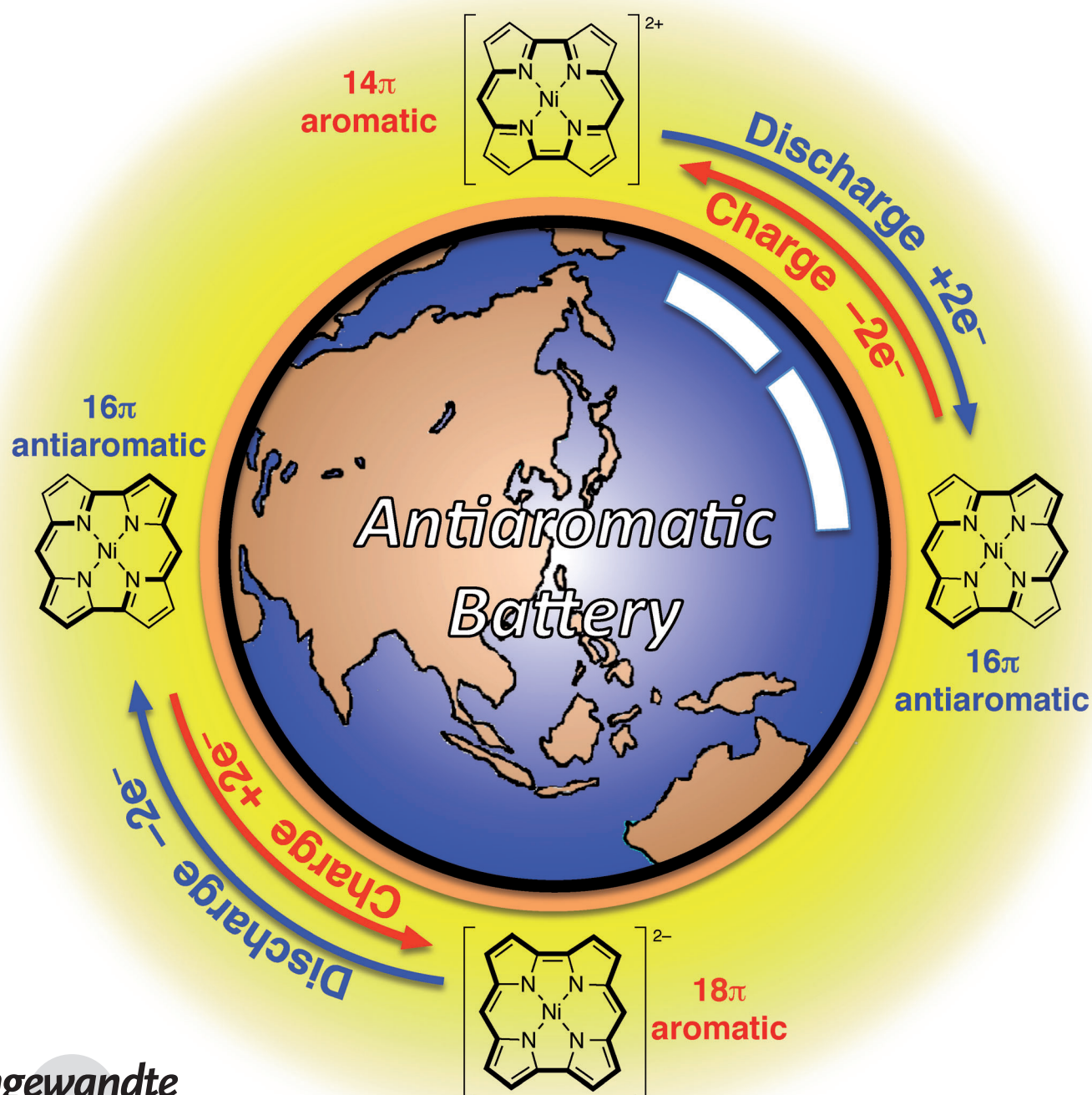




An Antiaromatic Electrode-Active Material Enabling High Capacity and Stable Performance of Rechargeable Batteries**

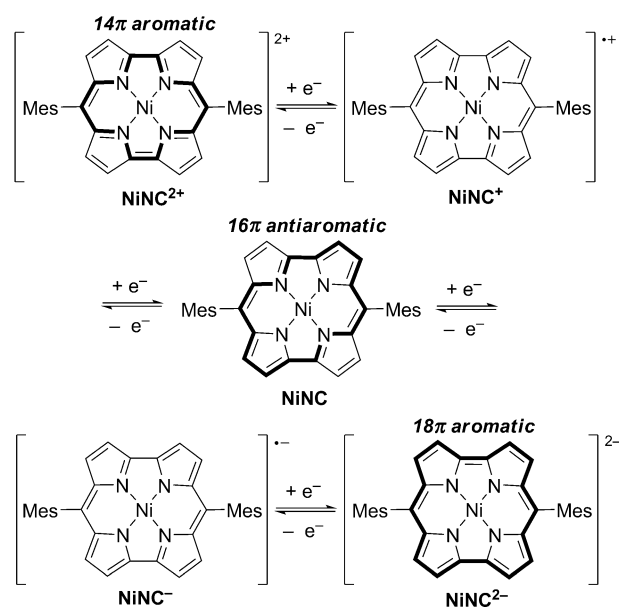
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Abstract: Although aromatic compounds occupy a central position in organic chemistry, antiaromatic compounds have demonstrated little practical utility. Herein we report the application of an antiaromatic compound as an electrode-active material in rechargeable batteries. The performance of dimesityl-substituted norcorrole nickel(II) complex (NiNC) as a cathode-active material was examined with a Li metal anode. A maximum discharge capacity of about 207 mAhg⁻¹ was maintained after 100 charge/discharge cycles. Moreover, the bipolar redox property of NiNC enables the construction of a Li metal free rechargeable battery. The high performance of NiNC batteries demonstrates a prospective feature of stable antiaromatic compounds as electrode-active materials.

Aromaticity is one of the most fundamental concepts in organic chemistry. According to Hückel's rule, a planar cyclic conjugated system with delocalized $(4n + 2)$ π electrons is aromatic, which results in a system that is particularly stable in terms of energy. In sharp contrast, a planar cyclic conjugated system with $4n$ π electrons is antiaromatic. In general, antiaromatic compounds are unstable as a result of antiaromatic destabilization. Consequently, they still lack meaningful practical applications. However, they have intriguing properties, such as small HOMO–LUMO gaps and high redox activities, which may potentially lead to practical applications.

Porphyrins and related analogues (porphyrinoids) have been the targets of active investigation.^[1] Although several antiaromatic porphyrinoids have been characterized,^[2] most of them are unstable and difficult to prepare in large quantities. Recently, we succeeded in the large-scale synthesis of the dimesitylnorcorrole nickel(II) complex (NiNC, Scheme 1) in over 90% yield.^[3] NiNC exhibits distinct antiaromaticity because of the 16 π electrons, but high stability toward air and water as a result of the effective steric protection by the mesityl groups, thus allowing easy handling under ambient conditions. Furthermore, NiNC has a very



Scheme 1. Two-electron oxidation and two-electron reduction of NiNC. The bold line indicates each π -conjugation circuit. Mes = 2,4,6-trimethylphenyl.

small HOMO–LUMO gap that allows the facile injection and removal of electrons.^[4] As shown in Scheme 1, the two-electron oxidation and two-electron reduction of NiNC provide dicationic and dianionic species, respectively. Notably, these redox species are stabilized because of their 14 π and 18 π aromatic systems. In addition, NiNC has been the smallest antiaromatic porphyrinoid so far. The relatively small size of NiNC is favorable for high-density energy storage. We expected that NiNC would be suitable for electrode-active materials in rechargeable batteries.

Rechargeable batteries are one of the key technologies for achieving a sustainable society.^[5] Several organic compounds have been extensively explored as cathode-active materials.^[6] Stable organic radical monomers and polymers are promising candidates for such organic materials.^[7] Several redox-active organic molecules have also demonstrated high charge/discharge capabilities.^[8] Here we describe the use of NiNC as electrode-active materials for Li-organic and Li metal free poleless batteries to achieve excellent charge/discharge capacity and durability. To the best of our knowledge, this is the first report of an antiaromatic compound that exhibits practical performance as an electrode-active material in rechargeable batteries.

Analysis of the electrochemistry of NiNC by cyclic voltammetry (CV) showed two reduction and two oxidation waves (Figure 1). To evaluate the stability of the redox species, the redox processes were monitored in situ by UV/Vis/NIR absorption spectra. Each absorption spectrum of the NiNC redox species was assigned on the basis of TD-DFT calculations (see Figures S2 and S3 in the Supporting Information). Upon the first oxidation (Figure 2a), broad absorption bands arising from NiNC⁺ were observed at 690 and 1160 nm. Subsequently, new lower energy absorption bands of the dication NiNC²⁺ became evident at 400, 720, and

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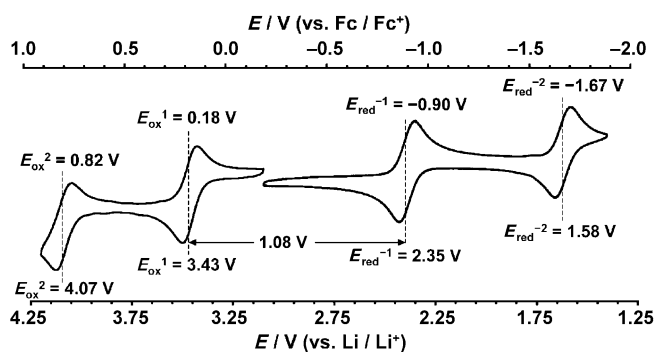


Figure 1. Cyclic voltammogram of NiNC in CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NPF}_6$): the working electrode is glassy carbon, the counter electrode is Pt, and the reference electrode is Ag/AgClO_4 . $\text{Fc}/\text{Fc}^+ = \text{ferrocene}/\text{ferrocenium}$ couple.

980 nm around the second oxidation potential (Figure 2b). For the first reduction, we detected absorption bands at 480, 810, and 920 nm in the spectrum corresponding to the radical anion NiNC^- (Figure 2c). It is of interest, however, that NiNC^- was reduced to NiNC^{2-} at higher potentials than the

second reduction potential, as judged from the disappearance of the band at 920 nm and the increase in the broad absorption band at approximately 660 nm (Figure 2c,d). On the basis of these results, the oxidation of NiNC is likely to proceed sequentially through NiNC^+ to NiNC^{2+} . In contrast, the radical anion NiNC^- is not very stable and is further reduced to stable NiNC^{2-} , probably through the disproportionation of NiNC^- to NiNC and NiNC^{2-} .

We then applied NiNC as a cathode-active material for Li batteries.^[9] Cathode electrode composites were prepared by mixing NiNC, polyvinylidene fluoride, and conductive carbon black with *N*-methyl-2-pyrrolidone. A Li-NiNC battery was assembled with a Li metal foil anode and the NiNC cathode, with a porous polymer film separator in an electrolyte solution composed of LiPF_6 in ethylene carbonate/diethyl carbonate (Figure 3a, and see Figure S1a in the Supporting Information).

The experimentally obtained voltage ranges of 1.8 to 4.2 V are approximately consistent with the lowest reduction and highest oxidation potentials of NiNC (versus Li/Li^+ , Figure 1), which correspond to the reduction of NiNC^- to NiNC^{2-} and the oxidation of NiNC^+ to NiNC^{2+} in the CV

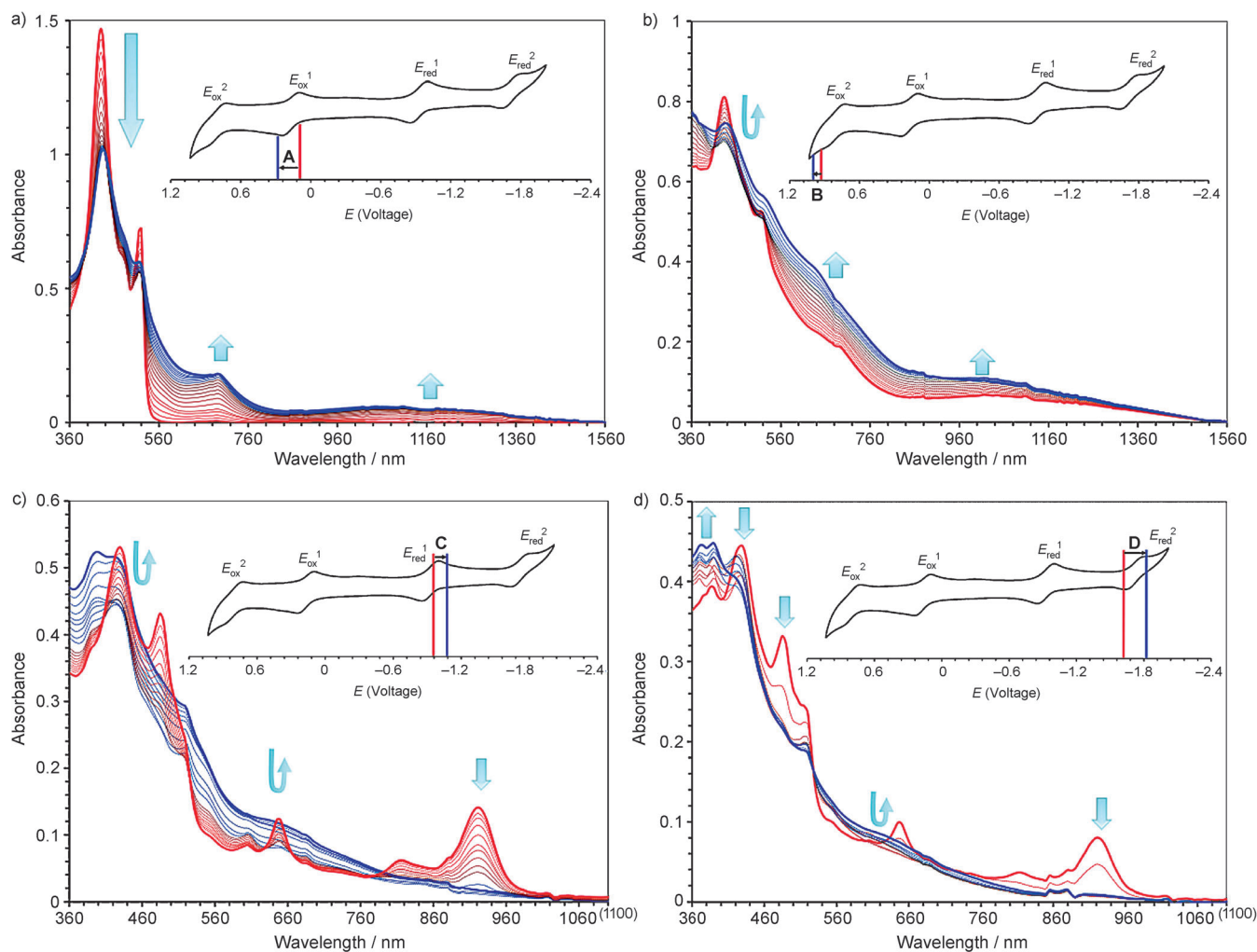


Figure 2. Changes in the absorption spectra upon a) the first oxidation, b) the second oxidation, c) the first reduction, and d) the second reduction of NiNC in CH_2Cl_2 .

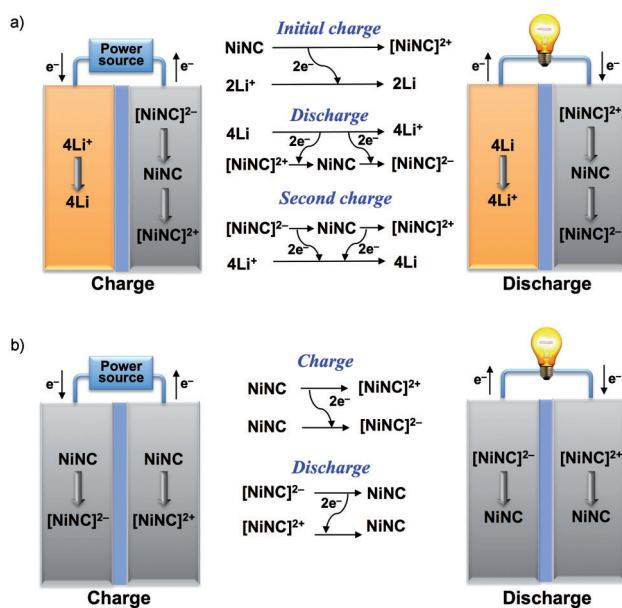


Figure 3. Charge/discharge reactions for a) Li-NiNC batteries and b) NiNC-NiNC batteries.

curves, respectively (potentials versus Li/Li^+ , as shown in Figure 1). Figure 4a shows selected charge/discharge curves of the fabricated Li-NiNC batteries over 100 cycles, measured at a constant current of 1 mA in the voltage range of 1.8 to 4.2 V.^[10] The capacities are normalized by the weight of NiNC. The initial voltage of the as-prepared cell was 3.2 V, and the voltage exhibited a plateau at 3.7 V in the first charge process, followed by an increase to 4.2 V. The first charge capacity was approximately 120 mAhg^{-1} , which is larger than the value estimated by two-electron oxidation from the initial neutral state NiNC to NiNC^{2+} (Figure 3a), since the theoretical charge/discharge capacity of the NiNC electrode is 46 mAhg^{-1} for a single electron. On the other hand, the first discharge curve gradually decreased to 1.8 V and reached 170 mAhg^{-1} . After the second cycle, the charge curves exhibited a gradual increase, while the discharge curves were nearly the same as the initial discharge, but the discharge capacity gradually increased and was maintained at approximately 200 mAhg^{-1} after the 50th cycle (Figure 4b). Although the enhancement of the charge/discharge capacity is not well understood at present, the capacity of 200 mAhg^{-1} is approximately reproduced by a four-electron reduction from the dication to the dianion species (Figure 3a).

Although a voltage plateau region in charge/discharge curves for Li-organic material batteries generally indicates a chemical redox reaction assigned to a redox wave in the CV curves, the charge/discharge profile of the Li-NiNC battery exhibited no plateau region. This may be the result of the instability of the intermediate radical ion species. The Li-NiNC battery demonstrated a stable cycle performance and a high charge/discharge efficiency of approximately 100% after the 100th cycle (Figure 4b). Considering that most rechargeable batteries using organic materials have exhibited poor cycle performance, this high stability and efficiency are noteworthy. This is probably due not only to its insolubility in

the electrolyte solution but also to the reduction and oxidation of the stable antiaromatic NiNC to stable aromatic NiNC^{2-} and NiNC^{2+} .

Replacement of the Li metal anode by organic materials is one of the most significant practical challenges.^[11] Since neutral NiNC can be readily oxidized and reduced, NiNC is considered as a bipolar electrode-active material. Only a small number of examples of organic bipolar electrode-active materials have been reported so far. Nishide and co-workers have employed a bipolar radical polymer to create a fully organic-based rechargeable battery.^[12] We next tested a Li metal free NiNC-NiNC poleless battery with a symmetric configuration, wherein NiNC was used as both the anode and cathode-active materials (Figure 3b, see also Figure S1b in the Supporting Information).

Figure 4c shows charge/discharge curves for the voltage increase and decrease processes over 100 cycles, measured at a constant current of 1 mA in the voltage range of -1.7 to 2.5 V. The maximum battery voltage of 2.5 V is in good agreement with the gap between the highest oxidation and lowest reduction potentials of 0.82 and -1.67 V (versus Fc/Fc^+), respectively, while the absolute value of the minimum voltage -1.7 V is slightly smaller. The capacities are calculated per weight of NiNC to enable discussion of battery performances based on the redox reaction of NiNC. The inset of Figure 4c shows that the first charge process exhibited a gradual increase from 0.0 to 2.5 V, with a small step at 1.2 V, and a capacity of 350 mAhg^{-1} . This value is much larger than the theoretical value of 92 mAhg^{-1} estimated from a two-electron redox process because of the conversion of NiNC into NiNC^{2+} and NiNC^{2-} at the cathode and anode, respectively (Figure 3b). This is probably explained by a supercapacitor effect of the carbon materials included in the electrode.^[13]

The generated NiNC^{2+} and NiNC^{2-} subsequently change to NiNC in the discharge process down to 0 V, while NiNC becomes NiNC^{2-} and NiNC^{2+} in the charge process from 0 to -1.7 V, and vice versa for the voltage increase from -1.7 to 2.5 V. The first discharge curve ($2.5 > V > 0$ V) showed a capacity of 86 mAhg^{-1} , which can be explained by a two-electron redox process between NiNC^{2+} and NiNC and between NiNC^{2-} and NiNC (Figure 3b). Each charge and discharge capacity is different, as indicated by the two-way arrows in Figure 4c, and this is probably because of inhomogeneous reactions of NiNC in each electrode, since both electrodes include slightly reduced and oxidized NiNC even at 0 V. The discharge capacities ($2.5 > V > 0$ V) plotted in Figure 4d illustrate that this battery also exhibited good cycle performance, with the capacity maintained at approximately 90% of the initial capacity even after the 100th cycle. The described electrode performances are one of the molecular properties peculiar to NiNC.

In conclusion, we have applied a redox reaction of NiNC to rechargeable batteries. The Li-NiNC battery exhibited a high discharge capacity of 207 mAhg^{-1} , which exceeds those of Li-ion batteries using LiCoO_2 as a cathode-active material when compared in capacities per weight of active materials. The high capacity arises because of the facile redox conversions of NiNC involving four electrons per molecule. The

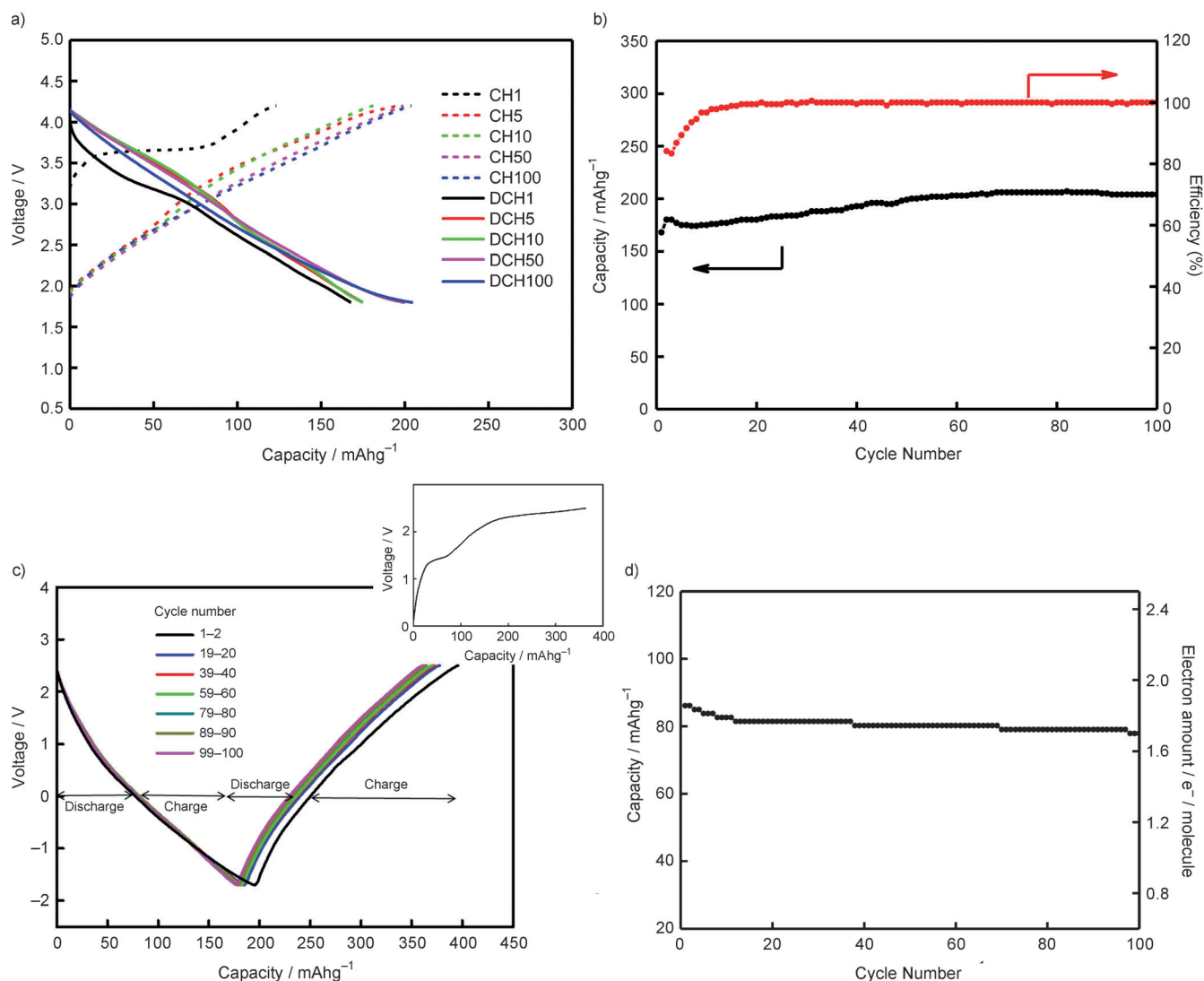


Figure 4. a) Selected charge/discharge curves, b) performance over 100 discharge process cycles of a Li-NiNC battery cell (1.0 mA step and 1.8–4.2 V set), c) selected charge/discharge curves (inset: first charge process), and d) cycle performances for 100 discharge process cycles of a NiNC-NiNC battery cell. These data were obtained at a charge (discharge) rate of ca. 1.5C. CH1 and DCH1 in (a) denote the first charge and discharge processes, respectively. Cycle number 1–2 in (c) refers to the first voltage decreasing and the second voltage increasing (1.0 mA step and –1.7–2.5 V set).

high discharge capacity was maintained even after 100 cycles. We have also demonstrated the performance of a NiNC-NiNC battery as a Li metal free rechargeable battery. The NiNC-NiNC battery exhibited a first discharge capacity of 86 mAhg^{-1} and maintained 90% of the initial capacity after 100 cycles. We believe that the aromatic stabilization of two-electron oxidized and two-electron reduced species plays an important role in sustaining excellent battery performance in Li-NiNC and NiNC-NiNC batteries.

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