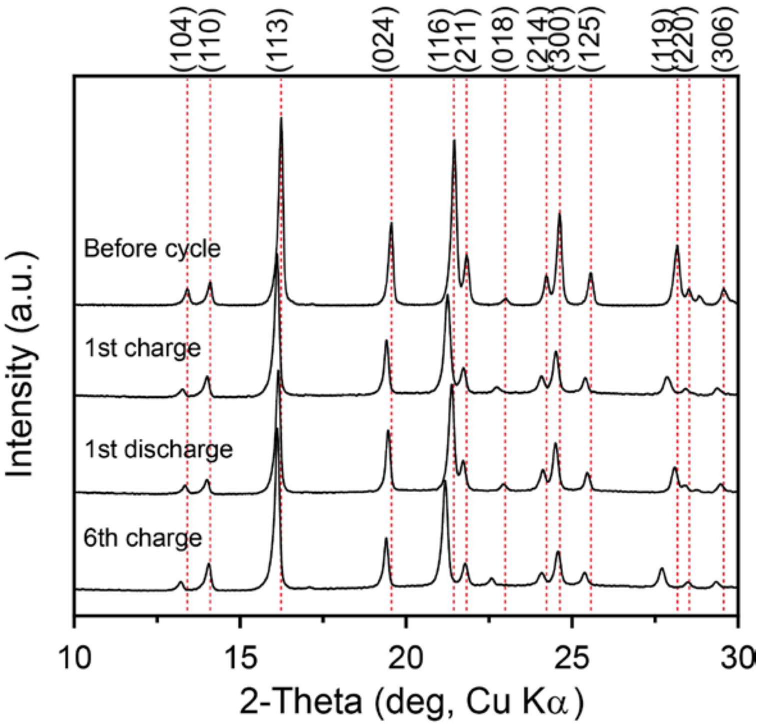

Fig. S2. *Ex-situ* XRD patterns for NZH at different electrochemical states with the electrolyte of 1 M $NaClO_4$ in PC. The potential range is 2.0-4.0 V vs. Na/Na^+.

Section D. Solvent properties

Table S1. Properties of solvents [6]

Properties (at 25℃)	**Water**	**PC**	**EC**	**DMC**
Molecular Weight	18	102.09	88.06	90.08
Density (g/cm^3)	0.997	1.2006	1.3214	1.063
Surface tension (γ, mN/m)	71.97	41.93	54.6	31.9
Electric dipole moment (μ, debye(D))	1.87	4.81	4.61	0.76
Dielectric constant (ε)	79.2	66.14	89.78	3.107
Viscosity (η, cP)	0.89	2.53	1.90 (40℃)	0.59 (20℃)

Section E. The cycle life and potential profiles of NZH in the electrolyte of $NaPF_6$ in EC/DMC (1:1 v/v)

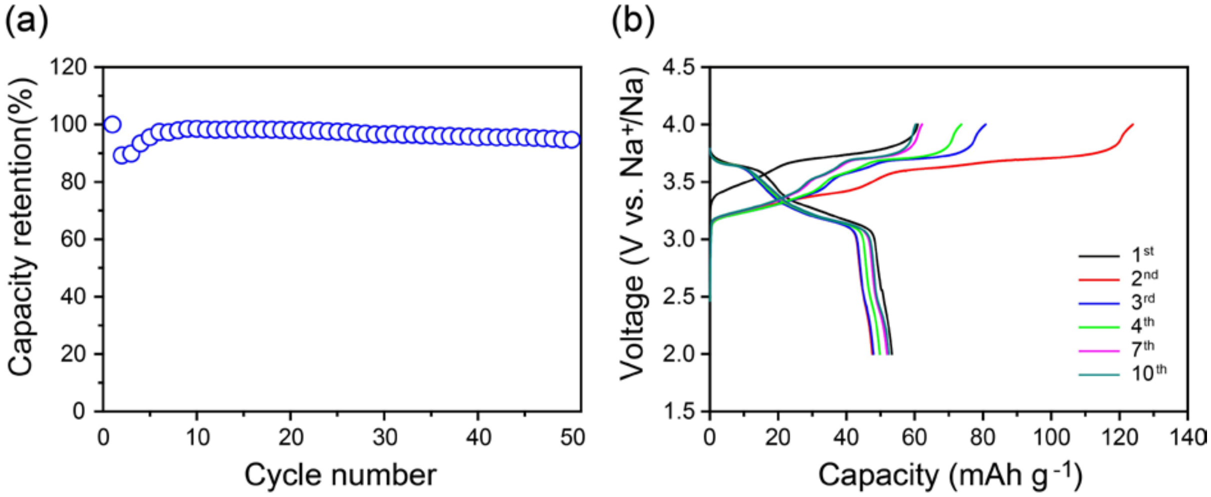

Fig. S3. (a) The capacity retention and (b) the potential profiles of NZH when tested with the electrolytes of 1 M $NaPF_6$ in EC/DMC (1:1 v/v). The potential range is 2.0-4.0 V vs. Na/Na^+.

Unlike other electrolyte cases, the NZH cell in the electrolytes of 1 M $NaPF_6$ in EC/DMC (1:1 v/v) exhibits smaller capacities in the first 10 cycles (Fig. S3a), which are likely to be associated with the fluctuating potential profiles in the charging processes during those cycles (Fig. S3b). Although in-depth analyses need to be performed to understand the fluctuation during the charging processes, it is speculated that the behavior originates mainly from the electrode-electrolyte reactions, perhaps SEI formation, that takes place during the early period of cycles. Apparently, the interfacial properties depend on the electrolyte and thus show distinctive behaviors among the different electrolytes. In fact, the more stable cycling with $NaPF_6$ in EC/DMC compared to other electrolyte cases (Fig. 3c in the main text) might be attributed to these SEI layers that stabilize the interface during cycling.

Section F. Rate capability of NZH

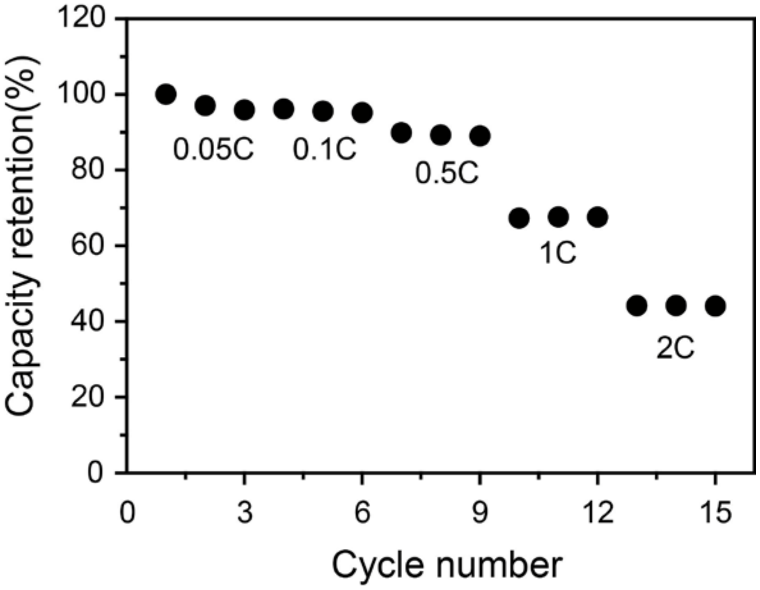

Fig. S4. Rate capability of NZH with the electrolyte of 1 M $NaClO_4$ in PC. The potential range is 2.0-4.0 V vs. Na/Na^+.

Section G. References

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