様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　３ 年 １０ 月 １８ 日現在

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課題番号：１８Ｋ０４９２５

研究課題名（和文）Self-healing antiaromatic batteries

研究課題名（英文）Self-healing anti aromatic batteries

研究代表者
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交付決定額（研究期間全体）：（直接経費）　　3,400,000円

研究成果の概要（和文）：有機電池の電極物に利用可能な有機分子を探索する目的として新し有機分子を合成し、その物理/化学的特性を研究、報告した（論文4編、研究発表4回）。　反芳香と芳香族間の相互変換能可能な拡張π共役分系を有機電池の電極物として投入し研究報告した（論文１編）。高い充放電性能、電池寿命の延長、急速充電率、有機電極の高い耐久性を持つ優れたナトリウム-有機電池を開発、研究し報告した（論文１編、論文表紙、リチウム-有機電池関連研究発表２回）。電極物質内の有効な空間と高濃度電解質の輸液イオン流動性が電池性能影響することを見出だした（論文１編）。

研究成果の学術的意義や社会的意義
Daily energy consumption is essential. Researchers have intended to devote to explore practically functioning energy devices. Organic rechargeable batteries thus have accumulated scientific attention. High-durable secondary organic batteries were invented through this project.

研究成果の概要（英文）：The principal investigator attempted to explore efficient battery electrode materials where new organic molecules were published with their physical/chemical properties (RSC Adv. 2019, 9, 40031; RSC Adv. 2021, 2, 2263; JPP 2020, 24, 191; Org. Lett. 2020, 22, 4400). Organic batteries with elongated π-conjugation molecules having interconversion capability between antiaromatic and aromatic conformations were investigated (Molecules 2019, 24, 2433). Also, high durable secondary organic batteries assembled with large composite (70%) NiNc electrodes and highly concentrated dual ion liquid provided high charge-discharge performances, enhanced working-life of batteries, fast charging rate, and high durability of organic electrodes (Mater. Adv. 2021, 2, 2263, front cover of the issue). Influential dual-ion mobilities of an ionic liquid through appropriate cavity spheres in electrodes furnished significantly improved battery performances were established (Batter. Supercaps 2021, 4, 1605).

研究分野：有機二次電池

キーワード：Porphyrinoid　electrochemistry　Li-organic battery　Na-organic battery

１．研究開始当初の背景

The exploration of efficient energy storage systems and the management of unworkable trash have been critical universal issues, with the increasing need for renewable energy and the rapid development of new electronic devices. Within the context, self-healing materials have attracted significant interest from scientists as well as engineers. Artificial self-healing materials developed for energy storage mainly were polymer-based. Furthermore, their healing mechanisms were not precise. Researchers have devoted their vital efforts to explore novel functional materials and nationally proposed structures to improve the capacity and efficiencies of practically functioning energy devices, and especially organic rechargeable batteries have accumulated scientific attention. Electrodes need to be fabricated with an increased volume to obtain high battery capacity. However, significant volume changes of electrodes for high-energy lithium-ion batteries often resulted in cracking the surface of electrodes and pulverizing the function of electrodes.

２．研究の目的

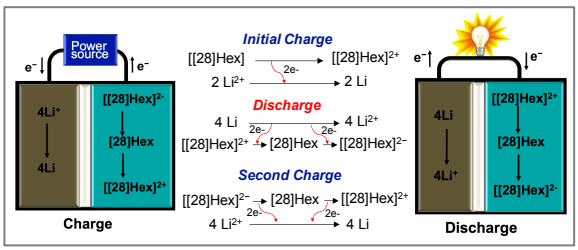
This research proposal aims to explore convenient self-healing organic batteries assembled with the electrodes having antiaromatic molecules. Researchers have intended to devote novel functional materials with rationally designed structures to improve the capacity and efficiencies toward practically functioning energy devices. Especially organic rechargeable batteries thus have accumulated scientific attention. As promoting an efficient battery system, the principal investigator and collaborators have produced efficient organic batteries involving an active electrode of antiaromatic porphyrinoid, namely norcorrole, which gave powerful battery performances. To advance to the next generation of organic batteries with active antiaromatic electrodes, the principal investigator considered inventing organic batteries capable of enhancing the durability of electrodes or self-healing the damages. Organic batteries with active antiaromatic molecular electrodes were the primary exploration for self-healable batteries. **This research proposal aimed to comprise convenient self-healing organic batteries with efficient active electrode organic molecules. To improve the battery performances, the principal investigator attempted to achieve (a) high charge-discharge performances, (b) high safeties, (c) enhanced working life of batteries, (c) fast self-healing speed and (d) high durability of organic electrodes.**

３．研究の方法

The principal investigator and collaborators attempted to prepare novel antiaromatic molecules capable of efficient organic batteries. Considerably suitable antiaromatic molecules were designed with sufficient synthetic methods. Furthermore, sufficient electrolytes were introduced in the assembly of organic batteries. Electrode materials showed efficient self-healing processes were polymer-based molecules. Hydrogel electrolytes were an applicable electrolyte of few examples reported. Antiaromatic nickel(II) nocorrole (NiNC) exhibiting significant charge/discharge behaviors in Li-NiNc batteries as an active battery electrode was examined for the advanced batteries, and then the structure of NiNC was modified to achieve additional functionality. Once organic batteries were prepared, the battery performances were compared with inefficient cases causing decomposition of organic electrodes, where the principal investigator fully comprehends the factors affecting the battery process. **The research was progressed in collaboration with the Kyoto University research group** (Profs. R. Hagiwara, K. Matsumoto, and J. Hwang at Fundamental Energy Science Department).

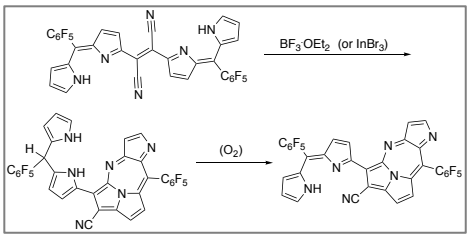
４．研究成果

1. There is no doubt that daily energy consumption is essential, associated with the quality of our lives. Li-organic batteries have been widely enquired by adopting distinct and suitable organic molecules. Elongated π-conjugation molecules with interconversion capability between antiaromatic and aromatic conformations were considered for organic batteries. Li-collaborating organic battery (Li-[28]hex) was investigated in the use of [28]hexaphyrin (1.1.1.1.1.1), where each hexaphyrin of [28]Hex cathode involved four electrons per unit cycle. The battery performance was reasonably stable over 200 cycles with a fast charging rate. (*Molecules* **2019**, *24*, 2433)



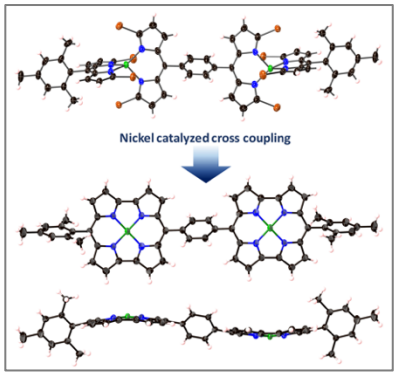
2. It is essential to characterize precise molecular structures and examine the chemical/photo-physical behaviors for investigating photo-responsible components toward functional battery materials. Since

the elongated π-conjugation molecules were produced in the metallation of a dipyrrin derivative, resembled reactions towards novel π-conjugation molecules were investigated. The principal investigator obtained diazepinopyrrolizine derivatives in reactions of a dicyanovinylene-dipyrrin derivative with $BF_3.OEt_2$ and $InBr_3$. The molecular structures were elucidated by X-ray diffraction analysis. (*RSC adv.* **2019**, *9*, 40031)



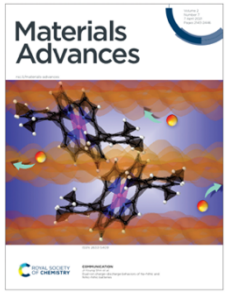
3. Metallation of the dipyrrin derivative was attempted with a cobalt source, where the principal investigator obtained a low spin-state and diamagnetic Co(III) complex. The crystal structure and spectroscopic analysis have been published (*RSC Adv.* **2021**, *2*, 2263). The corresponding results were reported at an international conference (Synthesis and Characterization of Octahedral Co(III) Complex of Pyrrolopyrrolizine Derivative; *ICPP-11*, Jun. 28 ~ Jul. 3, **2021**)

4. Since the principal investigator observed the probability of active battery electrodes using antiaromatic NiNc, dimerized molecular systems of NiNc were designed and newly prepared. IR and Raman vibrational behaviors of the NiNC-NiNC dimer were examined in consideration of the single-crystal structure. (*J. Porphyrins Phthalocyanines*, **2020**, *24*, 191)

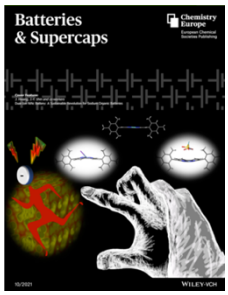


5. Reactivities of NiNc were investigated with carbene to provide novel NiNc molecules whose molecular structure was elucidated by X-ray diffraction analysis. (*Org. Lett.* **2020**, *22*, 4400)

6. Ni(II) norcorrole (NiNC) has exhibited excellent interconversions between antiaromatic and aromatic conformations (Electrochemistry of Antiaromatic NiNC; *NU-PKU Workshop*, Jan. 28 ~ 29, **2019**). Since excellent battery behaviors of Li-NiNc have been obtained with the NiNc cathodes, inexpensive and large abundant Na complementary batteries have been investigated with the NiNc electrodes. High composite (70 wt%) NiNc electrode has compromised nicely with the high redox durability and precise ion insertion, resulting in high discharge capacity, high stability, and high efficiency of Na-NiNc battery with high current densities. The research achievement was published (*Mater. Adv.* **2021**, *2*, 2263) and highlighted on the front cover of the journal issue.



7. Dual-ion mobilities of Na organic batteries are investigated with *in-situ* XRD analysis and computational estimation considering molecular alignments in the solid-state, signifying the interactive variations of ionic pairs of an ionic liquid electrolyte and an antiaromatic molecule, nickel(II) norcorrole (NiNc). An appropriate cavity sphere in three-dimensional molecular alignments dispensed mobilities of dual-ion in an ionic liquid, resulting in high battery capacities, supplemented with the comparison of Mes-NiNc and Ph-NiNc molecular alignments. *In-situ* XRD experiment, computation, and simulation perspectives afforded prospective insertion and desertion behaviors of cations and anions (*Batteries & Supercaps*, **2021**, *4*, 1605, cover feature). An oral presentation on NiNc batteries was provided at an international conference (Nickel(II) Norcorrole (NiNc) Batteries; *ICPP*-11, Jun. 28 ~ Jul. 3, **2021**).



This research proposal aimed to comprise convenient self-healing organic batteries with efficient active electrode organic molecules. The principal investigator attempted to discover advanced secondary organic batteries providing **(a) high charge-discharge performances, (b) enhanced working-life of batteries, (c) fast self-healing speed, and (d) high durability of organic electrodes.**

Due to the COVID circumstance, the research progress was slower than the initial plan. However, the principal investigator precisely explored **high durable secondary organic batteries** assembled with large composite (70%) NiNc electrodes and highly concentrated dual ion liquid through a research project, which provided **(a) high charge-discharge performances, (b) enhanced working-life of batteries, (c) fast charging rate, and (d) high durability of organic electrodes**. Furthermore, **the principal investigator established influential dual-ion mobilities of an ionic liquid through appropriate cavity spheres in three-dimensional molecular alignments of electrode organic molecules furnished significantly improved battery performances.**

５．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　7件／うち国際共著　0件／うちオープンアクセス　4件）

１．著者名 Shin Ji-Young、Zhang Zhongyue、Awaga Kunio、Shinokubo Hiroshi	４．巻 24
２．論文標題 Exploration of Li-Organic Batteries Using Hexaphyrin as an Active Cathode Material	５．発行年 2019年
３．雑誌名 Molecules	６．最初と最後の頁 2433～2433
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/molecules24132433	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Shin Ji-Young	４．巻 24
２．論文標題 Meso-1,4-phenylene bridged nickel norcorrole dimer	５．発行年 2020年
３．雑誌名 Journal of Porphyrins and Phthalocyanines	６．最初と最後の頁 191～199
掲載論文のDOI（デジタルオブジェクト識別子） 10.1142/S1088424619501074	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Shin Ji-Young	４．巻 9
２．論文標題 Synthesis of pyrrolo[3′,2′:4,5][1,3]diazepino[2,1,7-cd]pyrrolizine derivatives from dicyanovinylene-bis(meso-aryl)dipyrrin	５．発行年 2019年
３．雑誌名 RSC Advances	６．最初と最後の頁 40031～40036
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/c9ra08850d	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Liu Si-Yu、Fukuoka Takaki、Fukui Norihito、Shin Ji-Young、Shinokubo Hiroshi	４．巻 22
２．論文標題 Reactions of Antiaromatic Norcorrole Ni(II) Complex with Carbenes	５．発行年 2020年
３．雑誌名 Organic Letters	６．最初と最後の頁 4400～4403
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.orglett.0c01402	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

1．著者名 Shin Ji-Young	4．巻 11
2．論文標題 The synthesis and characterization of the octahedral CoIII complex of a pyrrolopyrrolizine derivative formed with dicyanovinylene-bis-(meso-aryl)dipyrrin	5．発行年 2021年
3．雑誌名 RSC Advances	6．最初と最後の頁 2315～2319
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/d0ra09452h	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

1．著者名 Hwang Jinkwang、Hagiwara Rika、Shinokubo Hiroshi、Shin Ji-Young	4．巻 2
2．論文標題 Dual-ion charge-discharge behaviors of Na-NiNc and NiNc-NiNc batteries	5．発行年 2021年
3．雑誌名 Materials Advances	6．最初と最後の頁 2263～2266
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/d1ma00007a	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

1．著者名 Hwang Jinkwang、Matsumoto Kazuhiko、Hagiwara Rika、Ukai Shusaku、Shinokubo Hiroshi、Shin Ji‐Young	4．巻 4
2．論文標題 Dual‐Ion NiNc Battery: A Sustainable Revolution for Sodium Organic Batteries	5．発行年 2021年
3．雑誌名 Batteries & Supercaps	6．最初と最後の頁 1605～1610
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/batt.202100193	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計6件（うち招待講演　2件／うち国際学会　5件）

1．発表者名 Ji-Young Shin
2．発表標題 Contracted and Expanded Porphyrinoids from Dipyrrin Precursors
3．学会等名 A3 Joint Seminar 2019（招待講演）（国際学会）
4．発表年 2019年

１．発表者名
Ji-Young Shin

２．発表標題
Electrochemistry of Antiaromatic NiNC

３．学会等名
NU-PKU Workshop "Solid-State Electrochemistry for Coordination Complexes"（招待講演）（国際学会）

４．発表年
2019年

１．発表者名
Ji-Young Shin, Nathan H. Faialaga, Hiroshi Shinokubo

２．発表標題
Synthesis of novel expanded porphyrinoids: NiII-induced nitrile cyclization of dicyanovinylene-bis(meso-aryl)dipyrrin

３．学会等名
10th International Conference on Porphyrins and Phthalocyanines (ICPP)（国際学会）

４．発表年
2018年

１．発表者名
辛　知映

２．発表標題
Some achievements on dipyrrin chemistry

３．学会等名
第2回集合有機分子機能研究会

４．発表年
2018年

１．発表者名
Ji-Young Shin

２．発表標題
Synthesis and Characterization of Octahedral CoIII Complex of Pyrrolopyrrolizine Derivative

３．学会等名
11th International Conference on Porphyrins and Phthalocyanines (ICPP)（国際学会）

４．発表年
2021年

１．発表者名 Ji-Young Shin
２．発表標題 Nickel(II) Norcorrole (NiNc) Batteries
３．学会等名 11th International Conference on Porphyrins and Phthalocyanines (ICPP)（国際学会）
４．発表年 2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関