

論文の内容の要旨

論文題目 Bis(diimino)metal Complex-based Coordination Nanosheets towards
Energy Storage Applications

(ビス (ジイミノ) 金属錯体を骨格とした配位ナノシートの
エネルギー貯蔵への応用)

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Introduction

On increasing demands from portable electronic devices or electric vehicles, rechargeable energy storage systems represented by lithium-ion batteries have attracted intensive attention in the past decades, aiming at further enhanced performances. For improvement of their properties including energy density and cycle lifetime, development of cathode materials is inevitable because they play a roll of redox activities to convert electric energy from/to chemical energy. Until now, the most widely used cathode materials are metal oxides such as LiCoO_2 , which show reasonably high capacity and stable cycles. However, improvement of those materials is reaching a limit, and thus finding other categories of materials are desired for sustainable advancement of technologies. In recent years, metal-organic frameworks (MOFs) are gradually attracting attentions as another type of cathode materials owing to the following advantages: (1) plenty of redox-active sites around metal ions, (2) porous structures for efficient counterion diffusion and (3) flexible designability owing to countless combinations of metals and linkers.^[1] In fact, several studies showed that some of MOFs could function as cathode materials in lithium ion batteries. On the other hand, MOFs are usually electronically insulating, which is a critical drawback as electrode materials.

As a solution of the above issue, our group has developed a novel type of MOFs having two-dimensional layers (coordination nanosheets). In addition to the advantages of MOFs, some of the coordination nanosheets have exceptionally high electronic conductivity thanks to the π -orbitals of the ligands that are widely expanded on the two-dimensional planes.^[2] Here, in my Ph.D. thesis, the coordination nanosheets based on bis(diimino)metal complex structures (MDI, $M = \text{Co}, \text{Ni}$ or Cu) were studied by experimental and theoretical approaches to understand their fundamental electrochemistry-related properties as well as performances as cathode materials in lithium ion batteries.

Synthesis of bis(diimino)nickel coordination nanosheet (NiDI) and investigation of its electrochemical properties as an electrode material in a secondary battery

NiDI (Figure 1a) has been reported to have high electronic conductivity. Additionally, bis(diimino)nickel complex, which is a composition unit of NiDI, is known to show redox activity with multi-electron transfer per metal (Figure 1b). Based on those properties, NiDI is expected to function as a cathode material in an energy storage system.

NiDI powder was synthesized following the reported procedure and characterized by several microscopic and

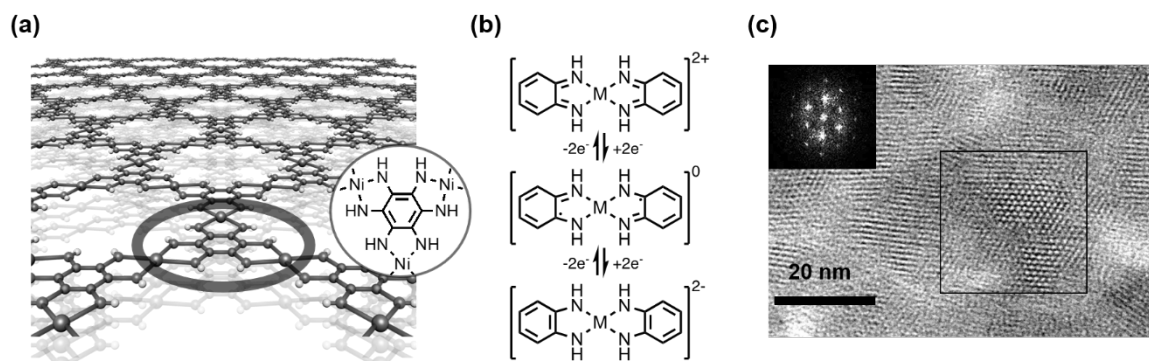


Figure 1. (a) Expected structure of NiDI. (b) Redox reactions of the bis(diimino)nickel complex. (c) HR-TEM image of NiDI. The Fourier transformed image in the inset was obtained from the square region.

spectroscopic techniques. The result of the powder X-ray diffraction (PXRD) measurement matched well the simulated pattern of the model structure, which revealed that the stacking manner of NiDI is mainly the AA pattern. The high-resolution TEM (HR-TEM) observation found the crystalline periodic lattices of NiDI with ~ 30 nm of the crystal domain size (Figure 1c). Formation of the targeted chemical structures were confirmed by the spectroscopic measurements.

The electrochemical measurements were carried out using a lithium-ion battery system. The NiDI-containing electrodes were prepared by mixing NiDI with multi-walled carbon nanotube to support current flow and polyvinylidene difluoride as a binder. Firstly, in the cyclic voltammetry of NiDI, it exhibited several pairs of redox waves, indicating that NiDI showed redox reactions with multi-electron transfer (Figure 2a). Furthermore, one pair of the waves occurred with the intercalation of Li^+ and the other did with PF_6^- , which is rarely seen in electrochemistry of solid materials. The electrochemical impedance spectra showed that the charge transfer resistance of Li^+ -related reactions was higher than the case of PF_6^- . This behavior is possibly originated from the change of electronic conductivity dependent on different oxidation states of NiDI. In order to investigate the battery performance of NiDI, charge-discharge tests were carried out, resulting in specific capacity of 155 mAh g^{-1} or energy density of 434 Wh kg^{-1} at 10

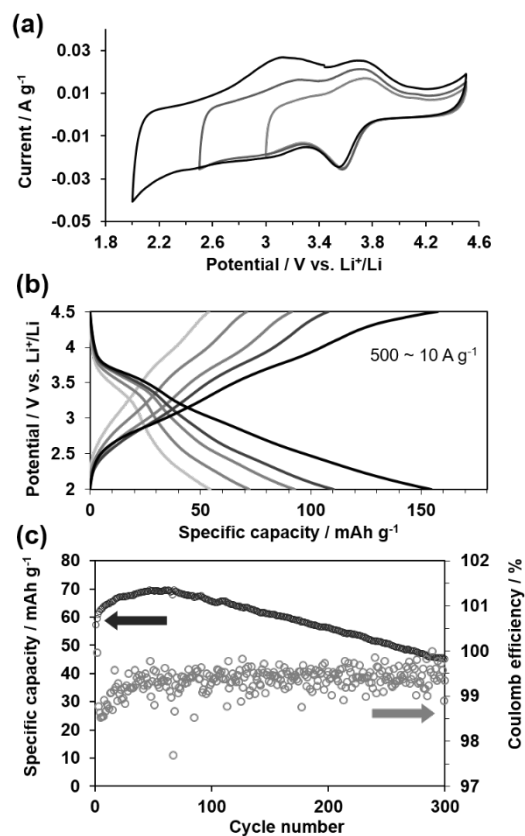


Figure 2. (a) Cyclic voltammograms at 0.1 mVs^{-1} and (b) the charge-discharge curves at several current densities of NiDI. (c) The capacity retention and the Coulomb efficiency

mA g⁻¹ (Figure 2b). These values are quite high as a MOF-based cathode material, and comparable to commercially used inorganic materials such as LiCoO₂. Additionally, NiDI showed relatively high stability as a MOF in the cycle test (Figure 2c). The electronic structure of NiDI was investigated by the DFT calculations to understand the mechanism of its electrochemical behavior. The result suggested that the redox reactions were largely concerned with the organic ligands, the electronic states of which are widely delocalized around the Fermi level.

Electrochemical study of the nanosheets with other transition metals: bis(diimino)cobalt coordination nanosheet (CoDI) and bis(diimino)copper coordination nanosheet (CuDI)

For improvement of performances of electrode materials, their properties are often tuned by modifying or replacing the chemical components, leading to drastic changes of electronic or crystal structures. In this study, cobalt or copper was embedded in the nanosheets instead of nickel to investigate the influence of those metal species on electrochemistry-related properties.

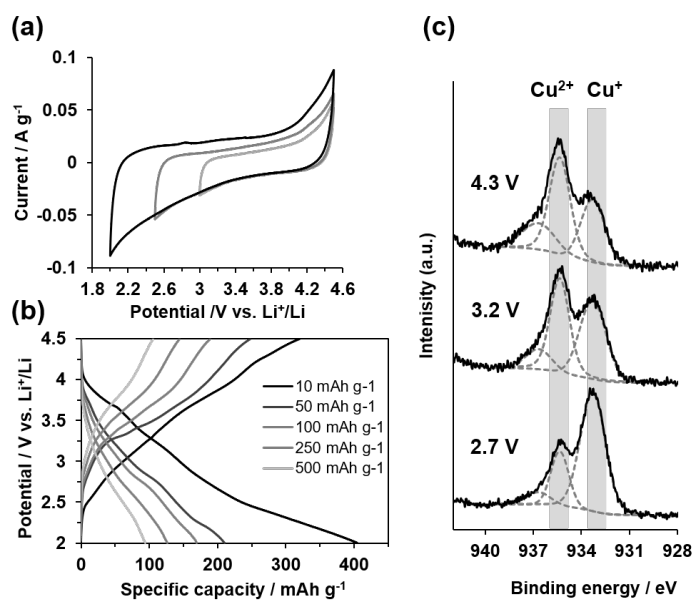


Figure 3. (a) Cyclic voltammograms of CoDI. (b) The charge-discharge curves of CuDI. (c) The X-ray photoelectron spectra of respectively charged CuDIs in Cu 2p_{3/2} region.

In the cyclic voltammetry measurements, CoDI did not show obvious redox waves in the potential range of 2 ~ 4.5 V vs. Li⁺/Li, indicating that CoDI was redox-inactive (Figure 3a). On the other hand, the electrochemical impedance spectra of CoDI exhibited the feature of a redox reaction. Those results suggest that the redox reactions of CoDI are possibly suppressed by kinetic factors such as sluggish diffusion of the counterions in the bulk. This hypothesis was supported by the temperature-dependent cyclic voltammetry measurements; the redox waves gradually showed up at elevated temperatures.

The cyclic voltammograms of CuDI revealed that it underwent the redox reactions with Li⁺ or PF₆⁻ intercalations as observed with NiDI. Although the redox potentials of CuDI was more positive than NiDI for about 0.1 V, their signatures had the same trend because their redox-active sites are mainly their ligands. Regarding the properties as a cathode material, the specific capacity of CuDI was nearly 400 mAh g⁻¹ at maximum in charge-discharge tests (Figure 3b), the value of which was significantly higher than the other two MDIs. The origin of this high capacity was examined by X-ray photoelectron spectroscopy (XPS). The spectra of CuDI at respectively charged states clearly

CoDI powder and CuDI powder were synthesized by the same procedure as NiDI, except for the used metal sources. The crystal structures of the synthesized materials were determined by PXRD measurements. The obtained patterns suggested that the crystal structure of CuDI was almost the same as NiDI while CoDI had a slightly different structure, but both patterns could be matched with AA stacking models. In the HR-TEM observation, both CoDI and CuDI were found to have the crystalline honeycomb lattices with the expected periodic length. The observation also found that the crystal domain size of CuDI was the largest among three nanosheets (~100 nm) while the domains of CoDI were only about 10 nm diameters.

In the cyclic voltammetry measurements, CoDI did

suggested the existence of Cu^+ and Cu^{2+} , and the ratio of those valences changed by charge or discharge of the material (Figure 3c). On the other hand, in the XPS study of NiDI, drastic change of the oxidation states of Ni was not observed. Therefore, it can be concluded that cooperation of the metal ions and the ligands in CuDI is the main reason for such high capacity.

Heterometal bis(diimino)cobalt-nickel coordination nanosheets ($\text{Co}_x\text{Ni}_{1-x}\text{DI}$) for the study of metal constitution effect on electrochemistry-related properties

In the studies of bis(diimino)metal coordination nanosheets, their electrochemical properties were found to be largely varied depending on the metal species. Therefore, employment of heterometal structure would enable us to further tune their electrochemical properties. Based on the above motivation, bis(diimino)cobalt-nickel coordination nanosheets ($\text{Co}_x\text{Ni}_{1-x}\text{DI}$) were synthesized with various metal compositions, and their electrochemical properties including energy storage functions were investigated.

For characterization of the compounds, PXRD measurements, and other spectroscopic/microscopic analysis were carried out, revealing that $\text{Co}_x\text{Ni}_{1-x}\text{DI}$ had a solid-solution state rather than separated two phases of CoDI and NiDI. As a result, it was found that the interlayer distance of the materials can be controlled by changing content ratio of Co and Ni ions. In the electrochemical measurements of $\text{Co}_x\text{Ni}_{1-x}\text{DI}$, the initially redox-inactive CoDI structure was activated by addition of little amount Ni ions in 2.0 ~ 4.5 V vs. Li^+/Li , which is possibly due to the change of the crystal structure for faster counterion diffusion, or more efficient electron transport between the material and current collectors. When the amount of Ni was further increased, $\text{Co}_x\text{Ni}_{1-x}\text{DI}$ exhibited the redox reactions that were originated from heterometal (Co-Ni-L, L = ligand) motifs. The electrochemical measurements were also carried out in more negative potential window of 1.0 ~ 3.5 V. Under the condition, $\text{Co}_x\text{Ni}_{1-x}\text{DI}$ at specific metal composition showed higher specific capacity than CoDI and NiDI. The mechanisms of the above properties were analyzed by DFT calculations, which implied that crystal structure changes during the reactions and also electronic structure around the respective metal ions played a key roll for the unique electrochemical behavior.

Conclusion

In these studies, several types of MDIs were synthesized, and their electrochemistry-related properties were investigated. The electrochemical measurements of NiDI revealed its unique redox reaction mechanism: multi-electron transfer with both Li^+ and PF_6^- intercalations. This energy storage principle realized high specific capacity and stable cyclability as a MOF-based cathode material. When the metal ion was replaced by Co or Cu, the materials showed quite different electrochemical properties. CoDI was nearly redox-inactive at room temperature because of the kinetic factors. On the other hand, CuDI exhibited far higher specific capacity than the other MDIs owing to the transitions of the metal valence states. The results demonstrated in my Ph.D. thesis suggest that complex-based materials could be candidates for energy storage materials in the next generation.