様　式　C－１９、F－１９－１、Z－１９　(共通)

科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

平成 ２９ 年　 ５ 月 ２６ 日現在

機関番号：１３９０１
研究種目：研究活動スタート支援
研究期間：2015～2016
課題番号：１５H０６２６５

研究課題名（和文）Metal-Organic Framework-based Cathode Active Materials for Lithium Batteries

研究課題名（英文）Metal-Organic Framework-based Cathode Active Materials for Lithium Batteries

研究代表者
張　中岳（Zhang, Zhongyue）

名古屋大学・物質科学国際研究センター・助教

研究者番号：００７５５７０４

交付決定額（研究期間全体）：（直接経費）　　2,100,000円

研究成果の概要（和文）：レドックス活性リガンドとアントラキノン官能基およびMn（II）カチオンとを組み合わせることにより、新しい金属有機骨格、すなわちMn-AQDCが調製されました。このMOFは、リチウムイオン電池のカソード材料として使用されたときに、新規な電気化学的メカニズムも見られる。高い比容量、200mAh / gも達成される。 Mn-AQDCに関するさらなる研究は、有機ゲスト分子を用いてその物理的性質を調整しました。新しいゲストMOF錯体の構造が達成され、固体反射率、EPRおよび磁気で電荷移動現象が観察されました。

研究成果の概要（英文）：Three major projects have been done for this research. 1), by combining redox-active ligand with anthraquinone functional groups and Mn(II) cations, a new metal-organic framework is prepared, namely Mn-AQDC. This MOF exhibited not only a flexible structure, but also a novel electrochemical mechanism is observed when it was used as a cathode material of Li-ion batteries. A high specific capacity, 200mAh/g is also achieved. 2), the attempt of hybridizing carbon nanotubes and nanoparticles of MOFs are performed, while the result is not positive. In most case, amorphous product was obtained. 3) A further study on the Mn-MOF is to tune its physical properties with electron donor organic guest molecules. With a crystal sponge method, the structures of new guest-MOF complexes are achieved and charge transfer phenomena were observed with solid-state reflectance, EPR and magnetism. Referencing with the charge transfer between pure donors and ligands, charge transfer was promoted in MOFs.

研究分野： Coordination chemistry

キーワード： Electrochemistry　Metal-Organic Frameworks　Redox activity

１．研究開始当初の背景

The electric storage technology is critical for the modern society as it provides a portable, affordable and clean energy resource to various devices. Among the well-developed techniques, the Li-ion batteries (LIBs) are of interest as it carries a relatively larger energy density and a desirable high output voltage. Metal-organic frameworks (MOFs). have been extensively investigated for their application on the gas storage, gas separation, catalysis, molecule recognition and molecule sensing. From the perspective of electrochemistry, only a few examples of MOFs have been examined, and fewer ones were studied for the application of the electron storage materials. Given large accessible space can be in the MOF structures, it was rational to assume a minor volume expansion upon the intercalation of Li-ions. Such properties may contribute to the stability of the crystalline frameworks and therefore lead to an outstanding cycle performance.

２．研究の目的

The purpose of the research includes the development of new redox active MOFs and explore their application as novel, high performance cathode active materials of Li-ion batteries with outstanding cycle stability, large electronic capacity and energy density. To enhance the performance, MOF nanoparticles and carbon-based materials, such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO) will be hybridized to promote the electron transfer in MOF materials. Finally, the interactions between the electron donor guests and redox active MOFs will be investigated and new charge-transfer complexes will be developed.

３．研究の方法

New MOFs are prepared by combining redox active metal cations (such as Mn(II)) and ligands, like anthraquinone, and the electrochemical properties are assessed by the coin cell method, while the physical insight was obtained via a series of *in situ* measurement. The hybridization between CNTs and MOFs were performed by growing MOF crystals in a well dispersed solution of CNT. Using “crystal sponge” method, we are able to insert organic donor molecules into the MOF framework with electron acceptor-type ligands.

４．研究成果

Three major research achievements have been obtained and it will be briefly introduced as below.

(1), inspired by the former synthesis of a MOF with both a redox active ligand and Cu(II) cations, a continuing work of combing anthraquinone dicarboxylics and redox active Mn(II) cations have led the formation of a new redox active MOF: $Mn_7(2,7\text{-}AQDC)_6(2,6\text{-}AQDC)(DMA)_4$ (Mn-MOF). Without analyzing the electrochemistry of this Mn-MOF, its structural characteristics is already interesting. With single crystal X-ray analysis, the Mn-MOF exhibited a phenomenon, namely “breathing behavior”, with the removal and re-introduce of guest solvent molecules. Without the solvent molecules, all the one-dimensional channels that could be observed in the X-ray structure disappeared and the structure was distorted to a tight-packing motif. This phase transition was reversible when the guest-free crystals were merged into common solvents, such as dichloromethane, DMF and so on. The flexibility of Mn-MOF was confirmed.

By analyzing the electrochemical behaviors of this MOF, we realized that this Mn-MOF suggested a new mechanism, which has never been observed in regular Li-ion batteries. Such mechanism is named as “Bipolar charging” by us. In a full charge-discharge cycle, the Mn(II) was oxidized to Mn(III) during the charge step, and reduced to Mn(II) in the discharge step, followed by the reduction of quinone groups. When the Mn(II) was oxidized, the anions in the electrolytes, which is PF_6^- in our study, and the PF_6^- was released during discharge and followed by the insertion of Li-ions to balance the charge of reduced quinone groups. (**Figure 1**) The Mn-MOF also showed a highly reversible charge-discharge process, with a specific capacity of ~200mAh/g.

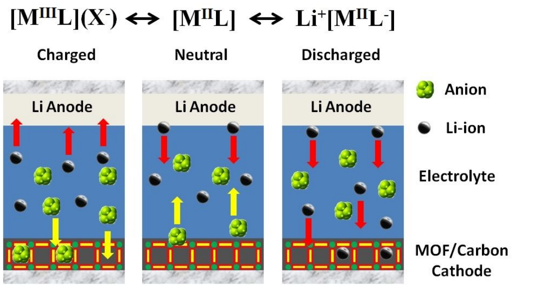

Figure 1. The "Bipolar charge" mechanism that is discovered in the electrochemistry of the Mn-MOF.

(2) The hybridization between the MOF nanoparticles and carboxylic group functionalized single wall carbon nanotubes (SWCNTs) has been attempted as well. The main method is try to grow MOFs with a mother liquor solution in which the functionalized CNTs were well dispersed. Various conditions and concentrations were tested, unfortunately, no positive result has been achieved. Most obtained materials are carbon nanotubes with amorphous metal-organic complex products. Future strategy will be carried from the mixture of metal hydroxide fiber and CNTs.

(3) Since the hybridization between CNTs and MOF nanoparticles was not successful, we proposed new research topics: to alternate the physical properties of redox active MOFs with guest molecules. In this study, the Mn-MOF with electron accepting group, anthraquinones are studied and the organic electron donor guest molecules, such as tetrathiafulvalene (TTF) and tetramethylphenyldiamine (TMPDA) are introduced. With a "crystal sponge" procedure reported from Fujita *et. al.*, the guest@MOF structures were successfully analyzed and two complexes with formula Mn-MOF·5TTF and Mn-MOF·7TMPDA were prepared. In both case, a self-aseembly of structure is realized: the donor molecules are found beside the location of anthraquinone groups (**Figure 2**) and charge transfer was evidenced by solid-state reflectance, EPR and magnetism. Referencing with the solution UV-vis spectrum of donor and ligand mixture, MOF is able to separate the donor molecules and create a close contact. The charge transfer between a weak donor and a weak acceptor could be promoted in this case.

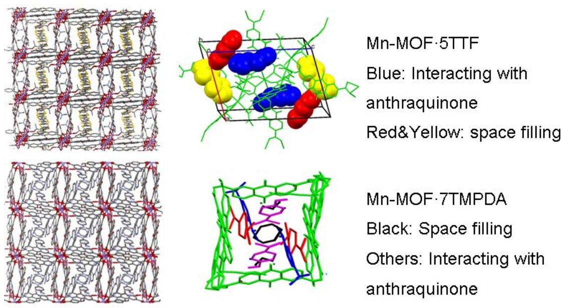

Figure 2. The structures of Mn-MOF·5TTF and Mn-MOF·7TMPDA.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　３件）

1, Discovery of a "Bipolar Charging" Mechanism in the Solid-State Electrochemical Process of a Flexible Metal–Organic Framework. Zhongyue Zhang, Hirofumi Yoshikawa and Kunio Awaga, *Chem. Mater.*, **2016**, *28*, 1298-1303. (Peer reviewed)

2, Synthesis of Vanadium-Incorporated, Polyoxometalate-Based Open Frameworks and Their Applications for Cathode-Active Materials. Zhenxin Zhang, Hirofumi Yoshikawa, Zhongyue Zhang, Toru Murayama, Masahiro Sadakane, Yasunori Inoue, Wataru Ueda, Kunio Awaga and Michikazu Hara, *Eur. J. Inorg. Chem.*, **2016**, *8*, 1242-1250. (Peer reviewed)

3, Redox-active metal–organic frameworks as electrode materials for batteries. Zhongyue Zhang and Kunio Awaga, *MRS Bulletin*, **2016**, *41*, 883-889. (Peer reviewed, invited literature review.)

〔学会発表〕（計　４件）

1, "Redox Active Metal-Organic Framework Brings New Mechanism to the Lithium Batteries." The 42th International Conference of Coordination Chemistry (ICCC42), Brest, France.

2, "Redox Active Metal-Organic Framework Brings New Mechanism to the Lithium Batteries." Pre-ICMM 2016, Nagoya, Japan.

3, "Redox Active Metal-Organic Framework Brings New Mechanism to the Lithium Batteries." 5th International Conference on Metal Organic Frameworks & Open Framework Compounds (MOF 2016), Long Beach, USA.

4, "Redox Active Metal-Organic Frameworks: Innovative Mechanisms in Lithium Batteries and Property Manipulation with Inserted Guest." The 12th Japan-China Join Symposium on

Conduction and Photoconduction in Organic Solids and Related Phenomena, Tokyo, Japan

〔図書〕（計　0 件）

〔産業財産権〕

○出願状況（計　1　件）

名称：二次電池
発明者：阿波賀 邦夫、吉川 浩史、張 中岳
権利者：国立大学法人名古屋大学
種類：　特許
番号：特願 2015-042831
出願年月日：平成 27 年 3 月 4 日(2015.3.4)
国内外の別：　国内

○取得状況（計　0　件）

名称：
発明者：
権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕
ホームページ等

６．研究組織
(1)研究代表者
張　中岳（ZHANG, Zhongyue）
名古屋大学・物質科学国際研究センター・助教
研究者番号：００７５５７０４

(2)研究分担者
なし

(3)連携研究者
なし

(4)研究協力者
なし