Supporting information for

Dual-Ion Charge-Discharge Behaviors of Na-NiNc and NiNc-NiNc Batteries

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Experiments

Electrochemical measurement

All air-sensitive materials were handled under a dry argon atmosphere in a glove box (H_2O < 1 ppm, O_2 < 1 ppm).

The salts used for electrolytes, Na[FSA] (FSA = bis(fluorosulfonyl)amide)(Mitsubishi Materials Electronic Chemicals, purity > 99%) and [C_2C_1im][FSA](C_2C_1 = 1-ethyl-3-methylimidazolium)(Kanto Chemical, purity > 99.9%) were dried under vacuum for 24 h at 80 °C. 1 mol dm^{-3} Na[PF_6]-EC/DMC(1:1 in volume) (Kishida Chemical, battery grade) was used as purchased. The typical water contents of the electrolytes were below 20 ppm, according to Karl-Fischer titration (899 Coulometer, Metrohm).

Sodium metal (Sigma-Aldrich Chemistry, 99.95% purity) was cut into a disk (16-mm diameter) and fixed on an Al plate current collector as the negative electrode. The positive electrode was prepared by mixing the NiNc, Carbon black (Timcal, Super C 65), and PVDF (70:25:5 wt%) in N-ethylpyrrolidone and pasting the mixture onto Al foil (the mass loading of the active material in the electrodes was approximate ~2 mg-active material cm^{-2}). For the symmetric cell configuration, an additional NiNc electrode was used as a counter electrode instead of a Na electrode. A three-electrode cell configuration (EC Frontier co., LTD) was assembled using NiNc working, and counter electrodes with sodium metal ring as a reference electrode. Glass microfiber separator (Whatman GF/A) was impregnated with an ionic liquid at 80 °C under vacuum before the cell assembly. In the case of organic electrolytes, a separator was impregnated with the electrolyte just before assembling coin cells in the glove box.

The active electrode material, NiNc was prepared following the literature method.[S1]

The electrochemical properties were measured at 25 °C using the thermostatic chamber SU-242 (ESPEC). All the electrochemical measurements were performed at least 30 min after temperature adjustments. A current density of 100-2000 mAg^{-1} was applied for the charge/discharge tests and cycle tests. The charge-discharge properties and cycling performances were evaluated using an HJ1001SD8 charge-discharge test device (Hokuto Denko). The CV was measured with Na metal using a Bio-Logic VSP potentiostat. The NiNc electrodes were swept to 4.2 and 1.2 V vs. Na^+/Na at 1 mV s^{-1}.

References

S1. T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi and H. Shinokuo, *Angew. Chem.* 2012, **124**, 8670; *Angew. Chem. Int. Ed*. 2012, **51**, 8542.

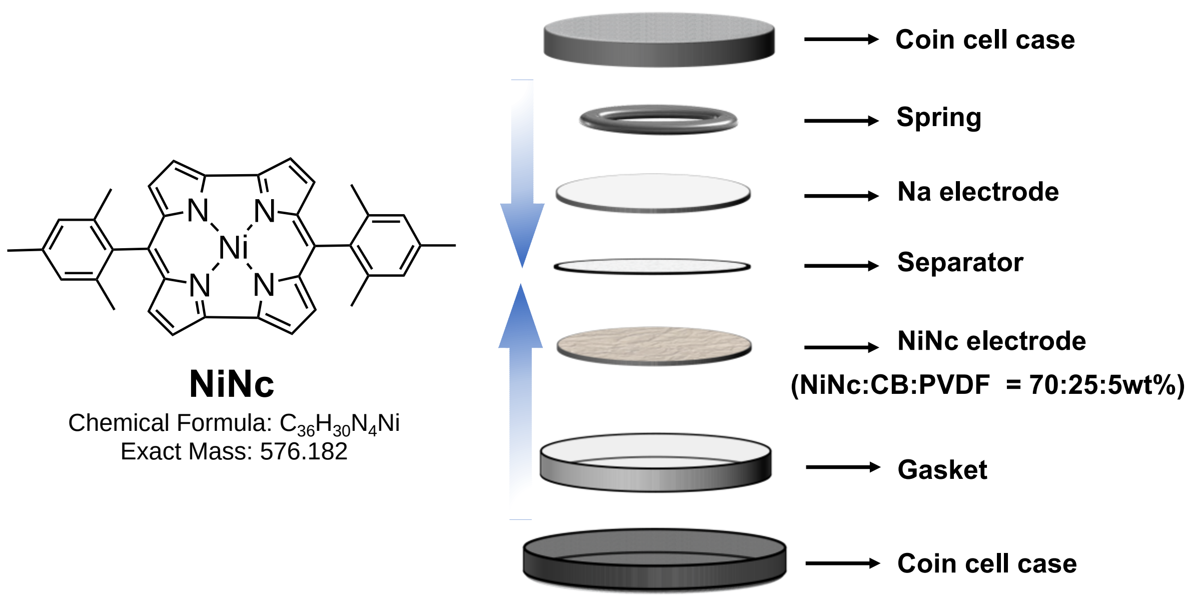

Fig. S1 Structure of nickel(II) norcorrole (NiNc) and a blueprint of Na-NiNc coin cells to represent the assembly: Different electrolytes such as 1 M Na[PF_6]-EC/DMC and 50 mol% Na[FSA]-[C_2C_1im][FSA] were selectively chosen to provide practical Na-NiNc batteries.

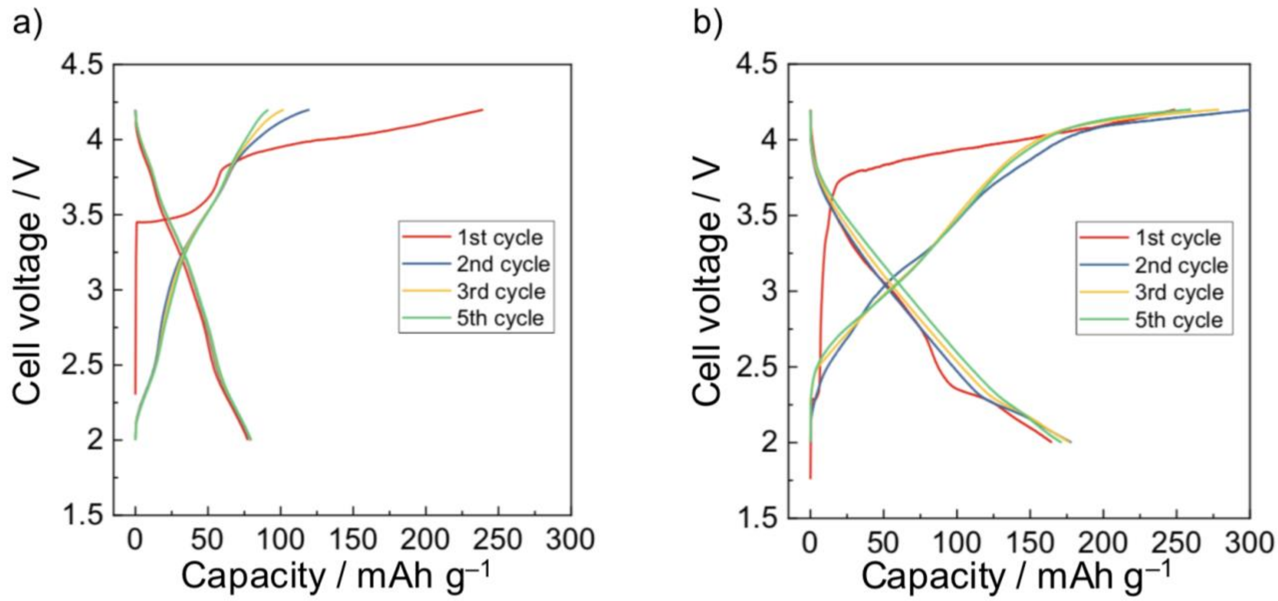

Fig. S2 Charge/discharge performances of Na-NiNc batteries fabricated with (a) 1 M Na[PF_6]-EC/DMC and (b) 50 mol% Na[FSA]-[C_2C_1im][FSA] electrolytes.

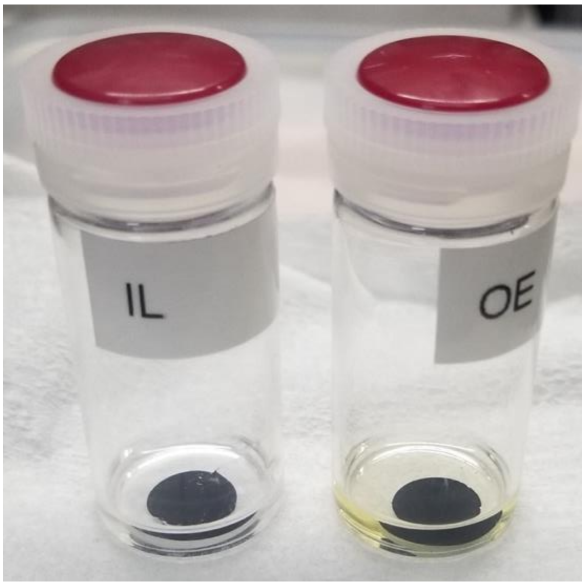

Fig. S3 A photograph representing solubilities of NiNc electrodes in 1 M Na[PF_6]-EC/DMC (right vial labelled with OE, organic electrolyte) and in 50 mol% Na[FSA]-[C_2C_1im][FSA](left vial labelled with IL, ion-pair containing liquid electrolyte).

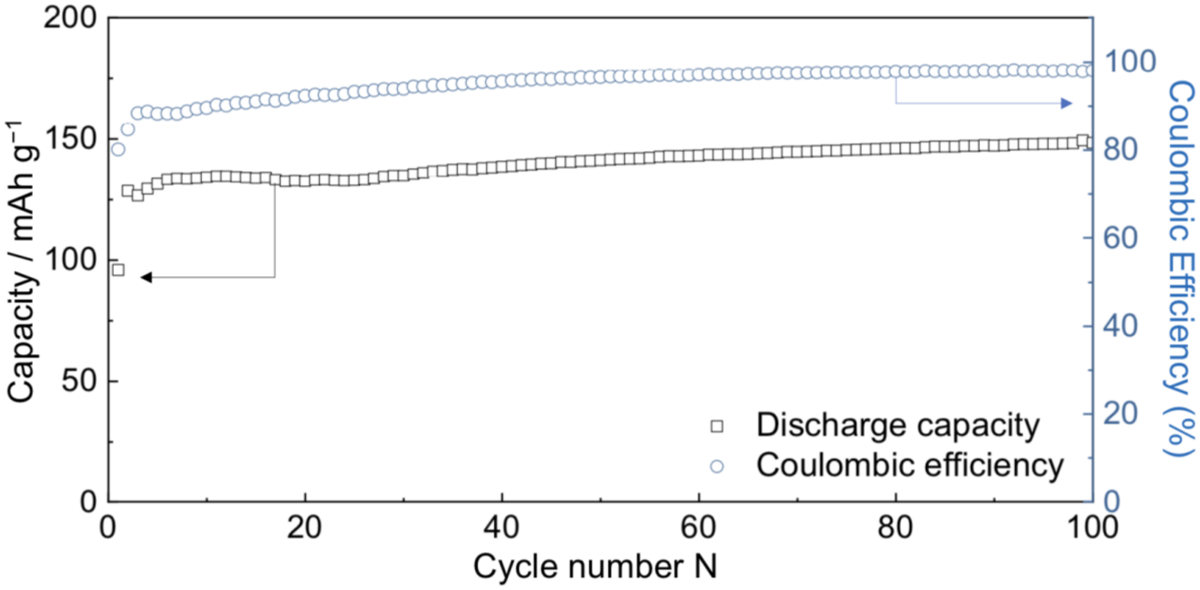

Fig. S4 Plots of 100 cyclic charge/discharge performances for a Na-NiNc battery: Composition of positive electrode = NiNc:CB:PVDF = 70:25:5wt%, Cut-off voltages = 2.0-4.2 V, and current density = 0.2 A g^{-1}.

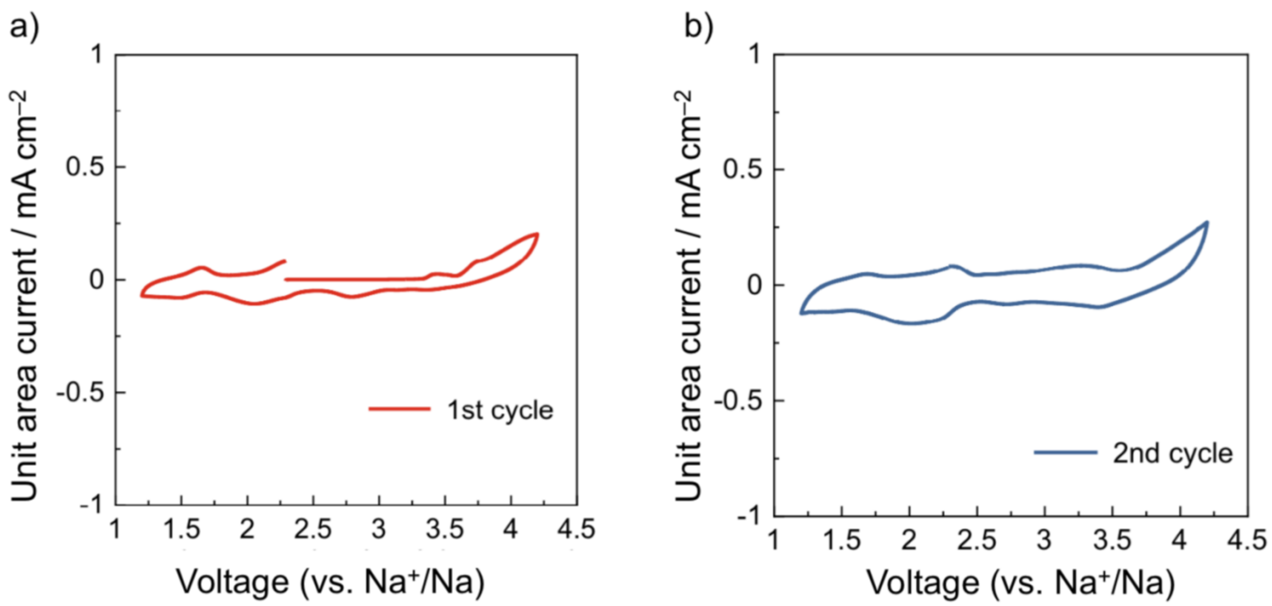

Fig. S5 Cyclic voltammograms of a Na-NiNc battery: Composition of positive electrode = NiNc:CB:PVDF = 70:25:5wt%, Cut-off voltages = 1.2-4.2V. a) presents the 1st redox cycle and b) represents the 2nd redox cycle. Scanning rate: 1 mV s^{-1}.

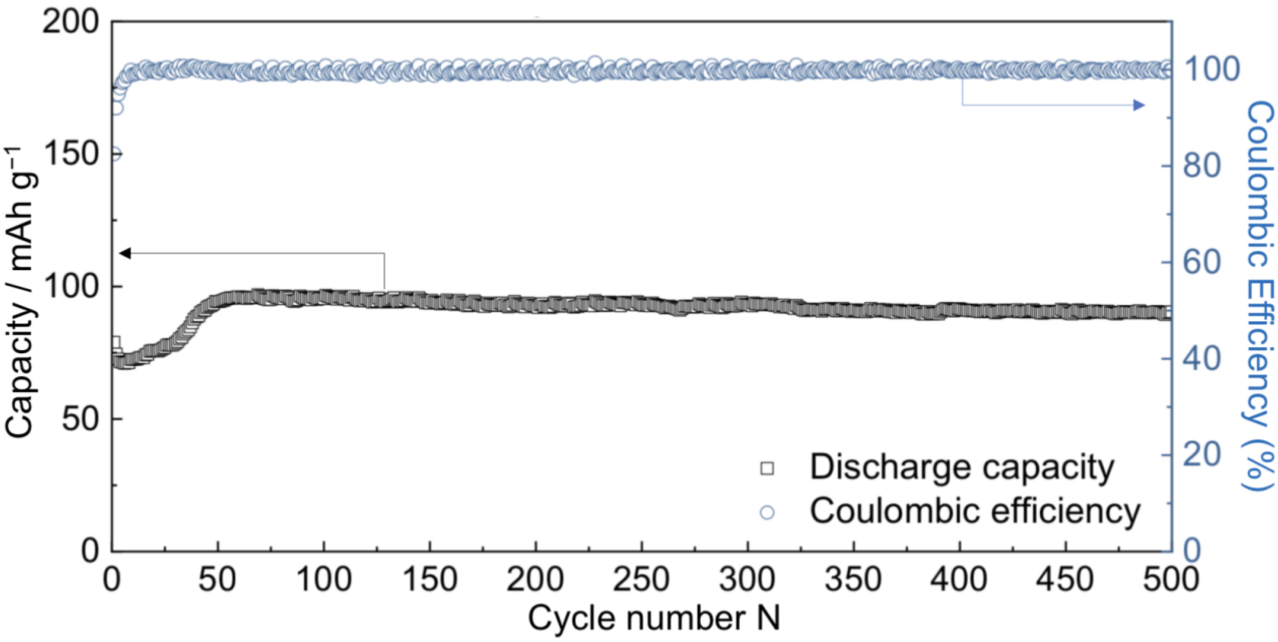

Fig. S6 Plots of 500 cyclic charge/discharge performances for a Na-NiNc battery: Composition of positive electrode = NiNc:CB:PVDF = 70:25:5wt%, Cut-off voltages = 1.2-4.2 V, and current density = 2A g^{-1}.

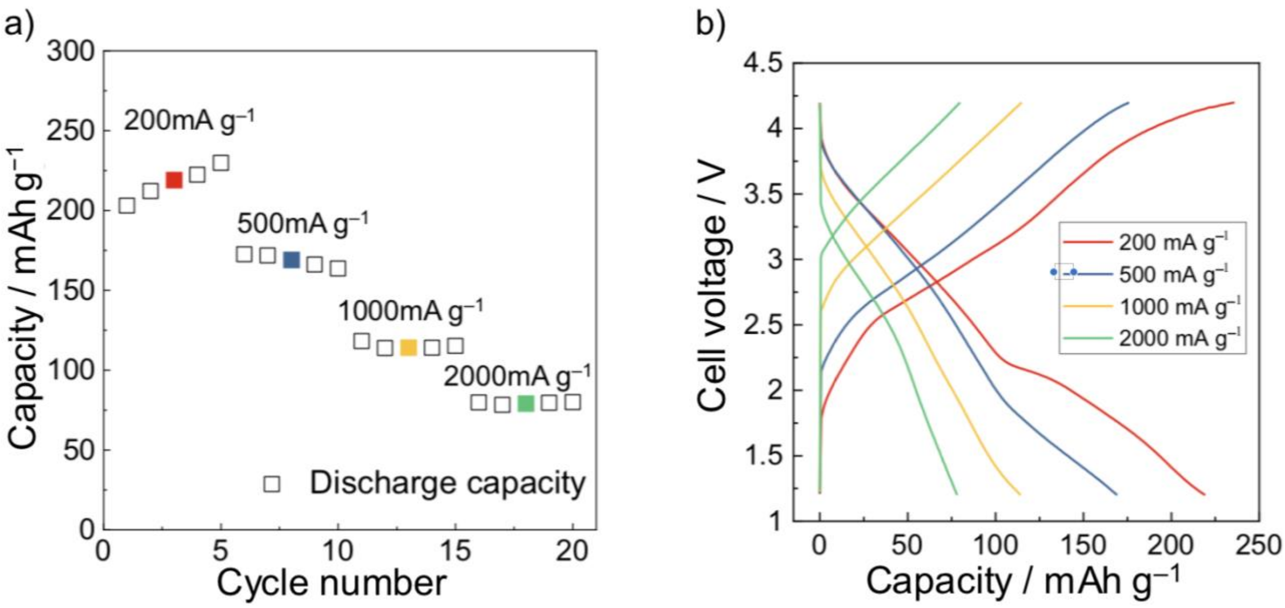

Fig. S7 Plots of charge/discharge performances for a Na-NiNc battery with different current densities: Composition of positive electrode = NiNc:CB:PVDF = 70:25:5wt%, Cut-off voltages = 1.2-4.2 V, and current densities (0.2, 0.5, 1.0, and 2.0 A g^{-1}) are given in the figures. The theoretical charge/discharge capacity of the NiNc electrode is 46.4 mAh g^{-1} for a single electron. Former charge/discharge capacities of a freshly prepared battery cell with the small current density, 200 mA g^{-1} exhibited slightly larger than the value estimated by the theoretical process, four-electrons oxidation. However, the capacities become normalized to a consistent value involving four electrons (186 mAh g^{-1}) in the first ten cycles, and the normalized value is maintained. We suspect it happened by either partial conversion reaction or electrolyte decomposition due to the wide cut-off voltages.

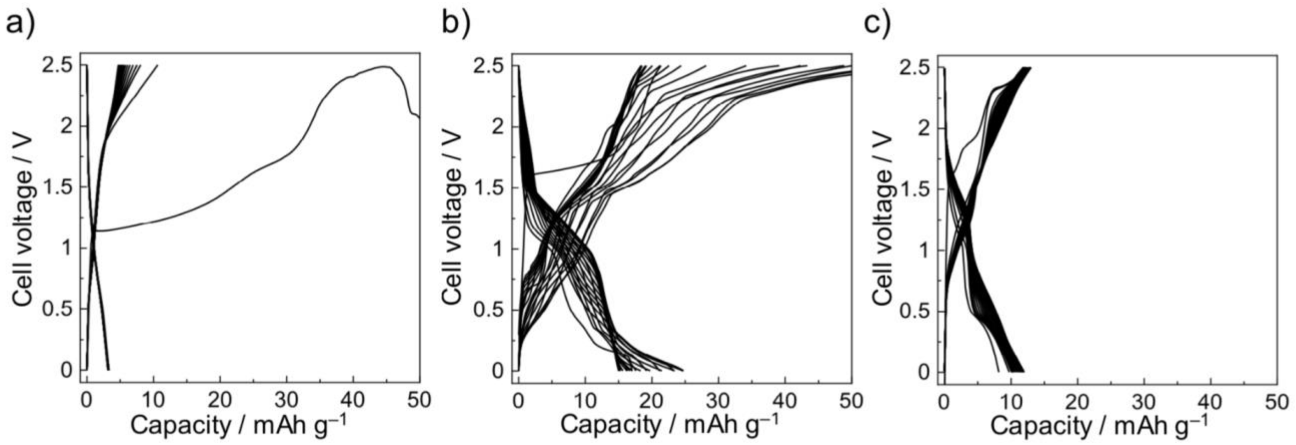

Fig. S8 20 Cyclic charge/discharge performances of symmetric NiNc-NiNc batteries fabricated with distinct electrolytes. a) EC/DMC, b) [C_2C_1im][FSA], and c) Na[FSA]-[C_2C_1im][FSA]. Cut-off voltages = 0-2.5 V, and current density = 50 mA g^{-1}.